Red Algae Pulp and Its Use in Papermaking

YUNG BUM SEO*, YOUN WOO LEE†, CHUN HAN LEE†, HACK CHUL YOU†, and SUNG MIN BOO‡

*: Professor, Dept. of Forest Products, Chungnam Univ., Daejun, Yousung-Gu, Gung-Dong, Republic of Korea, ybseo@cnu.ac.kr

† : Pegasus Research Co.

‡ : Chungnam National University

ABSTRACT

Red algae were used to make bleached pulp, from which paper handsheet samples were made. Red algae consists of rhizoidal filaments, epidermal tissues whose color were reddish, mucous carbohydrates, and other minor elements. Rhizoidal filaments of high brightness were obtained after extracting out mucous carbohydrates, and bleaching the remainder by using bleaching chemicals. The sizes and shapes of several rhizoidal filaments (or red algae pulp) from different red algae species were examined, and their handsheet properties were compared. Transparent and transluscent high density paper samples were made without applying refining process from the red algae pulp. White paper samples with good printability and excellent formation were made. We are developing pilot scale pulping and papermaking facilities at this time.

INTRODUCTION

There are over 10,000 described species of red algae[1]. Dring[2] reported that 27.1% of all known species of marine plants are red algae. Sheath[3] estimated the fresh water red algae represents about 3% of the total number of red algae species. Although red algae have been consumed by humans for at least 2,800 years, their full agronomic and biotechnological potential has yet to be realized. The utilization of red algae was suggested in the area of polyelectrolytes, pharmaceutical products, human nutrition, antimacrobial activity, polysaccharide production, etc[4].

Chemical composition of red algae consists of mostly polysaccharide, much less protein, trace of lipid, and inorganic materials. We tried to use red algae for the production of papermaking raw

material to replace wood fibers. In the cells of red algae, there are large amounts of mucilage materials such as agarose and carrageenan, which can be easily extracted by hot water and weak, environment-friendly chemical treatment. After extraction of mucilage materials, the red algae cells are bleached to be used for papermaking raw materals. We used mostly the red algae (*Rhodophyta* in scientific classification) in the family of *Gelidiaceae,* where three types of genera such as *Gelidium, Pterocladia,* and *Acanthopeltis* exist. The shape, the growing rate, and the amount of rhizoidal filament in the *Gelidiaceae* can be the criteria of utilization in pulp and paper area.

The extracted mucilage materials are mostly carbohydrates, whose chemical compositions are mainly agarose and carrageenan. People used to use mostly the extracted mucilage materials for food and other applications until this time, but almost no attention was given to the remainder after extraction. Some commercial agar plants in asia give the remainder after extraction away to farmers as natural fertilizer. In the preparation of papermaking raw materials, the quality and the amount of the remainder after extraction, most of which consist of rhizoidal filaments, are critical for economic potential. In this paper, we tried to introduce a new type of papermaking raw materials from red algae briefly, which could give more abundant quantity per year globally than wood fibers. The average growing rate of some red algae is more than 10% per day in mass during growing season[5,6].

PREPARATION OF RED ALGAE PULP FOR WHITE PAPER

Many species of red algae were used for the preparation of red algae pulp such as *Gelidium amansii, Gelidium asperum, Gelidium chilense, Gelidium robustum, Pterocladia capillacea, Pterocladia lucida, Acanthopeltis longiramulosa,* and so on. The shape and the amount of rhizoidal fillaments were different one another. The quality and the amount of mucous materials, which were extracted out in the extraction process, were different one another, too. Sometimes, we used chemicals in the extraction process to enhance the extraction, and to make ease in bleaching process. Some of the chemicals we used include oxygen, alkali, and sodium hydrosulfite. However, we will introduce the cases where no chemicals were used in the extraction process, and where only *Gelidium amansii* and *Gelidium chilense* were used in this paper.

Table 1 showed the extraction and the bleaching conditions of the two red algae species such as *Gelidium amansii* and *Gelidium chilense* for the preparation of white paper samples. Table 2 showed the properties of handsheets from those pulps.

From Table 1 and 2, it was observed that the red algae pulp yield decreased as extraction temperature increased or the number of extraction stage increased. When strong acid is add in the extraction process (GC3), pulp yield decreased by 5-8%. To make the pulp brightness up to

75%, red algae pulp yield by water extraction method seems to be around 14-17%.

