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Degardatrion of Cellulosic Fibers by Electron Beam Irradiation

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ABSTRACT

Henequen fibers were treated by electron beam irradiation and by NaOH to make surface modification for better bonding in the manufacture of biocomposite. Impurity removal and carbonyl group formation were noticed in the previous study by electron beam irradiation, but extensive cellulose degradation were also noticed. To evaluate the effects of electron beam irradiation on cellulosic fibers further, henequen fibers, cotton pulp, cotton fibers, and cellophane were irradiated by electron beam, and their changes of cellulose viscosity, chemical composition, and tensile strength were measured and analyzed.

Keywords : *electron beam irradiation, cellulose, henequen, cotton, cellophane, degree of polymerization, alpha cellulose, beta cellulose, gamma cellulose*

1. Introduction

Biocomposite from cellulosic fibers and biodegradable polymer is recently under extensive studies due to its environmentally friendliness and energy conservation effects, compared to the inorganic fibers reinforced polymer composite (1). Life cycle assessment on biocomposite revealed that its incineration generated less carbon dioxide and toxic gases than the incineration of the glass fibers-polymer composite did (2).

High strength biocomposite needs surface modification of cellulosic fibers for better bonding between components. Wet method of surface modification such as NaOH treatment on cellulosic fibers needs high energy (e.g. drying energy), produces pollutants, and complicates the process. Dry surface modification process such as electron beam irradiation on cellulosic fibers, if effective on surface modification, can overcome disadvantages caused by wet method.

Han et al. reported electron beam irradiation (EBI) is effective to achieve both impurity removal and functional group development on the surface of natural fibers for better bonding. Also, EBI can keep the inner structure of natural fibers intact, but the alkali

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solution treatment made the fibers free from the structure and collapsed (3). This result may give additional advantage of using EBI for biocomposite because the open and uncollapsed structure of natural fibers can result in higher insulation, and impact absorbing effects when biocomposites are applied to automobile and construction industries.

Polybutylenes succinate (PBS), the polymer matrix of biocomposite, is a thermoplastic aliphatic polyester and has excellent biodegradability in nature. It also has comparable mechanical properties with general thermoplastics such as polyethylene and polypropylene. PBS has stability in wet environment resulting in the good durability of biocomposites (4).

In the study of biocomposite (3), henequen was selected as natural fiber, and electron beam was irradiated on it to achieve both impurity removal and functional group formation for better bonding between components. EBI treatment on cellulosic materials always causes degradation of cellulose DP (degree of polymerization), which results in loss of cellulosic fiber strength (5-7). In this study, we investigated the chemical change of cellulosic materials caused by electron beam irradiation in several dose levels. For comparison, besides henequen, cotton and cellophane were used for the study of cellulose degradation by EBI.

2. Experimental

Henequen (Agave fourcroydes) fibers were obtained from Cordemax, S.A. of Merida, Yucatan, Mexico. Cotton pulp and natural cotton fibers were provided by Korea Minting and Security Printing Co. in Korea. Cellophane was provided by Shandong Henlan Cellophane Co. in China.

For EBI treatment, fibers and cellophane were put into polyethylene bag, and electron beam was irradiated on it with electron accelerator (ELV-4 type, EB-Tech Co., Ltd. Daejeon, Korea). The intensity from 10 to 500 kGy were applied to the fibers and cellophane. The properties of irradiated henequen fibers were analyzed and compared to those of alkali treated henequen fibers.

For alkali treatment of henequen fibers, they were washed and soaked in 2 wt%, 5 wt%, and 10 wt% NaOH for one hour in room temperature. After being washed with distilled water, they were neutralized with 2 wt% acetic acid, washed again with distilled water, and dried in vacuum oven.

Ash contents (KS M 7033), extractives (TAPPI T 204 os-76), lignin contents (TAPPI T222 om-83), holocellulose (Wise method), alpa and beta cellulose contents (KS M 7044), and viscosity of cellulose (ISO 5351-1- 1981(E)) of the specimens were measured.

The thermal stability of the fibers and cellophane was analyzed under a nitrogen atmosphere thermogravimetric analyzer from using a TGA2960 of TA Instruments. The heating rate was 10°C/min. Derivative thermogravimetric (DTG) and TGA curves were recorded for cotton pulp and cellophane.

