Wet Strength Improvement of Pineapple Leaf Paper for Evaporative Cooling Pad

T. Khampan, N. Thavarungkul, J. Tiansuwan, and S. Kamthai

Abstract**—**This research aimed to modify pineapple leaf paper (PALP) for using as wet media in the evaporation cooling system by improving wet mechanical property (tensile strength) without compromising water absorption property. Polyamideamine-epichorohydrin resin (PAE) and carboxymethylcellulose (CMC) were used to strengthen the paper, and the PAE and CMC ratio of 80:20 showed the optimum wet and dry tensile index values, which were higher than those of the commercial cooling pad (CCP). Compared with CCP, PALP itself and all the PAE/CMC modified PALP possessed better water absorption. The PAE/CMC modified PALP had potential to become a new type of wet media.

Keywords**—**wet strength, evaporative cooling, pineapple leaves, polyamideamine-epichorohydrin, carboxymethylcellulose.

I. Introduction

GLOBAL warming situation nowadays greatly affects worldwide agriculture industry. Such the environmental conditions directly impact on agricultural buildings, which in turn impact on quantity and quality of agricultural products. The inevitable consequences manifest itself in Thailand, known to be one of the world's major agricultural countries. Recently, the agro-industrial businesses in Thailand have grown rapidly and lead to exporting a large amount of agriculture products, e.g. rubber, canned pineapple, chicken meat, orchid, etc. In keeping pace of the business growth, conventional farming shelters of animals and plants have been changing into agricultural buildings such as animal houses and greenhouses. Ventillation and temperature of such farmings plays an important role in producing agricultural products. Agricultural buildings with air temperatures of higher than 40^{o}C may cause thermal stress [1]. The thermal stress in greenhouse affects stem strength, seed insemination, fruit set and size, and flowering negatively [2], [3]. Thermal stress in animal house can cause low weight, less egg and less milk [4], [5].

Evaporative cooling system has been employed to improve the agricultural building environment. The system could reduce temperatures by 4-13 ^{o}C [1] which leads to thermal stress reduction. Heat and mass exchange of water and air in the evaporative cooling system takes place in wet media (evaporative cooling pads). Currently, in Thai markets, most wet media and materials used to produce the wet media are imported. Their high costs limit the usages for small local farming enterprises. Development of local wet media using local raw material is an alternative to support the local farming.

The wet media in the evaporative cooling system require good water absorption, high antimicrobial strength, good weathering resistance, and high wet strength. At present, wet media can be made of varieties of materials such as paper, plastic, or glass fiber. All above mentioned, paper is the best due to its good water absorption. Major raw material for paper is cellulose, which can be obtained from agricultural waste. In Thailand as one of the top five biggest pineapple export country [6], pineapple leaves are abundant. Using pineapple leaves for wet media paper is not only cost reduction but also value-added to the waste, and conserves environment as well.

However, pineapple leaf paper, like other types of non-treated paper, still lacks of wet strength. The wet strength resin then comes into play. The functions of wet strength resin are to protect fibers from water and to provide reinforcement mechanisms in the paper [7]. Examples of these substances are urea-formaldehyde resins (UF), melamine-formaldehyde resins (MF), polyamideamine-epichorohydrin resins (PAE), and glyoxalated polyacrylamide resins (G-PAM) [8]-[13].

In general, these urea-formaldehyde resin and melamine-formaldehyde resins contain toxic formaldehyde group [8]. Glyoxalated polyacrylamide resin forms temporary bonding, which is not good for wet strength improvement. However, polyamideamine-epichorohydrin (PAE) resin does not contain formaldehyde group and bonds with fibers under neutral or weak base. Among other wet strength resins, PAE is the most widely used. However, it is due to its limitedadsorption to the cellulose fibers, another chemicals was added [10], [11]. PAE mixed with carboxymethylcellulose (CMC) was found to increase the surface adsorption on the cellulose fibers, which improves wet strength of handsheets more than using only PAE [10], [11].

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This research then aimed to prepare handsheet paper from pineapple leaves for wet media application. The PAE:CMC ratios were investigated to improve wet strength. A comparison between PALP and the commercial cooling pad paper was done to confirm the required properties.

