Morphology and surface properties of natural fiber treated with electron beam

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The surface morphological and topological properties and roughness of henequen fiber irradiated by electron beam (EB) with different intensities were investigated with SEM and AFM. EB irradiation is being utilized to modify the surface of natural fibers and the surface characteristics of henequen fiber were also changed by EB irradiation. The pectin and P layer were removed, but S layer was maintained without any degradation at an EB dose of 10 kGy. When impurities were removed, small pores of 1-10 µm were produced. Stronger EB irradiation results in striation having apparent height differences between doses of 10 kGy to 100 kGy because of removal of P layer and exposed of S layers. The degradation of S layer was observed with the higher EB doses over 50kGy. Morphological change was quantified by measuring porosity characteristics using mercury porosimetry and nitrogen adsorption. EB irradiation of 10 kGy and 30 kGy was effective to remove pectin, wax and P layer, and created many pores of 40 nm to 100 nm. Total surface area and pores increased with low doses up to 30 kGy. On the other hand, degradation of S layers was observed at higher doses.

Keywords Natural fiber; Electron beam; Scanning electron microscopy; Atomic force microscopy

1. Introduction

Cellulose is the most abundant natural polymer and has been used as a renewable raw material in a wide range of applications, such as paper, wood, and textile manufacturing [1]. With an increasing of environmental awareness, cellulose fibers such as cotton, flax, hemp, jute and henequen have recently received increased attention both industrially and scientifically, especially as reinforcements of polymer composites. Biocomposite consisting of a polymeric matrix reinforced with natural fiber possess several advantages such as high modulus and strength, relative to traditional materials such as glass fiber reinforced polymer composites. Also, these composites have the advantage of low density, low cost, recyclability, and biodegradability. Their uses are growing in areas where lightweight and strong structures are required, for example, in the aerospace, automobile, and building construction industries [2-6]. Despite the advantages of cellululosic fibers, the polymer composite reinforced with natural fibers have a problem in the poor bonding between the cellulose fiber and the polymer matrix. This is due to an opposite chemical nature between the highly hydrophilic property of cellulose fibers and the hydrophobic property of polymer matrix, which is associated with poor surface properties for association within the polymer matrix, and a degradation of mechanical properties [7,8].

The adhesion between the reinforcing fibers and the polymer matrix in composites plays an important role in the final mechanical properties of the material because the stress transfer between the matrix and fibers determines reinforcement efficiency [9]. Therefore, chemical or mechanical processing on the natural fiber is being utilized to overcome these problems. The chemical processes of mercerization [10], silane treatment [11], maleic acid [12], and acetylation [13] were developed to clean the fiber surface, modify the surface chemically, restrain moisture absorption and make the surface more hydrophobic, and remove the hydrophilic group of natural fiber. Also, physical treatments such as plasma treatment [14], corona treatment [15] and electron beam irradiation have been conducted to create a hydrophobic group, cause a cross-linking, and increase the interfacial surface area.

The electron beam (EB) irradiation technique is being increasingly utilized to modify the surfaces of various polymer materials, such as fibers, textiles, and films. Cotton fabrics have been coated with pigment colors using EB to improve color fastness, tensile mechanical, and crease resistance [16]. Takács et al. [17] studied the influence of gamma irradiation and sodium hydroxide on the structure of cotton cellulose. Kim et al. [18] and Han et al. [19] irradiated natural fibers with EB to improve adhesion between the fibers and thermoplastics. High dose of EB irradiation on cellulose resulted in the dehydrogenation and destruction of anhydroglucose, while cross-linking occurred at low irradiation dose [20,21]. Recently, the effects of EB irradiation on various types of cellulose fibers have been studied to treat surface and improve the reactivity of natural fiber for biocomposites. Han et al. [19] reported that EB irradiation is effective in both impurity removal and functional group development on the surface of natural fibers for better bonding between natural fiber and polymer matrix. EB irradiation can modify the surface structure and preserve the inner structure of natural fiber. EB irradiation on cellulose fibers has decreased alpha cellulose which has high DP, and increased beta cellulose which has low DP. The advantages of modifying fibers by using EB irradiation are that no
chemicals are used; the process can be done dry, in a clean environment, and at room temperature. The EB irradiation process saves energy, reduces processing time, does not require a catalyst, and is environmentally friendly \[22\]. Until now, research on interfacial adhesion between natural fiber and polymer matrix has been focused on opposite chemical properties such as hydrophilic natural fiber and hydrophobic polymer matrix. Other factors including surface area, surface structure, and porosity of fiber were relatively neglected in the consideration of interfacial adhesion between fiber and matrix \[23\]. Recently, the surface morphology and porosity of natural fiber have been recognized as significant factors for composite interfaces, and their effects on the performance of composites have been investigated. S. Luo et al \[24\] studied the interfacial shear strength resulting from the fiber surface roughness using Scanning Electron Microscope (SEM). Atomic Force Microscopy (AFM) \[25,26\] was used to investigate the morphology of the surface of natural fibers treated by pulping \[27\], bleaching and cellulase \[28\]. Mercury porosimetry and nitrogen porosimetry \[29\] are widely used to characterize the porous structure and surface area of fiber. The properties of natural fibers generally vary more than those of commercially produced synthetic fibers in terms of geometry, morphology, and surface characteristics. Understanding in details the structure of natural fibers has become increasingly important as the need increases to use renewable resources in technological applications. The surface properties of natural fibers play critical roles in high performance of composites, wicking, soil resistance, adhesion, and biocompatibility. In this study, the effect of EB irradiation on henequen fiber was investigated to improve the interfacial property between natural fiber and polymer matrix for biocomposites. We investigated the effect of EB irradiation on the surface morphology, surface structure, surface area, and porosity of henequen fibers. SEM and AFM were utilized to analyze the surface morphology and roughness. Also, surface area and porosity of henequen fiber were investigated with mercury porosimetry and nitrogen absorption.

