

# Chemical analysis of electron beam – treated henequen fibers

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## Introduction

Biocomposite made of 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 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 solution treatment made the fibers free from the structure and collapsed (3). This result may give additional advantage of 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.

Poly(butylene 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 (5,6,7). 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.

## **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. Taejun, Korea). The intensity from 10 to 500 kGy were applied to the

fibers and cellophane. The properties of irradiated henequen fiber was analyzed and compared to those of alkali treated henequen.

For alkali treatment of henequen fibers, they were washed and soaked in 2wt%, 5wt%, and 10wt% NaOH for one hour in room temperature. After being washed with distilled water, they were neutralized with 2wt% 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 pulp ( ) of the specimens were measured

## Results and Discussion

Chemical composition changes of henequen fibers by the treatment of EBI and NaOH are shown in Table 1. 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. No significant changes in gamma cellulose means no more reduction from beta cellulose to gamma cellulose by the EBI treatment. The reduction of alpha cellulose indicates the degradation of cellulose chain, which usually leads to reduction of fiber strength properties. Table 3 shows the viscosity reduction of EBI treated henequen fibers, which means the reduction of cellulose chain reduction (degree of polymerization).

We could not measure the individual fiber strength of the EBI treated henequens directly, but measured the straws of fiber bundles, that have very similar cross

section areas. The relationship between alpha cellulose and EBI dosage is shown in Fig. 1 and the relationship between EBI dosage and fiber bundle strength in Fig. 2, respectively. From these tables and figures, we find that EBI treatment remarkably reduces cellulose chain length and results in fiber strength reduction.

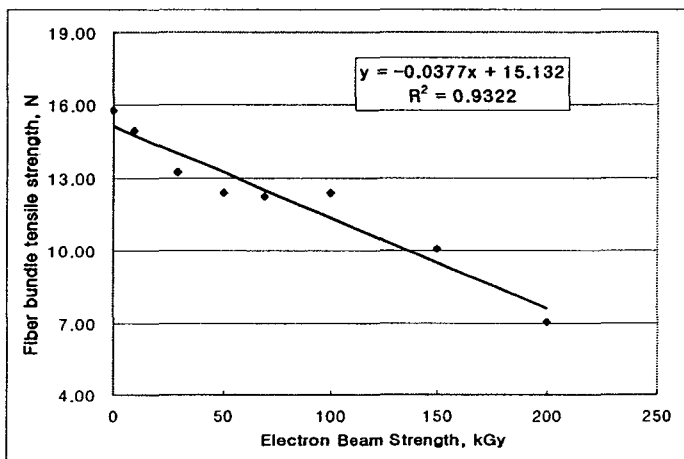


Figure 1. Relationship between henequen fiber strength and EBI dosage

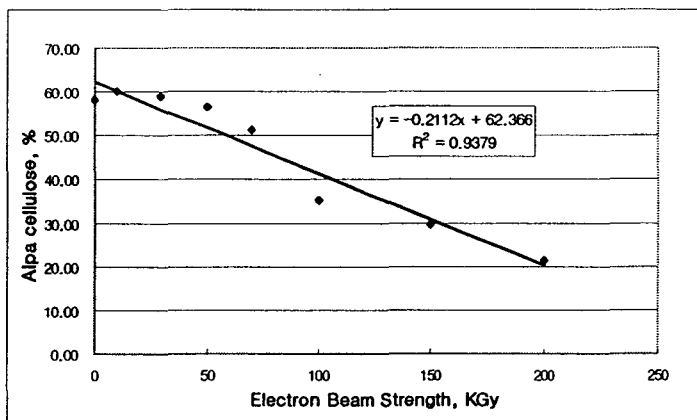
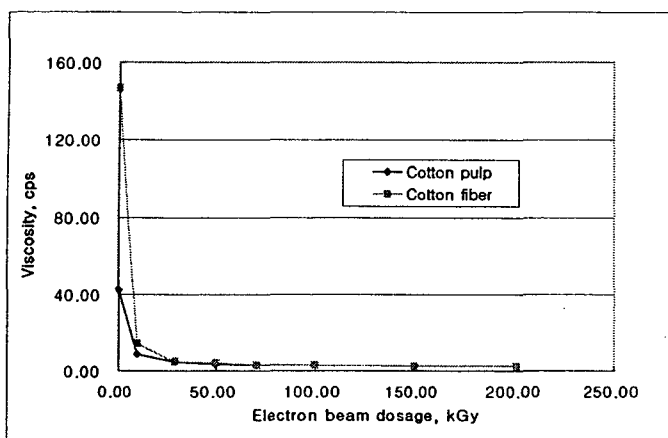


Figure 2. Relationship between henequen fiber alpha cellulose content and EBI dosage

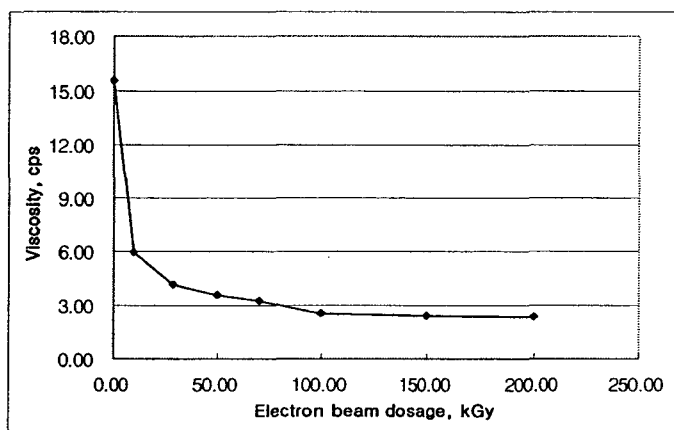
In the literature (8), beta and gamma cellulose have cellulose DP of 15-90 and under 15, respectively. Obviously, alpha cellulose has DP of more than 90, and wood chemical pulp usually has DP of 1000-3000. By the treatment of EBI, extensive degradation of cellulose chain occurred. Alkali treatment showed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

We selected pure cellulosic materials that have high and low cellulose DP to know the effects of EBI on cellulose more closely. Natural cotton fiber and cotton pulp, in which impurities such as extractives including wax are removed, 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 2, Table 3 and Table 4.