II. Materials and Methods

A. Materials

Materials used in this work were Pineapple leaves from Prachuab Kiri Khan province Thailand, Sodium hydroxide (NaOH) commercial grade for pulping process, NaOH analytical grade for pH adjustment, wet strength resin - Polyamideamine-epichorohydrin resins (PAE) with solid content of 12.5% from Clariant, Carboxymethylcellulose (CMC) - Finnfix30 from Noviant, and a commercial cooling pad (CCP).

B. Experimental Procedure

Preparation of paper and coating solutions:

a) Pineapple leaf paper (PALP)**:** PALP was made from closed system soda pulping process using 4% w/w based on oven dried raw material, liquor to material ratio of 10:1 (ml/g) at 105°C for 40 min. Each handsheet was 120 g/m^2, which was comparable to that of CCP.

b) PAE solution: PAE with solid content of 12.5% was diluted with water to 2.5% wt. NaOH analytical grade was used to adjust the solution pH to 7.

c) CMC solution: CMC 5g was dissolved in 1 litre of water using magnetic stirrer at 50-60 °C.

d) PAE - CMC solution: Mixed solution b) with solution c) in the following ratios: 100:0, 0:100, 80:20, 60:40, 40:60, and 80:20 (v:v).

Strengthening of paper

Soaked the paper prepared in a) into solution b), c), or d) for 20 s, and heated at 110 °C for 10 min in an oven. All the samples were signified as shown in Table I

TABLE I
SHEETS DESCRIPTION

Paper	Label
Commercial cooling pad	CCP
Non- treated pineapple leaf paper	PALP
PAE treated PALP	PAE
CMC treated PALP	CMC
PAE:CMC of 80:20 treated PALP	P80:C20
PAE:CMC of 60:40 treated PALP	P60:C40
PAE:CMC of 40:60 treated PALP	P40:C60
PAE:CMC of 20:80 treated PALP	P20:C80

C. Characterization

Samples were tested according to TAPPI standard test methods: T494 om-96 for dry tensile strength and T441 om-90, cobb's test, for water absorption. All testing standards were conducted at 23°C and 50%RH. The test methods were applied to both dry and wet papers. For dry ones, all samples were left at the conditions for 24 hours prior to testing. For wet ones, papers were soaked in distilled water for 10 min, then dried by blotting paper.

Fibers and their arrangements were studied using scanning electron microscope (SEM), JEOL JFM580, at 20 kV. Samples were gold coated prior to entering the vacuum chamber.

III. Results and Discussion

TABLE II
MECHANICAL PROPERTIES PAPER TREATED WITH PAE, CMC, AND PAE/CMC

Type of paper	Tensile index (kNm/kg)		Water Absorption (g/m^2)
	Dry	Wet	
CCP	34.13±0.55	16.75±0.15	81±0.95
PALP	31.41±0.49	1.44±0.23	134±1.5
PAE	32.26±1.21	13.57±0.42	115±1.64
CMC	33.58±0.45	1.22±0.12	154±1.43
P80:C20	35.39±0.73	17.57±0.37	117±1.73
P60:C40	36.41±0.8	14.97±0.85	126±1.8
P40:C60	28.63±0.91	6.5±0.58	149±1.83
P20:C80	26.01±1.41	3.51±0.56	148±1.91

Tensile indices and water absorption of all types of paper were presented in Table II. The findings were discussed separately in the followings:

A. Mechanical Properties

The tensile indices of non-treated and treated pineapple leaf papers were shown in Table II and Fig. 1.

