E3S Web of Conferences **576**, 06004 (2024) https://doi.org/10.1051/e3sconf/202457606004
EIC 2024

Carrageenan and bentonite as wet strength agents in the process of making nautical chart paper

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Abstract. Indonesia is a strategic maritime country, especially in terms of trade and economy. The most vital defense is Indonesian waters in the form of shipping by the Indonesian Navy. The support is in the form of nautical chart paper which is strong and waterproof. Natural paper reinforcement needs to be added because synthetic materials contain monomer groups, can damage the environment and are difficult to grade. Examples of natural agents are carrageenan and bentonite which work to form hydrogen bonds with cellulose fibers, thereby increasing the strength of paper. The research aims to study the effect of carrageenan and bentonite on opacity, tearing, tensile, wet index, and Cobb. The highest opacity was 100.2% in carrageenan with a dose of 14%. The highest tearing was in the mixed agent, amounting to 745.87 mN at a dose of 14%. The highest tensile dose of 14% was 1.58 kgf/15mm. The highest wet index dose is 14%, which is 2.55% of the mixed agent. The best Cobb for mixed agents with a dose of 14% was 67.09 g/m2. In conclusion, carrageenan and bentonite have potential as wet strength agents in making nautical chart paper.

1 Introduction

As one of the largest archipelago countries in the world, Indonesia has 104,000 km of coastline which is claimed to be the second longest in the world, after Canada. The national attribute of being a maritime country certainly provides strategic value for Indonesia, especially from a trade and economic perspective. However, such situations and conditions also present potential threats to national defense. Wide geographical areas, especially water areas, require strong defense equipment, both in terms of human resources and facilities and infrastructure. Efforts to uphold national sovereignty are the responsibility of all components of the nation by empowering all the potential of the national resources they have. Therefore, the implementation of national defense, especially maritime defense, is very necessary [2].

One of the supporting equipment for shipping is an insight map of Indonesian waters, which requires paper material that is strong, waterproof and resistant to changes in weather, including temperature.

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In this case, a paper strengthening agent (wet strength agent) needs to be added. Wet strength agent is a material that is added to the pulp during the papermaking process, namely at the mixing chest stage, so that the strengthening material can be completely mixed into the pulp mixture [9].

There are two types of wet strength agents, namely synthetic and natural. Synthetic wet strength agents are generally made from polymers such as polyamidoamine epichlorohydrin (PAE), polyacrylamide (PAM), and polyethyleneimine (PEI). This material works by cross-linking the cellulose fibers in the paper, forming a strong network that resists paper damage when it comes into contact with water. On the other hand, natural wet strength agents come from natural sources such as carrageenan or bentonite. This material works to form hydrogen bonds with cellulose fibers, thereby increasing the paper's strength against water. Synthetic materials are generally added to the pulp during the papermaking process, while natural materials are often applied to the surface of the finished paper product [12].

Carrageenan is a sulfated polysaccharide, extracted from several species of red seaweed (Rhodophyceae). Carrageenan is a natural high molecular polymer that functions like pectin by bridging cellulose fibers, so it can be used to increase the physical strength of paper. Bentonite is a natural mineral consisting of alumino-silicate crystals which have a high cation exchange capacity and there are reactive hydroxyl groups on its surface so that it can increase the physical strength of paper [24]. The presence of hydroxyl groups in bentonite functions to form hydrogen bonds with the hydroxyl groups of cellulose fibers, thus making the bonds between cellulose fibers stronger and increasing the paper's resistance to water. Bentonite itself is a type of mineral that is useful for humans and can be used as a binding material in foundry molding sand, as a raw material for making ceramics, crayons, cement, cosmetics [5].

This research aims to develop the use of natural wet strength agents from bentonite and carrageenan as a substitute for synthetic wet strength agents in making map paper. The resin contained in these synthetic agents contains monomer groups which can damage the environment, are difficult to grade and are dangerous to health [22]. The agent dosages used are 10%, 12%, and 14% to produce 160 gsm paper grammage. Apart from this aim, this research also aims to study the effect of carrageenan, bentonite and carrageenan-bentonite mixtures on the characteristics of the resulting nautical chart paper, including opacity, tearing strength, tensile strength, wet strength index and cobb test. And the aim is to determine the optimum dosage of nautical chart paper produced by adding carrageenan and bentonite as wet strength agents.