3. Results and Discussion

Changes of chemical composition in henequen fibers by the treatment of EBI and NaOH are shown in Table 1. Cellulosic degration of cotton pulp and fibers were shown in Table 2. In Table 1, we find there are no remarkable differences in ash contents, extractives, insoluable lignin, and soluable lignin contents between two treatments on henequen, respectively. However, alpha cellulose contents of EBI treated henequen are reduced abruptly by the EBI treatment, and beta cellulose are increased as much as the reduced amount of alpha cellulose. The relationship between alpha cellulose contents and EBI dosage was shown in Fig. 1. No significant changes in gamma cellulose means little reduction from beta cellulose to gamma cellulose by the EBI treatment. We find the same pattern of cellulose degradation in cotton pulp and cotton fibers in Table 2. The reduction of alpha cellulose indicates the degradation of cellulose chain, which usually leads to reduction of fiber strength

Table 1. Henequen chemical composition analysis

Electron Beam (kGy)

E.Beam (kGy)	Ash %	Extraction %	Insoluble lignin, %	Soluble lignin, %	Holocellulose %	α-cellulose %	β-cellulose %	γ-cellulose %	Fiber tensile N
0	0.60	2.96	9.24	1.25	88.02	57.98	6.27	23.03	15.78
10	0.95	2.04	9.00	1.24	89.73	59.92	12.80	17.19	14.95
30	0.97	1.92	8.88	1.22	88.98	58.81	12.01	18.26	13.23
50	0.86	2.23	7.99	1.14	88.89	56.36	12.44	20.08	11.96
70	0.80	2.35	8.15	1.47	86.42	51.14	17.91	17.37	12.22
100	0.99	2.90	5.88	1.63	85.35	35.04	30.05	20.26	12.72
150	0.90	2.77	7.53	1.27	85.12	29.52	39.14	16.45	10.07
200	0.91	2.90	6.98	1.39	83.62	21.31	46.51	15.80	6.68

Alkali treatment (NaOH)

NaOH	Ash %	Extraction %	Insoluble lignin %	Soluble lignin, %	Holocellulose %	α-cellulose %	β-cellulose %	γ-cellulose %	Fiber tensile N
0%	0.60	2.96	9.53	1.25	87.15	57.98	6.26	22.90	-
2%	0.72	1.72	11.80	1.22	83.37	60.27	8.74	14.35	-
5%	0.58	1.95	11.64	1.26	82.79	54.89	9.56	18.34	-
10%	0.68	1.65	14.41	1.41	82.93	62.22	8.71	11.99	-

Ash% : Inorganic contents
Extraction,% : Extraction with (Alcohol + Benzene)
Insoulble Lignin,% : Klason lignin, %
Soulble lignin,% : Lignin solution. 257nm UV for lignin detection.
Holocellulose,% : Alpa Cellulose% + Beta cellulose% + Gamma cellulose%
Alpa cellulose,% : Cellulose with the DP over 95 (MW of 16,200. Ref. 1)
Beta cellulose,% : Cellulose with the DP between 15 - 95 (Ref. 1)
Gamma cellulose,% : Cellulose with the DP under 15 (Ref. 1)
Fiber tensile, N : Fiber bundle tensile strength

Ref. 1 : Stamm, A.J., Wood and cellulose science, The Ronald Press Co., U.S.A., p105, 1964

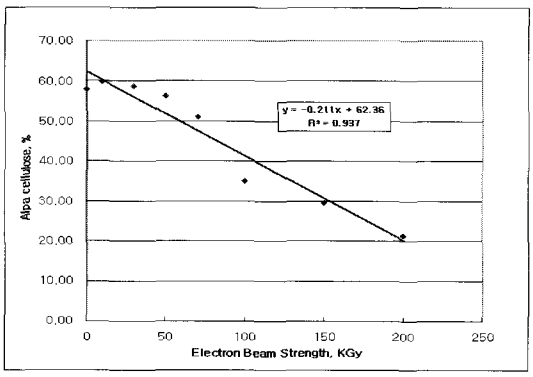

Fig. 1. Relationship between henequen fiber alpha cellulose content and EBI dosage.

properties. Table 3 shows the viscosity reduction of EBI treated henequen fibers, which means the reduction of cellulose DP (degree of polymerization).

