Henequen/Unsaturated Polyester Biocomposites: Electron Beam Irradiation Treatment and Alkali Treatment Effects on the Henequen Fiber

Young Hee Han,[1] *Seong Ok Han,**[1] *Donghwan Cho,*[2] *Hyung-Il Kim*[3]

Summary: Henequen natural fiber reinforced unsaturated polyester biocomposites were fabricated and characterized. Henequen fibers were treated with various electron beam irradiation (EBI) dose or different concentrations of alkali solution. The effects of EBI or alkali treatments on the both henequen fiber and the properties of biocomposites made of unsaturated polyester and henequen fiber were compared by Fourier transform infrared spectra, thermal gravimetric analysis and dynamic mechanical analysis. Characteristics of the henequen fiber surface showed differently depending on the treatments and there is a close relationship between the optimal surface treatment of henequen fiber and the highest performance of the biocomposite resulting from the good adhesion between fiber and matrix.

Keywords: alkali treatment; biocomposite; electron beam irradiation; henequen fiber; unsaturated polyester

Introduction

Recently, there has been an increasing interest in the use of biocomposites. Biocomposites utilize natural fibers as reinforcement and polymers as matrix for composites. Biocomposite can be used as an alternative to glass fiber reinforced polymer composite in automotive and construction industries. Biocomposite has several advantages such as eco-friendly, lightweight and energy-saving characteristics.[1–5]

Electron beam irradiation (EBI) technique has been utilized for surface modification and properties enhancement of various polymer materials like fibers, films and composites for many years because it is a dry, clean and cold process with energy saving, high speed and environmental friendliness.[6] Also, EBI can maintain the inner pore structure of natural fibril comparing to the destruction of pore structure of natural fiber treated by alkali solution.[7] It gives the additional advantage of biocomposite because the pore structure of natural fiber can result in the insulation and collision absorbing effects when biocomposites apply to automobile and construction industries.

Unsaturated polyester (UP) has many industrial applications because of their good mechanical, chemical, and weather-resistant properties especially when reinforced with fiber. Therefore, it has been a popular thermoset polymer matrix in composites.[8] In this study, we investigated the effects of EBI on the characteristics of henequen fiber and the dynamic mechanical properties of biocomposites fabricated with UP resin and henequen fiber. The properties of EBI treated henequen fiber and its biocomposites were compared to those of the alkali treated henequen fiber and its biocomposites.

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Experimental

Henequen fibers (Agavo fourcroydes), originated from Mexico, in 30–40 cm long filament form, were used as reinforcement throughout this research.

Unsaturated Polyester (UP-GR235) is supplied from Sewon Chem. Co., Korea. It has the styrene content of 35wt%. Methyl ethyl ketone peroxide(MEKP) was used as catalyst. Figure 1

Fiber Treatments

For EBI treatment henequen fibers were put into a polyethylene bag, and then they were irradiated by an electron beam accelerator (ELV-4 type, eb-TECH Co. Ltd., Daejeon, Korea).[9] The henequen fibers were irradiated with different EBI dosages of 100, 200 and 500 kGy, respectively. The EBI processing was successfully conducted at EB-Tech Co., Korea. For alkali treatment henequen fibers were washed and soaked in NaOH solutions of 2, 5 and 10 wt% for 1 hour, respectively. Then, the treated fibers were washed with distilled water, neutralized with 2 wt% acetic acid, washed with distilled water again, and then finally dried at room temperature for 3 days. Untreated (0 kGy) henequen fibers were also used for comparison.

Biocomposite Fabrication

The fiber contents and chopped fiber lengths were 30 wt% and 1 cm for henequen/UP biocomposites, respectively. The biocomposites were fabricated by a compression molding technique using a hot press (Carver 2518). The molding compounds were heated with heating rate of 2 °C/min. The pressure of 1000 psi applied to the compounds at 40 °C and maintained at 70 °C for 1 hr, then cooled down to room temperature. The biocomposites were post-cured at 70 °C for 24 hr in the vacuum oven.

FT-IR Analysis

Fourier transform Infrared spectra were acquired using a FT-IR-610 spectrometer (Jasco Co.) The fibers were mounted on an ATR accessory and the ATR-FTIR spectra were obtained with an accumulation of 128 scans and with a resolution of 4 cm^{-1}.

Thermogravimetric Analysis

The thermal stability of the henequen fibers and biocomposites was analyzed in the range of 30 °C∼500 °C under the nitrogen atmosphere using a thermogravimetric analyzer (TGA Q500, TA Instruments). The heating rate was 5 °C/min.