2 Methods

This research uses the parameters of waterproof paper used as nautical chart paper by Pushidrosal TNI AL, referring to samples of map paper produced by the Drewson Germany factory which can be seen in Table 1. The pulp raw material is obtained from pulp stock originating from the mixing chest, with a composition ratio of pulp and water of 30 g : 1000 ml, grinding degree of 250 CSF (Canadian Standard Freenes) with a consistency of 3%. The experiment was carried out by adding a wet strength agent from carrageenan, adding a wet strength agent from bentonite, and a mixture of carrageenan and bentonite in a 1:1 ratio with variations in the wet strength agent ratio of 10%: 12%: 14%. Then the 160 gsm handsheet was made.

Table 1. TNI AL Pushidrosal Sea Chart Paper Parameters

Parameter		Unit	Range Specification
Gramature		g/m^2	152 – 165
Thickness		Micron	150 – 210
Opacity		%	95 – 100
Tearing Strength	MD	mN	1254 – 1412
	CD		1275 – 1364
Tensile Strength	MD	kgf/15mm	10.63 – 15.47
	CD		11.21 – 18.36
Wet Strength	MD	%	20.6 – 21.1
	CD		24.8 – 25.5
Cobb Test		g/m^2	20 – 35

2.1 Preparation of Agent Materials

Carrageenan is cooked in demineralize water at a temperature of 60-70 °C, stirring at a speed of 650 rpm for 15 minutes. Dissolve bentonite with demineralize water for 120 minutes, stir at 650 rpm for 120 minutes.

2.2 Making Handsheets

The stock pulp mixing chest is prepared and tested for wet end properties which include pH, consistency and freeness. Then, stirring is carried out to obtain a homogeneous stock condition. The first experiment was carried out with the addition of the wet strength agent carrageenan. Then the second experiment was with the addition of the wet strength agent bentonite. And then the mixture of bentonite and carrageenan was added in the third experiment, with each experiment varying the wet strength agent ratio by 10% : 12% : 14%. Then a load test was carried out on each experimental variation and then 160 gsm handsheets were made using a handsheet former with a drying temperature of 110 °C for 5 minutes. Soak in oxidation starch solution for 30 seconds, then dry at 110 °C for 1 minute. After completing the handsheet production, it was continued with testing the physical properties of the handsheets from each experiment.

Tabel 2. Research Results Data

Agent	Dose	Opacity (%)	Tearing Index (mN)	Tensile Index (kgf/15 mm)	Wet Strength (%)	Cobb Test (g/m^2)
Blank LBKP	0%	93.70	320.00	0.38	0.61	95.92
Carrageenan	10%	96.30	475.92	0.71	1.20	91.13
	12%	97.33	480.00	0.89	1.44	82.40
	14%	100.20	495.19	0.90	1.45	70.68
Bentonite	10%	94.60	392.50	1.48	2.37	75.71
	12%	96.03	400.00	1.49	2.40	70.04
	14%	96.90	413.30	1.58	2.55	68.37
Carrageenan + Bentonite (1:1)	10%	94.80	709.95	1.16	1.87	75.87
	12%	95.47	720.00	1.27	2.05	72.10
	14%	98.90	745.87	1.32	2.12	67.09

3 Results and Discussion

Making nautical chart paper using organic materials including carrageenan, bentonite and a mixture of both as wet strength agents is shown in Table 2. Table 2 is data from experiments on making map paper using carrageenan and bentonite as wet strength agents. This data shows that there is an increase in the resistance of map paper for each variable compared to blank samples or without a wet strength agent.