2. Experiment

2.1. Materials
Henequen (\textit{Agave fourcroydes}) fibers from Yucatan, Mexico were used, with filament lengths in the range of 60–70 cm. The average density was about 1.45 g/cm\(^3\). The diameter of filament was in the range of 150–200 µm. Henequen fiber is composed of approximately 77% cellulose, 4-8% hemicellulose, 13% lignin and 2-6% pectin and waxes by weight.

2.2. EB irradiation
Henequen placed in polyethylene bag was irradiated by an electron beam. The accelerator Elv*4 from eb-TECH Co. Ltd. (Daejeon, Korea) was used for modification of natural fiber. The beam’s current was 4.95 mA. The voltages of 1.0Mev and transport velocity of 10 m/min were applied for EB irradiation doses of 10, 30, 50, 70, 100, 150, 200, and 500 kGy. A raw sample was used as the control for comparison.

2.3. Observation of surface morphology

2.3.1. Scanning electron microscopy (SEM)
The surface characteristics and cross-sectional structures of henequen fiber were all observed by scanning electron microscopy (SEM), (S4700, HITACHI). The acceleration voltage was 10 kV. The samples were coated with Os using a vacuum sputter coater.

2.3.2. Atomic force microscopy (AFM)
The commercial XE-Series Atomic force microscopy (AFM,XE-100, Park Systems, Suwon, Korea) equipped with a 12µm Z-scanner was used for the research. The henequen fibers were immobilized on stubs with adhesive tabs for imaging using the AFM. All images were obtained using the True Non Contact Mode with silicon cantilever under atmospheric conditions. Experiments were performed with a 0.3-0.5Hz. Vibrating frequencies and amplitude were 280-330 kHz and 15-25nm, respectively. Root mean square (RMS) roughness data were obtained by analyzing topography images using the size of 20 µm × 20 µm specimens.

2.4. Measurements of pore structures

2.4.1. Mercury porosimetry
In order to measure the total surface area, the pore size distribution and porosity, mercury porosimetry was carried out with an Autopore IV 9500. In mercury porosimetry, gas is evacuated from the sample container and pressure is applied to force mercury into the sample. Henequen fiber of 180-300 mg was placed into a glass dilatometer. Measurement was
made in a pressure range to 60,000 psi. The pore distribution, porosity, and total surface area of henequen fiber were calculated from the relationship between the pressure necessary for penetration and the volume of penetrated mercury [30,31].

2.4.2. Nitrogen absorption
The specific surface area of henequen fibers was obtained from a BET analysis of nitrogen absorption isotherms using a Micromeritics ASAP*2420. The total pore volume is obtained as the volume of adsorbed nitrogen at a relative pressure approximating unity. Sample of 2.8-3.4 g were weighed, placed into sample tubes, and dried under vacuum at 100°C for 4 hours. Measurements were made of adsorption and desorption in a liquid nitrogen atmosphere and with liquid nitrogen flushing. The pressures 0.05< p/p° <0.30 was used to calculate the specific surface area for a monomolecular covering [32].