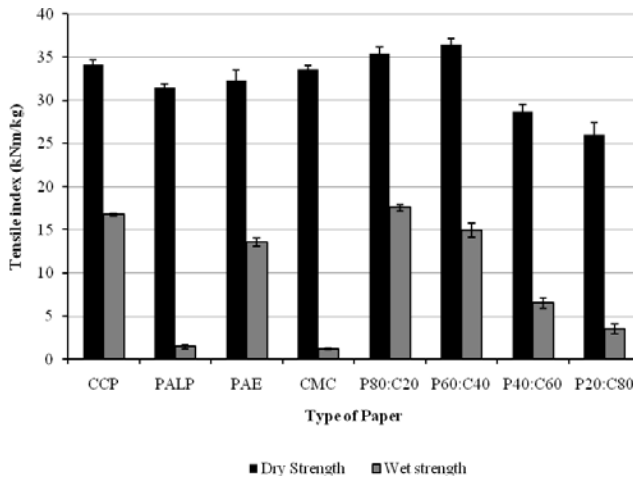

Fig. 1 The wet and dry tensile indices of different types of paper

The sole PAE and sole CMC treated samples gave higher dry tensile indices than non-treated PALP. For PAE, T. Obokata and A. Isogai [12] and D. Braga, G. Kramer, R. Pelzer, and M. Halko [13] stated that co-crosslinking and homo-crosslinking were responsible for paper strengthening. However, the two groups of researchers reported different mechanisms. T. Obokata and A. Isogai [12] explained that azetidinium groups of PAE forms ester bonding with carboxyl group of fibers called co-crosslinking (polymer-fiber bonding); and carboxyl group at the end of PAE and azetidinium group of PAE forms ester bonding called homo-crosslinking. On the other hand, D. Braga, G. Kramer, R. Pelzer, and M. Halko [13] presented co-crosslinking as the reaction of azetidinium groups with hydroxyl group of cellulose; and homo-crosslinking as the reaction of azetidinium groups with secondary amine. For CMC, E. Kontturi, M. Mitikka-Eklund and T. Vuorinen explained that fiber-fiber bond (inter-fiber bond) was strengthened upon CMC sorption [14].

Among the samples treated with PAE combined CMC, P80:C20 and P60:C40 had the highest dry tensile indices. Reference [11] mentioned that PAE in combination with CMC were polyelectrolyte complexes which imparted synergistic property. However, the dry tensile indices of P40:C60 and P20:C80 were less than that of non-treated PALP. Generally, in dry condition, there are contacts between fibers by hydrogen bonding of hydroxy groups. In wet condition, water would penetrate through fiber causing swelling [15]. This action went on until inter-fiber bonding was completely broken resulted in less strength in treated paper comparing to non-treated. Rather than one time experience of chemical solution in the pulping process, treated PALP, upon treatment, was again soaked with different chemical solutions. As a result, fibers were wet for the second time which weakened the inter-fiber bonding. Unlike the P80:C20 and P60:C40 samples, precipitations from the chemical solutions of P40:C60 and P20:C80 were observed. Activities of the PAE in combination with CMC in strengthening the paper may be reduced via the precipitation reactions. The origin of the reaction is out of the scope of this study.

For the wet strength, while the sole PAE treated sample gave higher wet strength than the non-treated PALP, CMC did not so contribute. CMC under the wet condition may rather form hydrogen bonding with abundant H_2O than with cellulose which lessened the fiber-fiber bonding achieved in dry condition. However, synergy between PAE and CMC were still observed for all PAE in combination with CMC treated samples even though some precipitations were found in the case of P40:C60 and P20:C80. All the PAE - CMC treated samples gave higher wet strength than non-treated PALP. The same reason of inter-fiber bond weakening in the second time experience of wetting mentioned beforehand can be applied. Under the wet testing condition, inter-fiber bond of the non treated PALP was weakened, whereas, in the treated samples had polyelectrolyte complexes to function.

As the amount of PAE in the PAE:CMC decreased from 80:20 to 20:80 for the treated PALP, the wet strength decreased. It can be explained that PAE played a major role in strengthening the paper since it is a wet strength resin which formed covalent bond with cellulose, while, CMC attracted cellulose with hydrogen bond.

In Fig.1, PALP appeared to have lower dry and wet tensile indices than did CCP. Usually, the strength of paper was dependent on the extent of bonding and the strength of fiber-fiber bond [14]. Fig.2 depicted that PALP was composed of shorter fiber than CCP resulted in lower the extent of inter-fiber bonds which, in turn, lowered the mechanical property.

