IMPROVEMENT OF HARDWOOD KRAFT PAPER WITH NARROW-LEAVED CATTAIL FIBER, CATIONIC STARCH AND ASA

WARANYOU SRIDACH[*] and RUETHAMRONG PALADSONGKHRAM[**]

[*]*Prince of Songkla University, Faculty of Agro-Industry, Department of Material Product Technology, Songkhla, Thailand*
[**]*Phuket Rajabhat University, Phuket, Thailand*

Received May 21, 2013

The mechanical properties of short-fibered papers can be improved by non-wood fibers and wet end additives. Hardwood (*Trema orientails* (L.) Blume) affords short-fibered pulps, which are generally characterized by a lower strength. The blending with narrow-leaved cattail (*Typha angustifolia* L.) pulps, which are non-wood fibers, can greatly enhance the strength of short-fiber papers. This enhancement is due to the fiber length and fiber bonding of non-wood fibers, which closely resemble those of softwood pulps. An increased ratio in the mixing of non-wood fibers has resulted in an increase in paper strength. Cationic starch has been used as a wet end additive to improve dry strength with significant success. All mechanical properties were found to be increased by increasing the cationic starch added. However, the optimal dosage of cationic starch was of about 5% by dry weight of pulp. The water repellence in paper-making was improved by the use of an alkenyl succinic acid anhydride (ASA) emulsion. ASA emulsion doses of 0.5 kg/t pulp slurry (1% consistency) contributed to a desirable level of water absorption. Therefore, the blends of narrow-leaved cattail pulps, cationic starch and ASA emulsion that were prepared resulted in considerable improvement in the hardwood pulps used for packaging paper.

Keywords: short-fibered pulp, non-wood fibers, narrow-leaved cattail, cationic starch, ASA emulsion

INTRODUCTION

The increasing shortage of wood as a raw material has driven paper makers to search for alternative fiber sources. Research on new alternative sources of cellulosic fiber has been underway during the last three decades to find and develop new fiber supplies for paper-making. Plants and annual crops growing naturally have been studied for their suitability as alternative sources of raw material for paper-making. Fiber prepared from timber sources can be successfully supplemented by non-wood fibers. The benefits of non-wood plants as a fiber resource include their fast growth and smaller amounts of lignin content, which alleviates the amount of energy and chemicals used during pulping.[1-4] They can be used as an effective substitute for the depleting forest wood resources.

However, the source of the non-wood pulp is limited and these materials come from crops planted specifically to yield fiber.[5-6] Furthermore, the specific physical and chemical characteristics of non-wood fibers have an essential role in the technical aspects involved in paper production. Thus non-wood fibers are usually mixed with the wood fibers for substituting part of the hardwood kraft pulp in paper-making. The reason for the use of fiber mixtures is that certain fibers contribute to strengthening the properties of paper.

Many non-wood fibers are currently used in the pulping and paper-making process. Straw, bagasse, jute, kenaf and bamboo are the primary agricultural fibers used in commercial pulping operations.[7-9] Other agricultural fibers, such as narrow-leaved cattail, also possess characteristics suitable for paper-making.

The narrow-leaved cattail (*Typha angustifolia L.*) is a member of the *Gramineae* grass family, which includes rice, corn, wheat, oats, barley, and rye. Cattail is an easy-growing water plant that can be found throughout wetland areas. It is widely used in constructed wetlands for the treatment of wastewater and contaminated soil.[10-

[11] Leaves and stems have been used as bedding, thatching, matting and in the manufacture of baskets, boats, rafts, shoes, ropes, and paper.[12] Cattail is a source of lignocellulosic fibers. Narrow-leaved cattail fibers have an average length of 19 mm and an average diameter of 41 μm. Thus they have been proposed as a source of long fiber to mix with hardwood fibers for strengthening and enhancing paper. However, the improvement of the mechanical properties arising from these constituents in a paper sheet can be achieved by increasing the bonding among the cellulose fibers. A number of polymer materials have been applied to increase the interfiber bonding among cellulose chains in the paper sheets formed.