3. Results and discussion

3.1 Observation of surface morphology
The cell walls of henequen fiber have complex structure on surface. Like many other botanical tissue, the cell walls of henequen are a rigid multi-layered structure composed of middle lamella, a primary (P), and a secondary wall (S) that has been subdivided into the outer layer (S1), the main layer (S2) and the inner layer (S3), respectively. Each layer contains cellulose, hemicellulose and lignin. Lignin is mainly distributed the middle lamella and primary wall. Cellulose is the main component of S layer, especially S2 layer which is about 5μm thick and forms the main portion, comprising about 95 wt% of the natural fibers. The S2 gives the greatest contribution to the mechanical strength and the fiber in the longitudinal direction [20, 21]. Additionally, hemicellulose is distributed mainly between the lignin and cellulose. Fig. 1 shows a scheme of a cell wall and the thickness of the different layers of natural fiber.

Electron beam irradiation gives effects on the surface properties of henequen fibers significantly. Fig. 2 shows SEM micrographs of the surface and cross-sectional images of henequen irradiated with different intensities of EB. It shows that the surface morphology of untreated henequen fiber is different from that of irradiated fibers particularly in terms of their level of smoothness and roughness. Also, the cross-section view shows the clear evidence that the henequen fibers are composed of multi-layer. It is shown that the surface of the raw henequen was covered with wax, pectin, and P layer, which makes the surface smooth. The fibrillar structures of irradiated henequen fibers are revealed in the SEM images, and this is due to the leaching of waxes and pectin substances by electron beam irradiation. Fig. 2(b) shows the SEM image of 10 kGy irradiated fiber. It can be observed that almost all impurities have been removed from the fiber surface. As shown in Fig. 2(c), (d), (e), (f), the irradiated fibers show a prominent high over ravine and fibrillar structure on the surface from 30 kGy to 100 kGy. At the high doses of 200 kGy and 500 kGy, the surface of cellulose fiber looks jagged and flattened again and the inner part of the structure disappeared due to the degradation of S2.

![Fig. 1 The scheme of cell wall and thickness of the different layers of natural fiber.](image-url)
AFM was employed to monitor the topological changes of the heterogeneous surface morphologies and the roughness of henequen fibers. After EB irradiation, the henequen fibers exhibited significant changes in their surface characteristics. Fig. 3 and Fig. 4 show representative two-dimensional and three-dimensional AFM phase images of henequen fibers irradiated by different EB doses, and Table 1 shows the roughness information obtained by analyzing topographic images. The surfaces of raw henequen fibers have an irregular phase and fine corrugations which were also observed in the SEM images. It is observed that the surface roughness value is 59 nm because of a layer of pectin and waxy material, which covers the surface of fiber [33]. After EB irradiation, the henequen fibers exhibited significant changes in their surface characteristics with the different doses. For the images in Fig. 3 from 10 kGy to 100 kGy, the brighter areas were determined to be higher than surrounding regions. It can be confirmed by three-dimensional image, Fig. 4. As shown in SEM image, AFM results also show that EB irradiation at 10 kGy was effective for the removal of outer layers such as pectin and waxy material, and thereby the P layer, network morphology, was exposed and damaged [34,35]. The surface morphology irradiated by 30 kGy shows that the fibril structure is well-aligned and there is a distinctive striation in the longitudinal direction. It can be explained that the S layer was exposed as P layer was removed at 10 kGy and also it seems that S2 layer was exposed at 30 kGy. The stronger EB irradiation condition results in the striations having apparent surface height differences, and a clearer surface because pectin and waxy impurities have been removed. However, the surfaces of henequen fibers irradiated with high doses of 200 kGy and 500 kGy show irregular phase. It can be explained by the fact that the exposed secondary cell wall is degraded. A roughness indicated by surface roughness value corresponds with the fibrillar structures on the surface as shown in AFM images.

As shown in Table 1, surface roughness reached 226.2 nm at 10 kGy and up to 268 nm at 30 kGy. The surface roughness increased to some extent with the irradiation condition. The reason for these phenomena is that the outer layer of the henequen fiber was removed during the irradiation. A roughness indicated by RMS value is correlated with the increasing amounts of the fibrillar structures on the surface of fiber. However, the surfaces of henequen fibers irradiated severely such as 200 kGy and 500 kGy, again show fine corrugations and an irregular phase. The surface roughness values also decreased to a minimum 97 nm at 500 kGy. This is evidence of the degradation of the S layer. This is also in agreement with the results of SEM.