Table 1. Extraction and bleaching conditions of the red algae

Species	Extraction process		Bleaching Process		
	1st	2nd	O_3	ClO_2	H_2O_2
Gelidium amansii (GA1)	50°C 3hr	-	-	Y	Y
Gelidium amansii (GA2)	120°C 2hr	110°C 1hr	Y	Y	Y
Gelidium amansii (GA2)	110°C 2hr	120°C 1hr	Y	Y	Y
Gelidium chilense (GC1)	120°C 2.5hr	-	Y	Y	Y
Gelidium chilense (GC2)	130°C 2.5hr	-	Y	Y	Y
Gelidium chilense (GC3)[1]	130°C 2.5hr	-	Y	Y	Y
Gelidium chilense (GC4)	100°C 3hr	-	Y	Y	Y
Gelidium chilense (GC5)[2]	100°C 3hr	-	Y	Y	Y
Gelidium chilense (GC6)[3]	100°C 3hr	-	Y	Y	Y

1: Starting pH 2.5 by HCl addition; 2: Electrolyzed anode water; 3: Electrolyzed cathode water

Table 2. Properties of handsheets prepared from red algae

Species	Yield (%)	Density (g/cc)	B. Length (Km)	Tear index (mNm^2/g)	Bekk smooth (sec)
Gelidium amansii (GA1)	22.0	0.51	9.26	-	-
Gelidium amansii (GA2)	10.0	0.62	4.58	-	-
Gelidium amansii (GA2)	10.1	0.61	4.01	-	-
Gelidium chilense (GC1)	14.3	0.63	4.36	3.20	43.3
Gelidium chilense (GC2)	14.0	0.65	4.64	3.20	51.6
Gelidium chilense (GC3)[1]	8.5	0.70	5.72	3.30	81.6
Gelidium chilense (GC4)	15.7	0.77	6.31	2.44	44.2
Gelidium chilense (GC5)[2]	17.2	0.72	5.32	3.05	68.0
Gelidium chilense (GC6)[3]	15.2	0.73	5.76	3.06	31.0

1: Starting pH 2.5 by HCl addition; 2: Electrolyzed anode water; 3: Electrolyzed cathode water

To compare the physical properties of red algae pulp to those of the commercial SwBKP and HwBKP, handsheets from those were prepared. Table 3 showed the results.

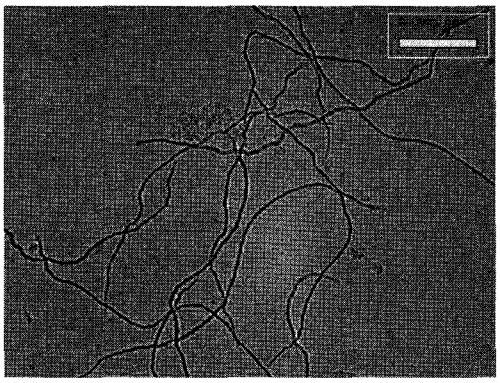
Table 3. Comparison of bleached chemical wood pulp and red algae pulp properties

Furnish	Density (g /㎤)	Bekk smooth. (sec)	Breaking Length (Km)	Stretch (%)	Tear index (mN ㎡/g)	CSF
SwBKP 1	0.53	3.21	2.59	2.40	18.13	680
SwBKP 2	0.59	5.43	8.58	3.98	11.53	560
SwBKP 3	0.63	8.78	8.96	4.22	9.82	457
SwBKP 4	0.67	7.15	9.55	3.70	8.53	362
HwBKP 1	0.59	2.98	1.96	1.06	2.31	634
HwBKP 2	0.66	4.63	2.40	1.24	2.43	597
HwBKP 3	0.72	6.83	3.95	2.05	3.79	504
HwBKP 4	0.74	9.15	4.74	2.66	5.24	397
G.amansii (10% yield)	0.57	25.90	6.41	3.50	3.29	153

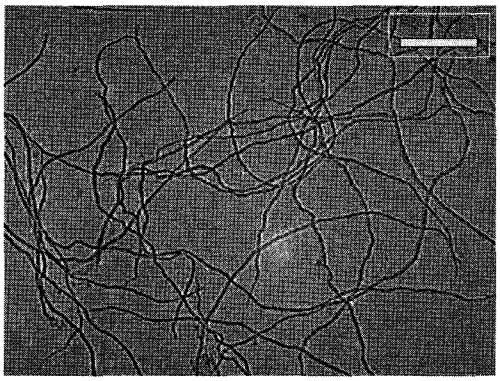
In the Table 3, SwBKP and HwBKP were refined by valley beater in four different levels, respectively, and one red algae pulp properties without refining were included for comparison. In Table 2 and 3, we observed that the properties of red algae pulp were in the middle of HwBKP and SwBKP properties when brightness levels were around 75%. However, the smoothness of red algae pulp was

exceptionally higher and freeness was much lower than wood pulps. Actually, the smoothness of red algae pulps listed in Table 2 were much higher than the one in Table 3.