3.1 Effect of Adding Agent on Opacity

Opacity is the level of opacity or see-through ability of an image on the reverse side of the paper. The level of opacity can be seen on the back side of the paper, the thicker or clearer the image on the back of the paper, the lower the opacity level. This opacity test uses the ISO 2471 method with units of percent (%). The test results with the addition of wet strength agent on opacity are shown in Figure 1.

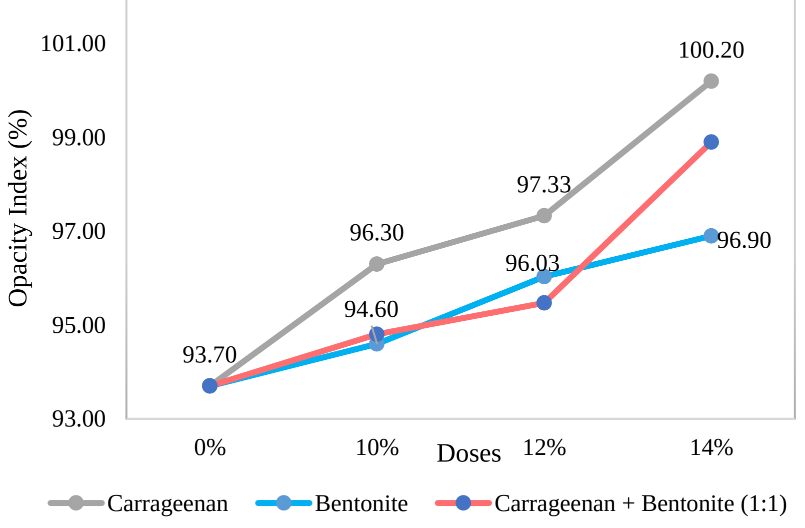

Fig. 1. Graph of the Effect of Adding Agent on Opacity

Based on Figure 1, the highest opacity value was 100.2% when the carrageenan agent was added at a dose of 14%, while the lowest value was 94.6% when the bentonite agent was added at a dose of 10%. The characteristic of carrageenan is that it forms a gel when it is dissolved in water. This gel makes the pores of the cellulose fibers become covered with gel, so that the ability to penetrate the image on the sheet will otherwise be reduced. Most of the research results have met the parameters of map paper produced by Drewson Germany with a range of 95-100%.

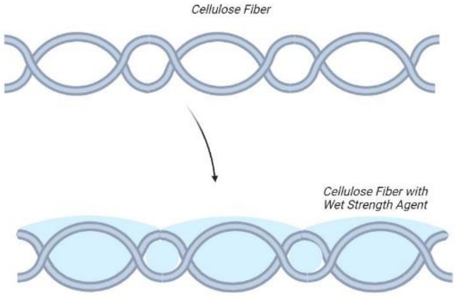

Fig. 2. Graph of the Effect of Adding Agent on Opacity

Figure 2 shows that the pores in the cellulose fibers are closed due to the addition of a wet strength agent. This causes the opacity of the paper to increase, so that the ability to penetrate an image on the reverse side of the paper is reduced.

3.2 Effect of Adding Agent on Tearing Strength

Tearing strength or tear resistance of paper is the force required to tear the paper. This tearing strength test uses the ISO 1974 method with measuring units (mN). The tearing strength test results are shown in Figure 3.