3.2. Measurements of pore structure

During the removal of the pectin, wax, and P layer from the surface of henequen fiber, large pores are produced in the fiber wall and these facilitate a more rapid dissolution of lignin from the secondary cell wall layer [36]. The size and
Fig. 3 2D Image (20 μm × 20 μm) of henequen irradiated by EB with different doses.

Fig. 4 3D Image (20 μm × 20 μm) of henequen irradiated by EB with different doses.
distribution of these pores affect fiber properties including their swelling in water, their accessibility to chemical reactants such as cellulase, fiber shrinkage, and fiber strength. For example, the increase of small pores results in a decrease in fiber strength. Pore structure, dependent on the pore size, contributes to the interlocking that takes place between the fiber and a polymer matrix closely related to the mechanical performance of composites which means the good adhesion between fiber and polymer matrix [37].

The surface changes of henequen fiber irradiated by EB were investigated by the total surface area, pore distribution, and porosity using mercury porosimetry. The result showed that large peak showed in the range of 10^3 nm to 10^5 nm which is the evidence of the striated structure of the cellulose fibers. Also, there is a small peak with diameter 10^3 nm to 10^4 nm and very small peak around 10^5 nm. It means that there are few small pores having a diameter 10^3 nm to 10^5 nm. There are longitudinal hollow tubes such as vessels and voids between the fibers, which affect the measured volume to a greater extent than do the internal pores of the fibers [38]. The untreated fiber has relatively larger pore diameter with the range of 10^3 nm to 10 nm, compared to the EB irradiated fibers. The peak for the smaller pores than 10^3 nm is created with EB irradiation on the henequen fiber. These phenomena can be explained that first, EB irradiation of 10 kGy separates pectin, wax, and P layer from henequen fiber. Second, the level-off degree of polymerization in henequen fiber results in a significant decrease in pore diameter in connection with remarkable enhancement of the micropore on the surface [37]. With increasing doses of EB such as 100 kGy and 150 kGy, the small pores decrease in henequen fiber, because pores are generated, existing pores are enlarged, and neighbouring pores are annexed. The decrease in small pores is also due to the removal of damaged S layer of henequen fiber. This results in a decrease of tensile strength. At an EB dose of 500 kGy, small pores between 100 nm and 10 nm increase again because the degradation of S layers. As seen in AFM images, the surface of henequen fiber was flattened at 500 kGy dose. It means that the small pores generated were enlarged and that neighbouring pores were annexed when the stronger EB irradiation doses were applied.

Total surface area associates with the pore size. When the pore size gets smaller, relatively surface area is increased. Total surface area shows the highest for the henequen fiber treated with 30 kGy as a result of increased small pores of 10^3 nm and 10 nm on the surface of henequen fiber. Then the total surface area was decreased due to the creation of larger pores with increased EB dose. However, the total surface area was increased again with the dose of 200 kGy. It is supposed from the microcrack and etching at 200 kGy. The lowest surface area is shown at 500 kGy. It is due to the fact that the small pores were enlarged by the excessive etching and annexation of pores because of the degradation. The increase of surface area is correlated with the roughness. Also, they provide the adhesion area between fiber and polymer. The highest porosity was observed for the henequen fiber irradiated with 10 kGy comparing with the fact that the highest total surface area was obtained for the henequen fiber irradiated with 30 kGy. It can be interpreted that EB irradiation of 10 kGy is effective the removal of P layer and the creation of many pores in the rage of 100 nm to 40 nm, however, EB intensity of 30 kGy contributes to the formation of the highest porosity for the henequen fiber. On the other hand, the lowest porosity for henequen fiber irradiated with EB of 100 kGy dose can be interpreted in terms of crosslink of cellulose [39].

The surface areas, micropore and BET C-value measured by N_2 absorption are summarized in Table 2. Generally, all cellulose fibers have very small specific surface areas. According to the EB dose, henequen fiber can be distinguished with two groups: one having ‘larger’ surface area but smaller C-values and the other with lower surface areas and larger C-values. The C-value is a measure of the difference of the adsorption free enthalpies of the first adsorbed gas layer to the subsequent multi-layers. There is dependency between surface area and C-value. The henequen fiber irradiated by 10 kGy was classified as having small surface pores. This structure can be a cause of high crystallinity and fiber stiffness. EB irradiation up to 100 kGy causes surface area to increase but simultaneously the C-value decreases. Also, the structure flattens with increasing EB doses as shown in SEM and AFM images, resulting in a diminished surface area but with increased C-values. However, these results did not perfectly coincide with the result of mercury porosimetry. Due to different measurement ranges, nitrogen adsorption (0.3-300 nm) gave markedly smaller total pore