The reasons of very high smoothness and low freeness can be explained easily by looking at the shape of the fibers and handsheets of red algae pulp. Figs. 1-4 showed the shape of fibers.

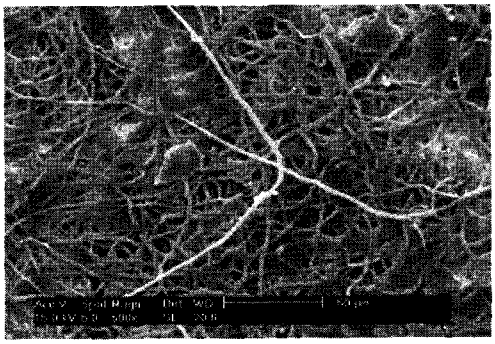


(a)

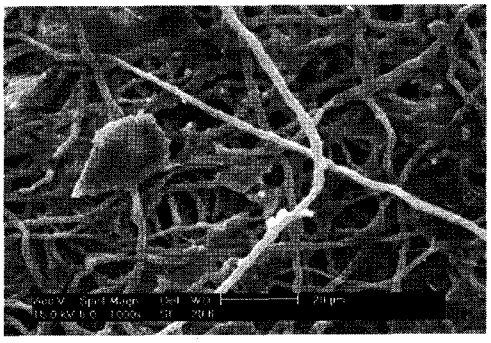


(b)

Figure. 1. Shape of rhizoidal filaments from red algae after extraction and bleaching process

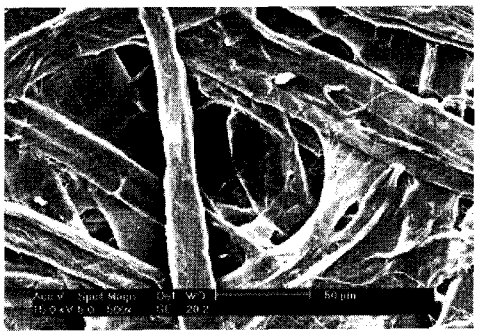


(a) 500x

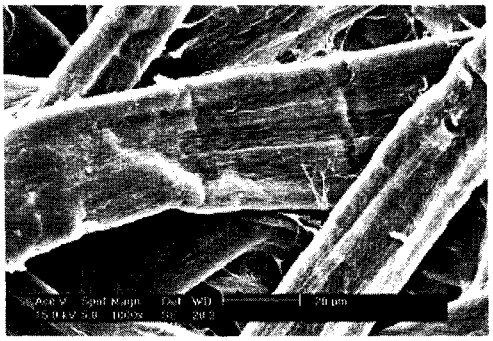


(b) 1000x

Figure 2. Shape of red algae pulp fibers in handsheet.