Dynamic Mechanical Analysis

The storage modulus and the glass transition temperature of each biocomposite were measured by means of dynamic mechanical analysis using the single cantilever mode at a fixed frequency of 1 Hz under the liquid nitrogen atmosphere. The oscillating amplitude used was 0.2 mm. The heating rate was 5 °C/min. The DMA thermograms were recorded with a dynamic mechanical analyzer (DMA Q800, TA Instruments). The glass transition temperature was determined from the peak temperature of each tan δ curve. Before each measurement, the instrument was calibrated to have the correct clamp position and clamp compliance. The specimen dimensions were 30 mm × 10 mm × 1.8 mm.

Scanning Electron Microscopy

The surface morphology of raw, EBI treated henequen fibers and the fractured surfaces of biocomposites were character-

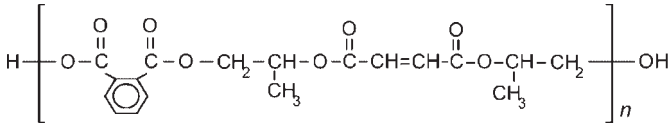

Figure 1.
Structure of unsaturated polyester.

ized by Scanning Electron Microscope (SEM, KL30, Philips, Netherlands). All specimens were coated with Au prior to the observation. The acceleration voltage used was 15~25 kV.

Results and Discussion

EBI and Alkali Effects on the Henequen Fiber

Figure 2 shows TGA and DTG thermograms of untreated and EBI-treated henequen fibers. The TGA result shows the removal of intrinsically absorbed water in the fiber around 100 °C and the decomposition of hemicellulose and cellulose in the range of 280~320 °C and 350 °C~360 °C, respectively. The main decomposition peak of cellulose for untreated henequen fiber was found at 360 °C. It was slightly decreased with increasing the EB dosage, shifting to 346 °C when irradiated at 500 kGy. Also, the decomposed portion of the henequen fibers treated at 500 kGy in the range of 200 °C~360 °C was increased, which means the formation of the lower molecular weight compounds resulting from the cleavage of the glycosidic bonds of cellulose.

Figure 3 shows TGA and DTG thermograms of untreated and alkali-treated henequen fibers. It is seen that there was no significant change in the decomposition peak temperature of cellulose. On the contrary, the small peak like a shoulder was due to the presence of hemicellulose component in the untreated henequen fiber and it completely disappeared even with the treatment of 2 wt% alkali solution. It has been known that the hemicellulose component can be removed easily by an alkali treatment.[10–13]

Figure 4 shows FT-IR spectra of untreated and EBI treated henequen fibers. The spectra of henequen fibers showed the absorption peaks at 3200–3400 cm^{-1} from the typical –OH stretching bonds, at 2750–2800 cm^{-1} from typical aliphatic (CH_2 and CH) stretching bonds, at 1738 cm^{-1} from carbonyl group stretching, at 1608 cm^{-1} from free carbonyl bond, at 1373 cm^{-1} from O–H in plane bending, at 1246 cm^{-1} from C–H, 1000–1500 cm^{-1} from aromatic region. No significant change was observed in

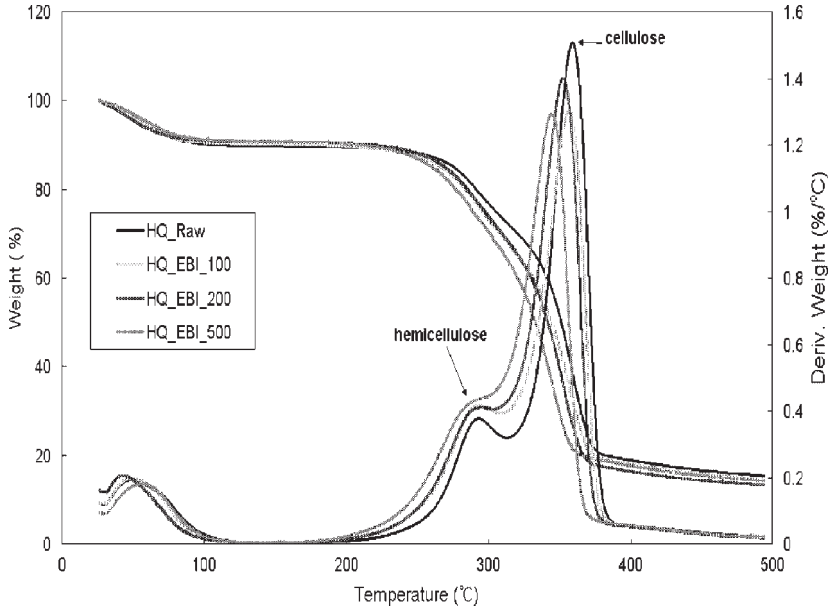

Figure 2.
TGA and DTG thermograms of untreated and EBI-treated henequen fibers.