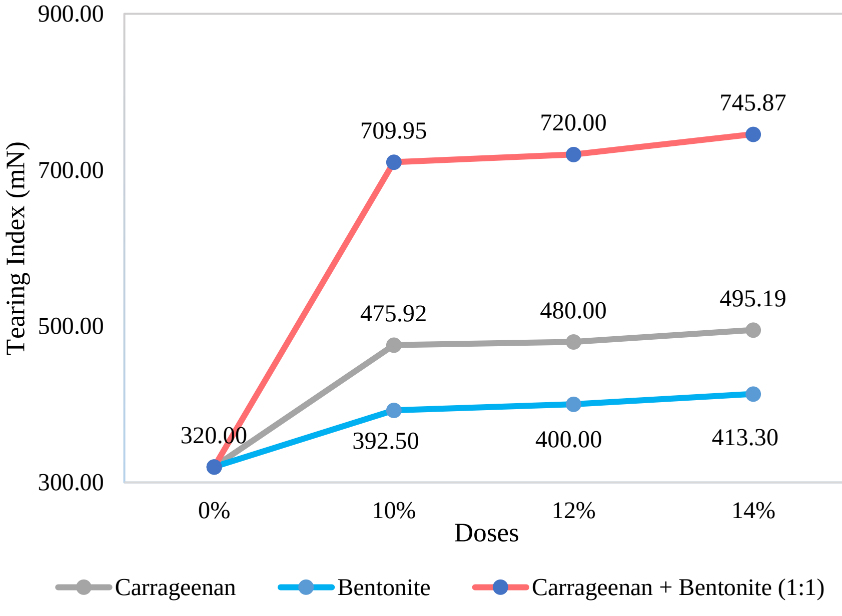

Fig. 3. Graph of the Effect of Adding Agent on Tearing Strength

The results shown in Figure 3, namely the addition of carrageenan as an agent, resulted in greater results compared to the blank sample. In the first experiment, the highest tearing strength value was found at a 14% dose increase of 495.19 mN, and the lowest value was at a 10% agent dose increase of 475.92 mN. The higher the dose given, the ability of carrageenan to increase the tearing strength value increased. The dose variations carried out in this experiment showed that the optimum point was at a dose of 14%, where carrageenan could work optimally in increasing the tearing strength value of the map paper obtained.

In the second experiment with bentonite as an agent, the lowest tearing strength value was obtained at a 10% dose of 392.50 mN, and the highest value at a 14% dose was 413.30 mN. The increase in physical strength of paper is due to the bonds between fibers when bentonite is added, this is because the negative charge on bentonite will be absorbed by the surface of the paper fibers [24]. In the third experiment, the addition of a mixture of carrageenan and bentonite increased the tearing strength value compared to the blank. The lowest value was at a 10% dose of 709.95 mN while the highest value was at a 14% dose of 745.87 mN. From the three experiments, the highest tearing strength value was obtained when adding a mixture of carrageenan and bentonite, including 709.95 mN at a dose of 10%, 720.00 mN at a dose of 12% and 745.87 mN at a dose of 14% because bentonite has the ability to adsorb. more effective, because bentonite colloidal particles are very small and capable of high cation exchange [24].

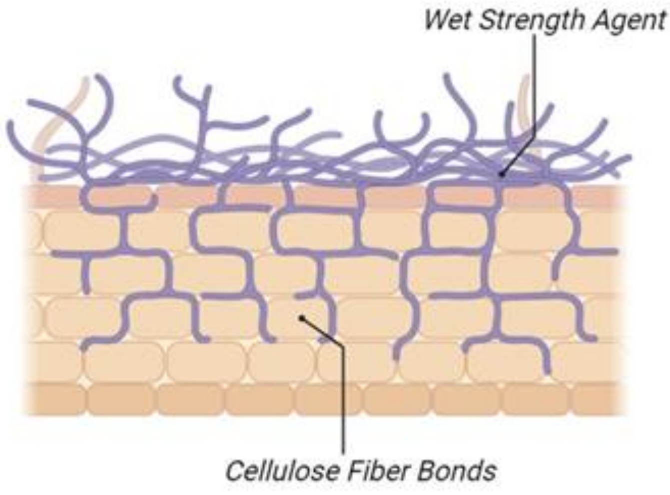

Fig. 4. The Agent is Absorbed by The Surface of The Paper Fibers

In Figure 4 it can be seen that the wet strength agent is absorbed by the cellulose fibers so that the bond between the cellulose fibers increases. This results in increased tearing strength of the resulting map paper.