We could not measure the individual fiber strength of the EBI treated henequen fibers directly, but measured the diameter of henequen fiber bundles, and selected bundles of very similar diameters. We measured the tensile strength of the henequen bundles of similar diameter, and found their tensile strengths in the range of 14~16 N. We further measured the electron beam irradiated henequen bundles of similar diameters. The relationship between EBI dosage and

Table 2. Chemical composition analysis of cotton pulp and fibers

	E. Beam kGy	Holocellulose %	α-cellulose %	β-cellulose %	γ-cellulose %
Cotton Pulp	0	98.8	96.36	3.59	-
	10	99.20	83.96	16.28	-
	30	98.20	55.15	45.16	-
	50	98.90	42.20	56.67	-
	70	99.10	30.55	69.07	-
	100	98.30	20.15	79.13	-
	150	99.20	12.20	88.59	-
	200	99.50	5.97	92.54	1.00
Cotton Fiber	0	96.67	90.88	4.34	1.45
	10	96.11	86.11	12.12	-
	30	98.63	84.40	18.02	-
	50	99.13	72.99	28.84	-
	70	98.07	59.46	35.94	2.67
	100	98.24	49.47	49.93	-
	150	98.20	42.20	54.30	1.67
	200	97.82	35.30	63.67	-

Table 3. Viscosity comparisons

E. Beam	Viscosity , cPs			
kGy	Cotton pulp	Cotton fiber	Henequen	cellophane
0	42.36	146.81	15.55	3.00
10	8.52	14.37	5.96	2.80
30	4.44	4.61	4.12	2.45
50	3.49	4.28	3.58	2.41
70	3.03	3.06	3.24	-
100	2.83	2.68	2.53	-
150	2.47	2.39	2.41	-
200	2.40	2.19	2.35	-

henequen bundle strength was shown in Fig. 2. From these tables and figures, we find that EBI treatment remarkably reduces cellulose DP and results in fiber strength reduction.

In the literature (8), beta and gamma cellulose have cellulose DP of 15-90 and under 15, respectively. Obviously, alpha cellulose has DP of more than 90, and wood chemical pulp usually has DP of 1000-3000. By the treatment of EBI, extensive degradation of cellulose chain occurred. Alkali treatment showed no significant changes in the amount of alpha and beta cellulose contents.

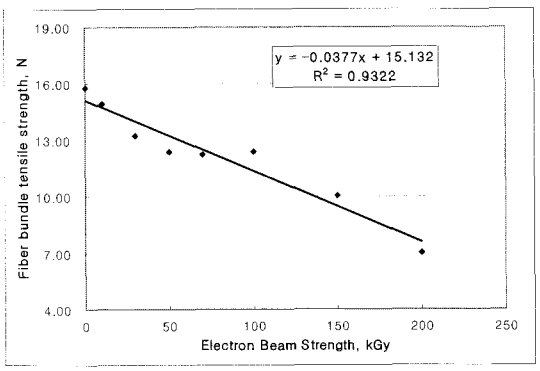

Fig. 2. Relationship between henequen fiber strength and EBI dosage.

Table 4. Viscosity comparison of henequen

E.Beam kGy	Viscosity(cPs) (E. Beam)	NaOH %	Viscosity(cPs) (NaOH)
0	15.55	0	15.55
10	5.96	2	14.96
30	4.12	5	13.26
50	3.58	10	7.33
70	3.24		
100	2.53		
150	2.41		
200	2.35		

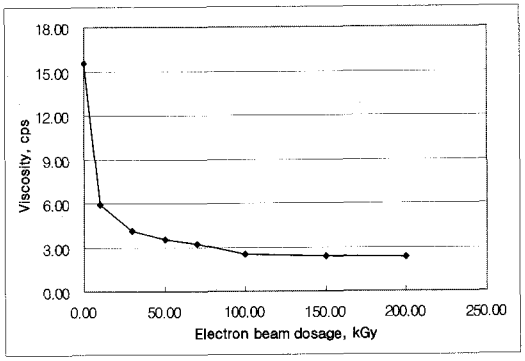

Fig. 4. Effects of EBI dosage on cellulose viscosity. (Henequen fibers)

We selected pure cellulosic materials that have high and low cellulose DP to know the effects of EBI on cellulose more closely. Cotton pulp was the purified cellulosic fibers by pulping and bleaching process, and was supplied by Korea Mint and Security Printing Co., while the cotton fibers were natural fibers without treatment. Natural cotton fibers usually have pectin and wax on their surfaces. They are selected as high cellulose DP material, and cellophane is selected as low cellulose DP material. The results of cellulose viscosity measurement were shown in Table 3 and Table 4.