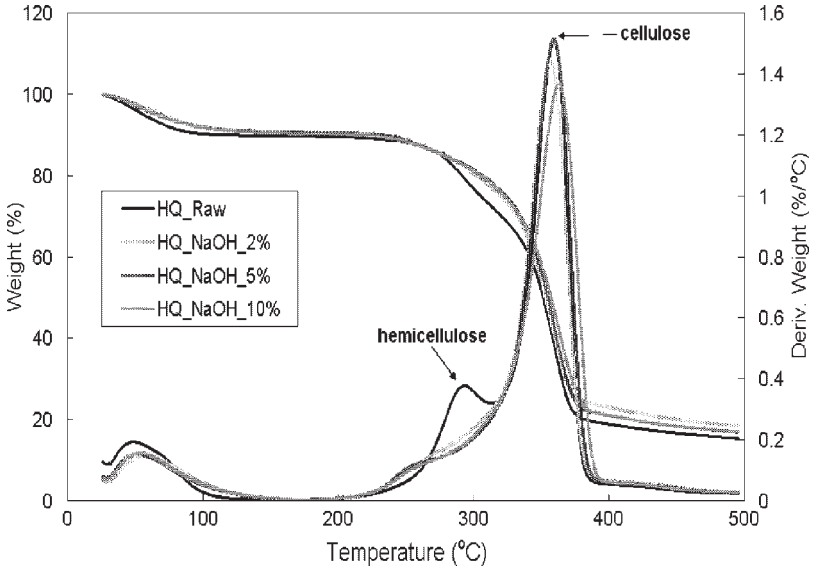

Figure 3.
TGA and DTG thermograms of untreated and alkali treated henequen fibers.

the spectra between untreated and the treated henequen fibers.

On the contrary, the henequen fiber undergoes very different chemical changes by the alkali solution treatment. Figure 5 shows FT-IR spectra of untreated and alkali treated henequen fibers. For the alkali treated henequen fibers, the intensity of the absorption peaks of 3200–3400 cm^{-1} from O–H stretching bond, 1373 cm^{-1} from O–H in plane bending were reduced because of the formation of glycoside bonding. Also, 1737 cm^{-1} from carbonyl group stretching was reduced due to hemicellulose removal. The decrease of 1608 cm^{-1} band can be explained by the removal of OH bending in the absorbed water molecules by alkalization.[11–15]

Characterization of Henequen/UP Biocomposites

Figure 6 shows the TGA and DTG thermograms measured for henequen fiber, UP, and henequen/UP biocomposites. The

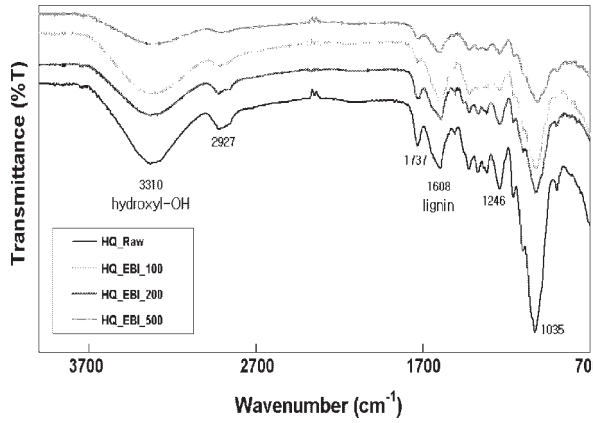

Figure 4.
FT-IR spectra of untreated and EBI treated henequen fibers.