3.3 Effect of Added Agent on Tensile Strength

Tensile strength is the tensile strength of paper when dry. Tensile strength or tensile strength is the main parameter of paper to measure how much influence the addition of chemicals has on the bond strength of the paper fibers. The higher the tensile strength value, the stronger the paper is against tension at both ends and sides. Tensile strength testing uses the ISO 1924-2 method with units (kgf/15mm) shown in Figure 5. Figure 5 shows that the first experiment adding carrageenan can increase the tensile strength value compared to blank. The lowest value was found with a 10% dose increase of 0.71 kgf/15mm, while the highest value was found with a 14% dose increase of 0.90 kgf/15mm, this result still exceeded the blank sample. So it can be concluded that the tensile strength value with carrageenan as an agent increases as the dose given increases. The number of hydrogen bonds formed will affect the strength of the paper obtained [24].

In the second experiment with the addition of bentonite as a wet strength agent, the lowest value was obtained at a dose of 10% with a value of 1.48 kgf/15mm and the highest value at a dose of 14% was 1.58 kgf/15mm, but still exceeded the blank value of 0.38 kgf/15mm. Based on the results of this experiment, it can be concluded that the higher the additional dose of bentonite, the higher the tensile strength value obtained, this is because the negative charge of bentonite will be absorbed by the cellulose fibers, so that the bonds between the fibers will be stronger [16].

The third experiment by adding a mixture of carrageenan and bentonite can increase the tensile strength value compared to without adding the agent (blank). The lowest tensile strength value was at a 10% dose of 1.16 kgf/15mm and the highest value was at a 14% dose of 1.32 kgf/15mm. Bentonite has the ability to adsorb more effectively, because bentonite colloidal particles are very small and capable of high cation exchange, as well as the presence of carrageenan which can help the performance of bentonite [24].

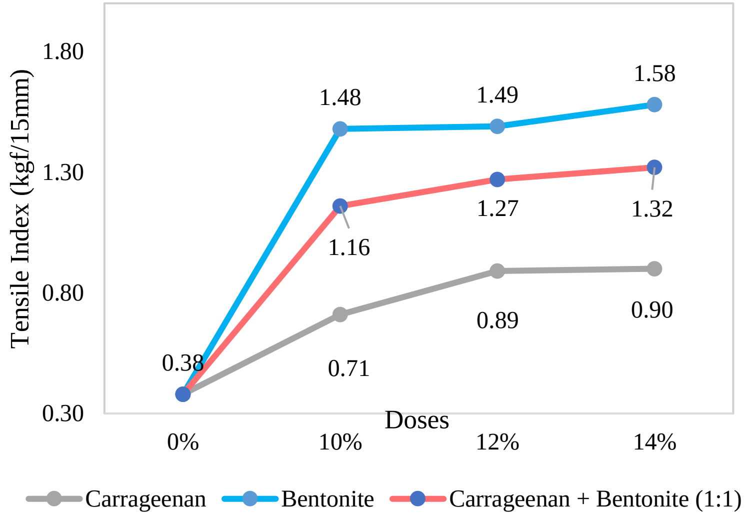

Fig. 5. Graph of the Effect of Adding Agent on Tealing Strength

3.4 Effect of Adding on Wet Strength Index

Wet strength index is the percentage of tensile resistance of paper when wet. The percentage value of wet strength or the ability of paper to survive in wet conditions is very necessary, considering the use of nautical chart paper for navigation of ships when sailing. The wet strength test results are shown in Figure 6.