Cationic starches are the most commonly used to add dry strength, but they can also be used as a fines retention aid in the paper industry.[13-14] They are chemically modified starches, which ionize with a positive charge. The cationic charges on the starch promote strength adsorption onto fibers, fines and fillers through electrostatic attraction to the negative charges on the surface of fibers and particles. The surface charge of fibers results from the carboxyl groups in cellulose and hemicellulose, which represent a source of negative charges on fibers for the adsorption of cationic starch. Cationic starch creates bridges between fibers and the free glucose hydroxyl groups of starch and participates in hydrogen bonding with the surface of cellulose fibers.[15] Therefore, it is added to the paper suspension to improve the mechanical properties of paper and the retention of the components of the paper.[16] Other advantages of cationic starch are a high degree of dispersion and high retention by wood fibers. It can be used as a stabilizer in sizing emulsion for paper-making.[17]

Alkenyl succinic acid anhydride (ASA) is the synthetic sizing agent used in alkaline paper-making. ASA size is a petroleum-derived liquid, which occurs from the reaction of the alkene chain and maleic anhydride. At room temperature, ASA is typically a yellow, oily liquid with extremely low water solubility. It is added to the pulp stock in the form of a cationic starch-stabilized emulsion, because this agent has limited stability in the pulp suspension. ASA is able to impart various degrees of resistance to the liquid penetration of paper products by altering the wettability of the cellulose fibers in the sheet making process.[18-19] It reacts relatively rapidly and develops sizing quickly on the paper machine and does not need external heat to proceed to a significant extent. ASA sizing emulsion is also easy to handle, need not be prepared in the paper mill and does not require special storage measures. ASA is used most often in fine papers, gypsum board, corrugated paper, envelope paper and for a few other applications.[18]

There are many studies available on the blending of hardwood fibers with softwood fibers.[20-26] However, the blending of hardwood fibers with non-wood fibers seems to have received less attention. Blending hardwood fibers with non-wood fibers is, possibly, a physical improvement that relies on interaction among fibers. This paper investigates the potential use of non-wood fiber (narrow-leaved cattail) for the partial substitution of hardwood pulp in paper-making and also the use of wet end additives, such as cationic starch and ASA size, for enhancing the quality of the paper produced.

EXPERIMENTAL

Materials

The fibrous raw materials used in this research were Peach cedar (hardwood fiber) and narrow-leaved cattail (non-wood fiber). They were collected from Pattani province, Thailand. Peach cedar (*Trema orientalis* (L.) Blume) was debarked and manually chopped to 2-3 cm pieces. Narrow-leaved cattail (*Typha angustifolla* L.) was cleaned, dried and chopped into 2-3 cm long pieces. The chemical composition of both was determined according to the respective standard methods: ash content (TAPPI T211 om-93); pentosan (TAPPI T223 cm-84); cellulose and lignin content.[27]

The chemicals used in the kraft pulping process were sodium hydroxide (NaOH) and sodium sulfide (Na_2S). They were purchased from AGC Chemicals (Thailand) Co., Ltd. The internal sizing agents were cationic starch and alkenyl succinic anhydride. Commercial cationic starch (ExcelCat@35) was obtained from Siam Modified Starch (Thailand) Co, Ltd. A commercial ASA sizing emulsion (18ASA) was obtained from Buckman Laboratories (ASIA) Pte Ltd (Singapore), and has been described in U.S. Pat. No. 20080277084A1.[28]

Methods

Kraft pulping process

The chips of Peach cedar and narrow-leaved cattail were cooked using the kraft pulping process. The sulfidity and the effective alkali (as NaOH) used on the Peach cedar were 40% and 23%, respectively. The pulping conditions of the Peach cedar employed were as follows: liquor-to-material ratio of 8:1; maximum temperature of 160 °C; time to maximum cooking temperature of 87 minutes; and cooking time of 150 minutes.