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>Roughness (rms)</th>
<th>SD (yEr±)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>58.59</td>
<td>4.69</td>
</tr>
<tr>
<td>10</td>
<td>226.21</td>
<td>33.39</td>
</tr>
<tr>
<td>30</td>
<td>267.97</td>
<td>27.67</td>
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<tr>
<td>50</td>
<td>240.23</td>
<td>21.87</td>
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<tr>
<td>70</td>
<td>230.76</td>
<td>28.51</td>
</tr>
<tr>
<td>100</td>
<td>170.30</td>
<td>15.98</td>
</tr>
<tr>
<td>150</td>
<td>105.17</td>
<td>22.42</td>
</tr>
<tr>
<td>200</td>
<td>103.28</td>
<td>30.33</td>
</tr>
<tr>
<td>500</td>
<td>97.90</td>
<td>11.99</td>
</tr>
</tbody>
</table>

Table 1 The roughness of henequen fibers irradiated by EB with different doses

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volume values than mercury porosimetry (3 nm-14 µm). Natural fiber contains pores larger than 300 nm, which is the maximum pore size detected by nitrogen adsorption. Also, mercury porosimetry measures the voids between the fibers, which affect the determined volume more than does the internal porosity of the fibers.

Table 2

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>BET surface area (m²/g)</th>
<th>Micropore volume (cm³/g)</th>
<th>C value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.230</td>
<td>0.00094</td>
<td>35.25</td>
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<tr>
<td>10</td>
<td>0.207</td>
<td>0.00059</td>
<td>47.94</td>
</tr>
<tr>
<td>30</td>
<td>0.223</td>
<td>0.00065</td>
<td>34.71</td>
</tr>
<tr>
<td>50</td>
<td>0.247</td>
<td>0.00079</td>
<td>31.50</td>
</tr>
<tr>
<td>70</td>
<td>0.286</td>
<td>0.00104</td>
<td>30.02</td>
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<tr>
<td>100</td>
<td>0.294</td>
<td>0.00093</td>
<td>28.61</td>
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<tr>
<td>150</td>
<td>0.280</td>
<td>0.00091</td>
<td>30.67</td>
</tr>
<tr>
<td>200</td>
<td>0.267</td>
<td>0.00111</td>
<td>29.34</td>
</tr>
<tr>
<td>500</td>
<td>0.237</td>
<td>0.00116</td>
<td>29.83</td>
</tr>
</tbody>
</table>

4. Conclusion

The effects of EB irradiation on henequen fibers were studied with respect to morphological and topological properties, roughness, surface area and porosity of fiber. The surface morphology of cellulose fiber has been recognized as significant factors for composite interfaces. The surface morphological and topological properties and roughness were investigated with SEM and AFM. The surface morphologies of henequen natural fiber were changed by EB irradiation. EB irradiation of 10 kGy showed the effective effects on the removal of weak boundary components such as wax, pectin, and P layer, which cover the surface of raw henequen fibers. Stronger EB irradiation results in striation having apparent height differences between doses of 10 kGy to 100 kGy. The pectin and P layer were removed, but S1 was maintained at an EB dose of 10 kGy. The increase in small pores indicates that the degradation of S1 occurs above doses of 30 kGy. This result corresponded with an increase in surface roughness value. The degradation of the S2 layer progressed as radiation dose increased over 50 kGy. With a very high EB irradiation of 500 kGy, the severe degradation of henequen fiber was observed with a flattened surface and decrease of the surface roughness value. Morphological change was quantified by measuring porosity characteristics such as distribution, total surface area, and pore volume, using mercury porosimetry and nitrogen adsorption. Pores of diameter from 1000 µm to 1 µm occurred in large numbers, originating from the striation or vessel and void between the fibers. Pore structures such as porosity and pore distribution were changed by EB irradiation. EB irradiation of 10 kGy and 30 kGy separated pectin, wax and primary layers, and created many pores of 100 nm to 40 nm. With increasing doses from 50 kGy to 150 kGy, small pores decreased, because pores generated and existing pores were enlarged and annexed with neighboring pores. Total surface area and pores increased with low doses up to 30 kGy. On the other hand, they decreased at higher doses

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