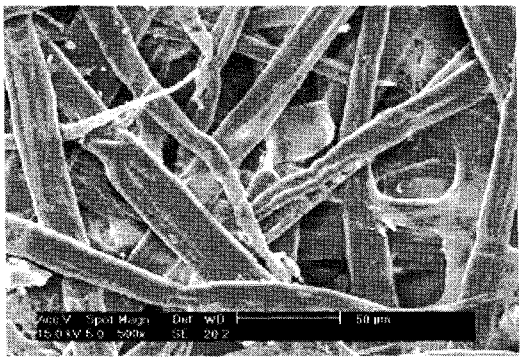


(a) 500x

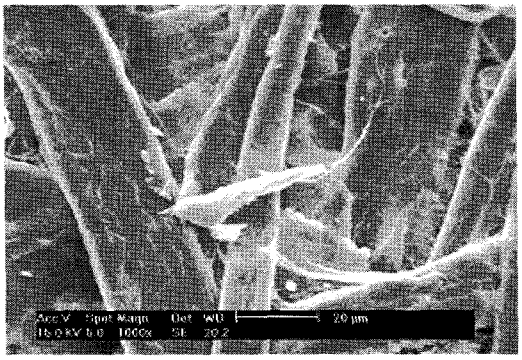


(b) 1000x

Figure 3. Shape of SwBKP in handsheet



(a) 500x

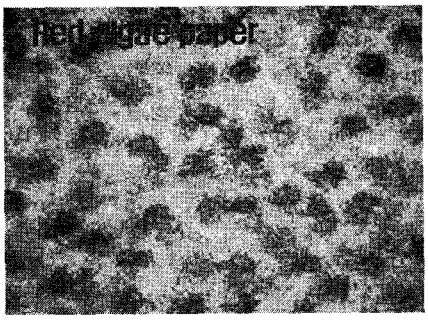


(b) 1000x

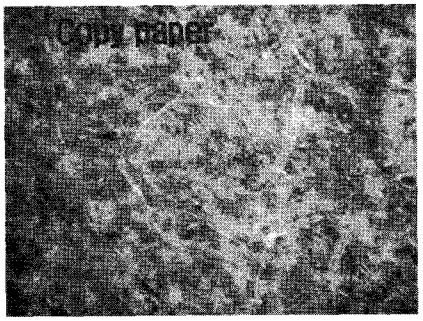
Figure 4. Shape of HwBKP in handsheet

Fig. 2 showed narrow and long fibers from red algae pulp, and one may expect very smooth paper. Figs. 3 and 4 showed the handsheet surfaces made from SwBKP and HwBKP, respectively, and one may expect rough surfaces. We measured the length and the width of typical red algae pulp fibers from Gelidium chilense, and they were about 500-1,000 μm, and 3-7 μm, respectively.

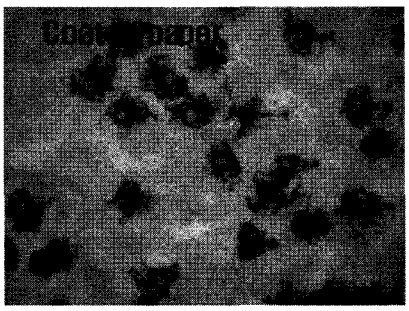
We printed in color on the red algae paper, commercial copy paper, and commercial coated paper, and compared the dot resolutions after magnification. Figure 5 showed the results. In the Figure, commercial copy paper showed its fibers in 50x magnifications, and no dots were identifiable. Red algae showed dots clearly as much as the commercial coated paper did. This means red algae paper may have potential to replace the coated paper in respect of print quality.



(a) Red algae paper, 50x



(b) Commercial copy paper, 50x



(c) Commercial coated paper, 50x

Figure 5. Blue color was printed on red algae paper, commercial copy paper and coated paper

PILOT TRIAL RESULTS OF RED ALGAE PULP

Pilot trial of red algae pulp for printing grade paper (40-50g/m^2) was made recently, and their properties were compared to the highest grade of commercial printing papers (about $2,500/ton in mill price in 2006). After lab calendaring, red algae paper gave Bekk smoothness value of around 150-200 seconds, whereas the highest grade printing paper gave 100-150 seconds, respectively. Commmercial white papers usually have 15-30 seconds in Bekk smoothness. Red algae paper gave higher opacity and brightness without lowering tensile strength at equivalent basis weight. There were some difficulties in runnability due to low freeness of the red algae furnish, but found to be manageable when the papermachine was slightly modified.

FURTHER DEVELOPMENT AND APPLICATIONS

We showed the glimpse of the red algae pulp fiber properties in the area of white paper application in this paper. The pulp yield of the red algae is not very attractive now, but should be raised more than 5% for white paper application in near future because the red algae, we used, were from wild habitat and were mixed with other species and inorganic substance. To give enough economic feasibility, cultivation of red algae is essential in near future, and the cultivated red algae will be clean and highly productive.

Application area of the red algae pulp described in this paper can be very broad. Filter paper, cigarette paper, surface layer of multiply paper or paperboard, security paper, edible paper, medical paper, and food paper are small examples of the application.

In the area of making high density or transparent paper, the red algae pulp yield goes up to 20 to 35% and drainage of the furnish is much faster than the one for white paper application. One of the advantages of the red algae pulp over wood fibers is no need of refining even in making high density paper.

The chemical composition of the red algae pulp fibers and their physical structure should be investigated in near future. More efficient extraction and papermaking processes are under development. Prototype machinery for red algae pulp production was developed and at work. A small papermaking pilot trial was successfully carried out to produce samples for distribution.

REFERENCE

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