As the cellulose viscosity of the specimen decreases, its cellulose DP decreases. In Fig. 3, cellulose viscosities of cotton fibers and pulp were dropped very fast as EBI dosage increased. It seems that around 30 kGy of EBI dosage, cellulose degradations were almost completed. It is also true for the henequen fibers in Fig. 4. Dosage increase of EBI more than 30 kGy did not cause further significant changes in cellulose viscosities (cellulose DPs) as shown in both figures.

ellophane has very low initial cellulose viscosity, and its viscosity did not drop much as EBI treatment was applied more than 30 kGy (Table 3). We found that the cellulose viscosity was dropped remarkably at low dosage of EBI when initial viscosity of the cellulosic material was high, but was no further changes when initial viscosity was low.

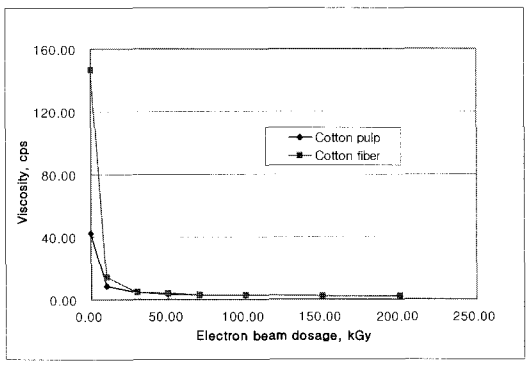

Fig. 3. Effects of EBI dosage on cellulose viscosity. (Cotton pulp and cotton fibers)

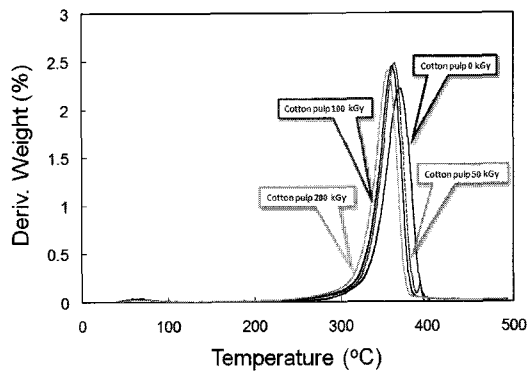

Fig. 5. Effects of EBI dosage on cotton pulp in DTG.

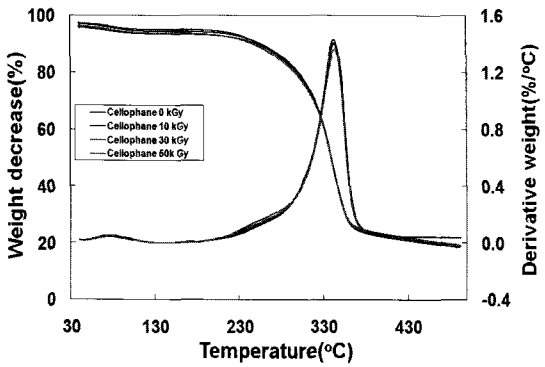

Fig. 6. Effects of EBI dosage on cellophane in TGA and DTG.

Fig. 5 shows DTG results of cotton pulp. The temperature of highest degradation rate of cotton pulp was decreased as the dosage of electron beam irradiation. Fig. 6 shows TGA and DTG results of cellophane. There are little differences in the curves of different electron beam dosages.

It was shown that electron beam was very effective to degrade the alpha cellulose and to increase beta cellulose, but was not effective on gamma cellulose. For the strength of cellulosic material such as henequen fibers, no more than 30 kGy EBI dosage was necessary to keep the fiber strength. Still, we should aware that there be remarkable amount of cellulose viscosity reduction by the application of low level EBI dosage.

4. Conclusions

In the study of EBI treatment on cellulosic material, we observed followings.

* EBI treatment on henequen, cotton pulp, and cotton fibers caused decrease in alpha cellulose, which has high cellulose DP, and increase in beta cellulose, which has low cellulose DP. There were no significant changes of gamma cellulose contents.

* EBI treatment on henequen did not cause much changes in chemical components except cellulose.

* Tensile strength of henequen fiber bundle was decreases in proportional to EBI dosage and alpha cellulose reduction.

* Electron beam irradiation on henequen fibers may enhance the surface modification for bonding in the manufacture of biocomposite, but should be limited less than 30 kGy for keeping their strength properties.

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