Fig.1 also showed that both wet and dry tensile strength could be improved upon treatment as treated PALP gave higher strength than CCP even though PALP fibers were shorter. The improvement was as well due to the prior mentioned mechanisms of polymer-fiber and/or fiber-fiber bondings.

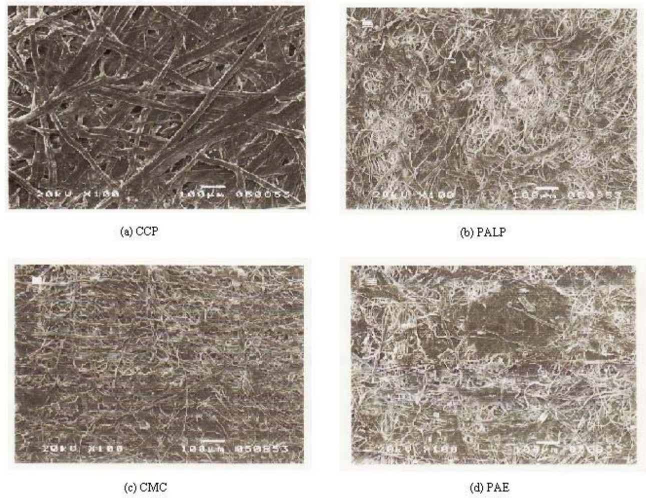

Fig. 2 SEM micrograph of different types of paper

B. Water Absorption Properties

Water absorption values of different types of paper were presented in Table II and Fig.3.

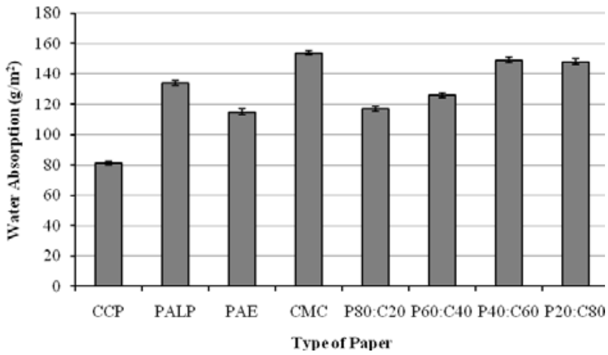

Fig. 3 The water absorption of different types of paper

Water absorption values of PAE treated PALP appeared to be lower than that of non-treated PALP. The PAE-cellulose bonding or polymer-fiber bonding in PAE treated PALP hindered contacts between water and fibers, On the other hand, CMC treated PALP gave higher water absorption than PALP. This could be due to the hydroxy groups of CMC formed hydrogen bonds with water. The water hindrance of PAE and the hydrophillic of CMC resulted in the increasing of water absorption as the amount of CMC increasing in treated PALP starting from PAE:CMC of P80:C20 to P20:C80.

Normally, CCP would be treated with wet strength resin which attained polymer-fiber bond. As a result, CCP exhibited lower water absorption than non-treated PALP and all treated ones.

Even though P80:C20 and P60:C40 did not give the highest water absorption, with the mechanical properties and water absorption which surpassed those of CCP, the treated PALPs were applicable to evaporative cooling pad.

IV. Conclusion

In this work, papers for evaporative cooling application were prepared employing waste from pineapple plantation, pineapple leaves. Handsheets of pineapple leaf paper (PALP) were formed using pulp obtained from soda pulping process. Dry and wet strengths of PALP were improved by modifying with Polyamideamine-epichorohydrin resin (PAE) and/or carboxymethylcellulose (CMC). PAE:CMC ratios investigated were 100:0, 0:100, 80:20, 60:40, 40:60, and 20:80. The treated PALPs with PAE:CMC ratios of 80:20 and 60:40 gave wet strengths of about 18 and 15 kNm/kg and water absorption of 117 and 126 g/m^2, respectively. The wet strengths of the samples were comparable to that of commercial cooling pad (17 kNm/kg), whereas, the water absorptions surpassed that of the commercial one (81 g/m^2). As a result, treated PALP showed a potential for evaporative cooling application.

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