For the narrow-leaved cattail, the cooking chemicals were 22% effective alkali (as NaOH) and 20% sulfidity. The liquor to narrow-leaved cattail was 8:1. The cooking temperature was raised from an ambient temperature to 160 °C in 87 minutes at the rate of 1.5 °C per minute. The cooking time at the maximum temperature was maintained for 120 minutes.

Figure 1: Contact angle of paper at 1 and 60 seconds

Table 1
Some chemical and morphological characteristics of Peach cedar and narrow-leaved cattail

Items	Type of fibers	
	Peach cedar	Narrow-leaved cattail
Chemical characteristics		
Cellulose content (%)	58.91	42.61
Ash content (%)	1.20	12.56
Lignin content (%)	16.20	5.75
Pentosan (%)	7.65	23.90
Morphological characteristics		
Fiber length (mm)	1.3	19.0
Fiber diameter (µm)	18.9	41.8

After the cooking was completed, the pulps were washed on a laboratory flat stationary screen, with a 200 mesh wire bottom, to remove the residual cooking chemicals. The screened pulps were characterized without being further refined. The fiber length and fiber diameter were determined by a projection microscope.

Blending and handsheet making

Peach cedar pulps was mixed with narrow-leaved cattail pulps in the ratios of 100:0, 90:10, 80:10, 70:30, 60:40 and 50:50 by weight. Handsheets of 60 g/m^2 were prepared according to the TAPPI standard method (T221 cm-99). The pulp sheets were conditioned at 23$\pm$1 °C and 50$\pm$2% RH for at least 24 hours before testing. The physical properties of the mixed pulp sheets were measured with the appropriate TAPPI Standard methods, such as assessing the tensile index (T494 om-88), bursting index (T403 om-91) and tearing index (T414 om-88). They were compared to the national standards applied to kraft paper specifications (wrapping paper) of Thailand.[29]

Addition of cationic starch to paper sheets

The cationic starch solution was prepared by dissolving in distilled water and heating in a water bath at 90 °C until the starch was completely gelatinized. The concentration of the cationic starch solution was in various dosages of 2.5, 5.0, 7.5 and 10% based on the oven-dried weight of the pulp. The mixed paper furnish was disintegrated at 5000 rounds before forming the handsheets. The mechanical properties of the paper sheets were then determined according to TAPPI Standard methods.

Addition of ASA sizing to paper sheets

The commercial ASA sizing emulsion was poured into the mixer and disintegrated with pulp suspension at 5000 rounds before forming a handsheet. The concentration of ASA sizing emulsion was in various dosages of 0.25, 0.5, 0.75 and 1.0 kg/t pulp slurry (1% consistency). The measurements using both contact angle and Cobb$_{60}$ tests were done to observe the wettability of the paper sheets formed. The water absorption of the blended paper sheets was measured by the Cobb test method (TAPPI T441). The contact angle of a liquid drop on the surfaces of the paper sheets was measured at 1 and 60 seconds after dripping took place (Figure 1). A contact angle measuring instrument was used (Model OCA 15 EC, from Data Physics Instruments GmbH, Germany). The mechanical properties, such as tensile index, bursting index and tearing index, were investigated according to the TAPPI standard methods.

RESULTS AND DISCUSSION

Chemical and morphological characteristics of Peach cedar and narrow-leaved cattail