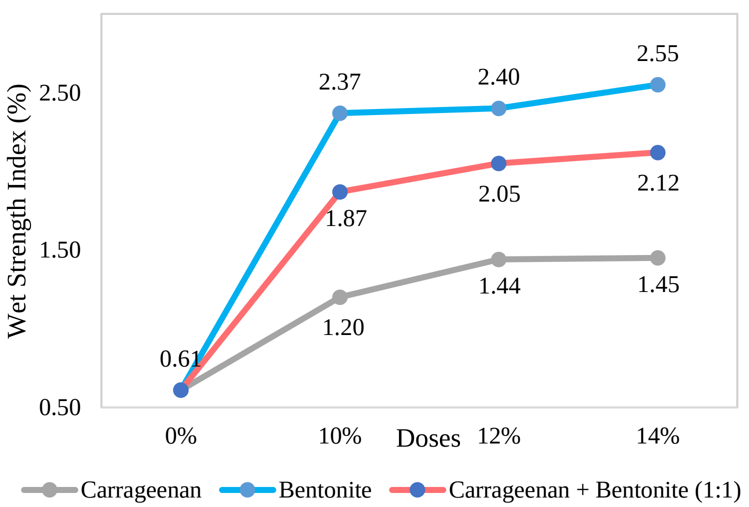

Fig. 6. Graph of the Effect of Adding Agent on Wet Strength

In Figure 6 it can be seen that the first experiment by adding carrageenan as an agent can increase the wet strength value compared to blank. The lowest value was at a dose of 10% at 1.20%, while the highest value was at a dose of 14% with a value of 1.45%. The more the dose of carrageenan is added, the more resistant the paper is to wet conditions. The hydroxyl groups and sulfate groups of carrageenan form hydrogen bonds with the hydroxyl groups of cellulose fibers, thereby increasing the physical strength of paper [24].

Experiments with the addition of bentonite as a wet strength agent can increase the resistance of paper in wet conditions compared to blank. From the second experiment, the following results were obtained, the lowest value was at a dose of 10%, which was 2.37%, while the highest value was at a dose of 14%, which was 2.55%. The negative charge of bentonite will be absorbed by the surface of the paper, thereby increasing the strength of the paper in wet conditions compared to without the addition of bentonite. If polyamidoamine epichlorohydrin (PAE) resin is added, the wet strength value will increase even more, because the negative charge of bentonite will bind to the positive charge of PAE and be absorbed by the surface of the paper fibers, so that more PAE is retained in the paper compared to without the addition of PAE [24].

In the third experiment, adding a mixture of carrageenan and bentonite as an agent could increase the ability of the paper in wet conditions. The value obtained from this experiment was with a 10% dose of 1.87% for the lowest value, while the highest value was obtained with an additional 14% dose of 2.12%. From these experiments it can be concluded that a mixture of carrageenan and bentonite can increase the ability of paper in wet conditions. If you add polyamidoamine epichlorohydrin (PAE), the wet strength value will increase even further, because bentonite has a high cation exchange capacity, so the negative charge of bentonite will bond with the positive charge on PAE and the addition of carrageenan will really help the performance of bentonite [24].

3.5 Effect of Adding Agent on the Cobb Test

The Cobb test or water absorption capacity is the ability of paper to absorb water between the fibers. Solvation or solution is formed from water which binds to cellulose fibers, causing the paper to become soft and damaged. How much water is absorbed in paper is very dependent on the bonds of the cellulose fibers [21, 22]. The Cobb test testing method uses ISO 535, shown in Figure 7:

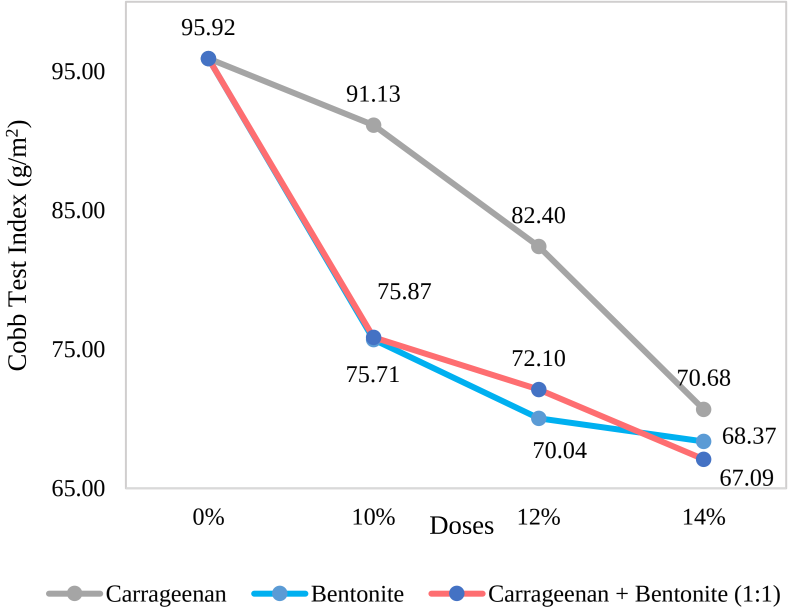

Fig. 7. Graph of the Effect of Adding Agent on the Cobb Test

Figure 7 shows that in the first experiment with the addition of carrageenan the highest value was at a dose of 10% of 91.13 g/m2, while the lowest value was with a dose of 14% of 70.68 g/m^2. In the second experiment with bentonite as the agent, the highest value was at a 10%