As the cellulose viscosity of the specimen increases, its cellulose DP increases. 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. 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.



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



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

Cellophane 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 kept little change when initial

viscosity was low. It seems that electron beam was very effective to degrade the structured cellulose region (crystalline structure), but was not effective in the amorphous cellulose region, where there might be large electron absorption site. For the structured cellulosic material, no more than 30 kGy EBI dosage was necessary to keep the cellulose viscosity from extensive degradation. Still, we should aware that there be remarkable amount of cellulose viscosity reduction by the application of low level EBI dosage.

## Conclusions

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

- \* EBI treatment on henequen and cotton caused decrease in alpha cellulose, which has high cellulose DP, and increase in beta cellulose, which has low cellulose DP. There were changes of gamma cellulose contents within experimental error.
- \* 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 was very effective to degrade the structured cellulose region (crystalline structure), but was not effective in the amorphous cellulose region, where there might exist large electron absorption site.

## References

1. Mohany, A.K., Misra, M., Drzal, L.T., J. of Polym. and Environ., 10(1/2), 19, 2002
2. Corbiere-Nicollier, T., Laban, B.G., Lundquist, L., Letierrier, Y., Manson, J.A.E.,

- Jolliet, O., Resources, Conservation and Recycling, 33, 267, 2001
3. Han, S.O., Han, M.H., Cho, D.H., Drzal, L.T., American Chemical Society(Polymer Chemistry Division) Preprint, March 28-April 2, Anaheim, CA, USA, 2004
  4. Han, S.O., Park, J.S., Kim, J.S., Kim, S.K., Cho, D., EUROMAT2003 Polymer session, Sept. 7-11, Lasanne, Switzerland, 2003
  5. Komarov, V.B., Gordeev, A.V., Samuilova, S.D., Fadin, A.V., Ershov, B.G., High energy chemistry, 33 (3), 156-160, 1999
  6. Bychkov, V.L., Vasilev, M.N., High energy chemistry, 31 (2), 117-120, 1997
  7. Aleksandrov, I.V., Bychkov, V.L., Vasilev, M.N., High energy chemistry, 31 (1), 44-49, 1997
  8. Stamm, A.J., Wood and cellulose science, The Ronald Press Co., 1964

## ACKNOWLEDGEMENTS

The authors acknowledge the financial support of the Korean Ministry of Science and Technology (Grant No. M6-0302-00-0041) in the funding of this work.



**Table 1. Henequen chemical composition analysis**

<b>Electron Beam (kGy)</b>									
E.Beam (kGy)	Ash %	Extraction %	Insoluble lignin, %	Soluble lignin, %	Holocellulose %	$\alpha$ -cellulose %	$\beta$ -cellulose %	$\gamma$ -cellulose %	Fiber tensile Newton
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

<b>Alkali treatment (NaOH)</b>									
NaOH	Ash %	Extraction %	Insoluble lignin %	Soluble lignin, %	Holocellulose %	$\alpha$ -cellulose %	$\beta$ -cellulose %	$\gamma$ -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

**Table 2. Chemical composition analysis of cotton pulp and fibers**

	<b>E. Beam kGy</b>	<b>Holocellulos e %</b>	<b><math>\alpha</math>-cellulose %</b>	<b><math>\beta</math>-cellulose %</b>	<b><math>\gamma</math>-cellulose %</b>	<b>Viscosity cps</b>
<b>Cotton Pulp</b>	0	98.8	96.36	3.59	-1.15	42.36
	10	99.20	83.96	16.28	-1.04	8.52
	30	98.20	55.15	45.16	-2.11	4.44
	50	98.90	42.20	56.67	-2.97	3.49
	70	99.10	30.55	69.07	-0.52	3.03
	100	98.30	20.15	79.13	-0.98	2.83
	150	99.20	12.20	88.59	-1.59	2.47
	200	99.50	5.97	92.54	1.00	2.40
	<b>Cotton Fiber</b>	0	96.67	90.88	4.34	1.45
10		96.11	86.11	12.12	-2.12	14.37
30		98.63	84.40	18.02	-3.97	4.61
50		99.13	72.99	28.84	-2.70	4.28
70		98.07	59.46	35.94	2.67	3.06
100		98.24	49.47	49.93	-1.17	2.68
150		98.20	42.20	54.30	1.67	2.39
200		97.82	35.30	63.67	-1.15	2.19

**Table 3. Viscosity comparisons (cps)**

<b>E. Beam kGy</b>	<b>Viscosity , cps</b>			
	<b>Cotton pulp</b>	<b>Cotton fiber</b>	<b>Henequen</b>	<b>cellophane</b>
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	-

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		