The chemical composition and fiber morphology of Peach cedar and narrow-leaved cattail are shown in Table 1. The chemical composition of Peach cedar had tremendous variations compared to the narrow-leaved cattail pulp. Peach cedar pulp was rich in cellulose (58.91%) and lignin content (16.20%), as illustrated in Table 1. These are important parameters for the pulping process and pulp yields. The ash content of Peach cedar (1.20%) was lower than normally found in non-wood fiber and in the narrow-leaved cattail, which was 12.56%. This high ash content, derived from silica and mineral substances, may have negative effects during the pulping and paper manufacturing processes, especially in the bleaching, refining and recovery of the cooking liquor.[2] Pentosan was found chiefly in the pulps that yielded xylose and arabinose on hydrolysis. The pentosan content of the narrow-leaved cattail (23.90%) was higher than that of Peach cedar and hardwood fibers. Thus there was a greater amount of hemicellulose available, which ensures a stronger paper pulp. This higher pentosan content is, therefore, desirable.[30]

The morphological characteristics of both are shown in terms of the fiber length and fiber diameter. The mean length and diameter of the Peach cedar fibers were of 1.3 mm and 18.9 µm, respectively. The narrow-leaved cattail fibers had an average length of 19 mm and a diameter with an average of 41.8 µm. The fiber length of narrow-leaved cattail fibers was practically similar to the bast fiber of hemp (*Cannabis sativa*). Dutt *et al*.[31] reported that the average length and diameter of hemp (bast) was 20 mm and 22 µm, respectively. It had characteristics similar to those of softwood fibers. The morphological characteristics of *Cannabis sativa* resemble those of the narrow-leaved cattail fibers.

Effect of pulp blending on paper properties

The effects of the mixing ratio between hardwood and non-wood fibers on the pulp sheet characteristics are discussed in terms of tensile index, tearing index and bursting index. These properties suggested the durability of the blended pulps for utilization. They are shown in Figures 2-4.

The tensile strength is one of the basic strength properties tested on pulps and paper. It is a measure of the breaking resistance of paper sheet under tension, which is dependent on the fiber strength, fiber length, the surface area of fibers, and also the bonding strength between them.[32] The tensile index is similar to the notion of tensile strength, but is obtained by dividing the tensile strength by the basic weight of the paper sheet.

The tensile indices of the blended pulp sheets (sheets composed only of pulps, with no additives such as starch, ASA etc.) are shown in Figure 2. The pulp sheets made of mixed pulp of Peach cedar (hardwood) and narrow-leaved cattail (non-wood plant) in the ratio of 50:50 (by weight) showed the highest tensile index (57.79 ± 2.26 Nm/g). However, it was not significantly different from that of the mixed pulp sheet in the ratio of 60:40, which was 57.51 ± 1.39 Nm/g. By comparing the tensile indices of the pulp sheets with the specifications for kraft paper, it can be seen that the pulp sheets with all ratios of mixing exhibited higher values in terms of tensile indices than those of kraft paper with standard specifications (32.31 Nm/g). The fiber length was considered to be important for the strength of the pulp sheets. The strength of pulp sheets was directly proportional to fiber length and dictated its final use.

Hardwoods are characterized by their short fibers, which makes developing their strength more difficult. Thus it is appropriate to blend long fiber pulp with short fiber pulps, because this enhances the strength and formation of the paper.[33] The higher the weight percentage of the narrow-leaved cattail fibers, the greater the interfiber bonding and paper strength of the pulp sheets. This was because the narrow-leaved cattail fibers were generally longer and more flexible than the hardwood fibers. Fiber length is believed to play a role in the tensile strength of paper.

Furthermore, the amount and quality of fiber bonding is another important factor affecting tensile strength.[34] The morphology of narrow-leaved cattail fiber, such as fiber width and cell wall thickness, correlated positively to the swelling and forming of interfiber bonds for the development of tensile strength.[35]

The burst strength is the amount of hydrostatic pressure required to rupture a piece of paper. It is highly correlated to the tensile strength.[36] The burst index is calculated by dividing the burst strength by the basic weight of the paper sheet. The results in Figure 3 indicate that the burst indices of the mixed pulp sheets increased with an increase of the long fiber in the paper furnishes. The pulp sheets mixed between Peach cedar and narrow-leaved cattail in the ratio of 50:50 (by weight) afforded the highest burst index, as seen in Figure 3.