dose of 75.71 g/m^2, while the lowest result was at a 14% dose with a Cobb value of 68.37 g/m^2. Finally, in the third experiment, by mixing carrageenan and bentonite as wet strength agents, the highest value was at a 10% dose of 75.87 g/m^2, and the lowest value was at a 14% dose of 67.09 g/m^2. Based on the overall results of the experiment, it can be concluded that the Cobb test value for each dose of carrageenan, bentonite or a mixture of the two decreases as the number of agent doses increases. The hydrophobic nature of the additive agent influences the decrease in the Cobb test value. The additives contained in this agent change the hydrophilic nature of cellulose to hydrophobic so that water absorption is reduced [21, 22].

Previous research used carrageenan and benonite as dry strength agents to improve the physical quality of MG paper. Optimal results for carrageenan at a dose of 7.5 Kg/T, bentonite at 5 Kg/T and a mixture of carrageenan and bentonite optimal results at a dose of 5 Kg/T. Based on this research, it can be implied that carrageenan, bentonite, along with a mixture of carrageenan and bentonite in a 1:1 ratio are wet strength agents [24]. However, previous research still included additional synthetic agents in its manufacture, whereas this research only uses natural agents.

4 Conclusion

After conducting research, it can be concluded that carrageenan and bentonite have potential as wet strength agents in making nautical chart paper. The optimal opacity obtained from adding carrageenan was found at a dose of 12%, amounting to 97.33%, when adding bentonite, it was found at a dose of 14% with a value of 96.90%, while adding a mixture of the two optimal results were obtained at a dose of 14% with a value of 98.90%. The optimal tearing index obtained from adding carrageenan was at a dose of 14% with a value of 495.19 mN, when adding bentonite at a dose of 14% with a value of 413.30 mN came out as the optimal value and by adding a mixture of the two the optimal value was obtained at a dose of 14% with value of 745.87 mN. The optimal tensile index when adding carrageenan was obtained at a dose of 14% with a value of 0.90 kgf/15mm, the addition of bentonite obtained optimal results at a dose of 14% at 1.58 kgf/15mm, while adding a mixture of the two optimal results were obtained at a dose of 14% with a value of 1.32 kgf/15mm.

The wet strength index for adding carrageenan obtained optimal results with a dose of 14% of 1.45%, optimal results for adding bentonite of 2.55% with a dose of 14%, while adding a mixture of the two obtained optimal results of 2.12% with a dose of 14%. %. Cobb test on the addition of carrageenan obtained an optimal result of 70.68 g/m2 with a dose of 14%, on the addition of bentonite the optimal result was 68.37 g/m2 with a dose of 14%, while adding a mixture of the two obtained an optimal result of 67.09 g/m2 with a dose of 14%. The most optimal result and close to the parameters of the TNI AL Pushidrosal nautical chart paper is the addition of a mixed agent between carrageenan and bentonite with the following tearing strength results obtained, at a dose of 10% a value of 709.95 mN is obtained, at a dose of 12% a value of 720.00 is obtained. mN and the highest value was found at a dose of 14% of 745.87 mN.

For further research, you can display the SEM (Scanning Electron Microscopy) test results, so you can determine the bond between the agent and the paper fibers. It is necessary to add synthetic resin so that the ability of carrageenan and bentonite to bind between cellulose fibers is more optimal and can meet the standardization of TNI AL Pushidrosal nautical chart paper. It is necessary to calculate the cost ratio between synthetic wet strength agents and organic wet strength agents, so that the costs incurred are more efficient.

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