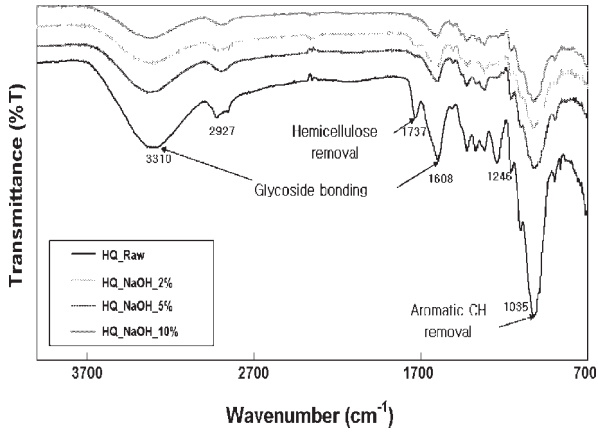

Figure 5.
FT-IR spectra of untreated and alkali treated henequen fibers.

biocomposites were made of untreated and treated henequen with different EBI dosages. The absorbed water showed the peak around 150∼220 °C. Hemicellulose and cellulose were decomposed of the temperature of 280∼320 °C and 350 °C∼ 360 °C, respectively. The main decomposition peak of UP showed at 390 °C. The main decomposition peak of cellulose of henequen fiber shifted from 360 °C to lower temperature with increasing EBI dose and the maximum decomposition temperature of cellulose for biocomposite made of EBI treated HQ with 500 kGy shifted to 346 °C. It means that the alpha-cellulose of higher molecular weight changed to the beta-cellulose of lower molecular weight by the EBI treatment. The decomposition of the UP was shifted from 388 °C to 396 °C in the henequen/UP biocomposite. It can be explained by that the henequen fibers were incorporated into the UP matrix of the biocomposite and the reinforcing by henequen fibers probably somewhat retarded the thermal decomposition of the UP matrix.

Figure 7 shows the TGA and DTG thermograms measured for henequen fiber,

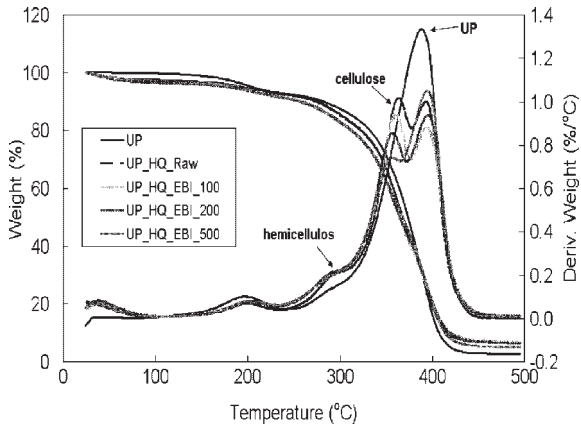

Figure 6.
TGA and DTG thermograms for henequen fiber, UP, untreated- and EBI treated-henequen/UP biocomposites.

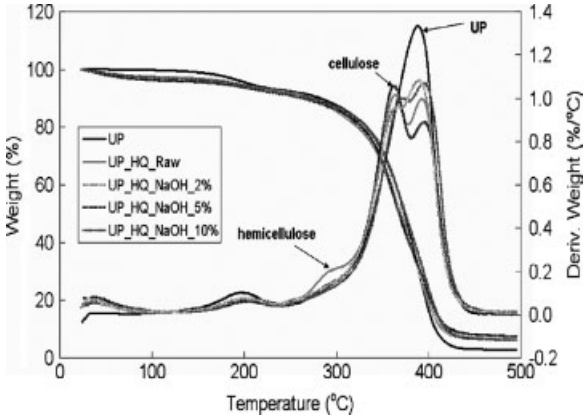

Figure 7.
TGA and DTG thermograms for henequen fiber, UP, untreated- and alkali treated-henequen/UP biocomposites.

UP, untreated and alkali treated henequen/UP biocomposites. The absorbed water showed the peak around 150∼220 °C. There was no significant change in the decomposition peak pattern from the cellulose and the UP in the henequen/UP biocomposites with alkali treatment. Regardless of the concentration of alkali solution used, the maximum decomposition peaks were occurred at 360 °C from the cellulose component and 390 °C from the UP matrix. The only difference for decomposition peaks between the untreated and the alkali treated henequen fibers was the peak for hemicellulose removal in the range of 280∼320 °C. The thermal stability study of henequen fiber/UP biocomposites is consistent with the results of characterization of treated henequen fibers with EB or alkali solution.

Figure 8 compares the storage modulus of UP, untreated and EBI treated henequen/UP biocomposites. The storage modulus of the untreated henequen/UP biocomposites (3.4 GPa) increase comparing to the UP matrix itself (2.7 GPa) due to the reinforcing effects of henequen fiber. Also, the storage modulus of raw henequen/UP specimen increased with an application of EBI. The storage modules of biocomposites at 30 °C changed with the different EBI dosages such as 4.0 GPa, 4.3 GPa and 3.8 GPa with 100, 200 and 500 kGy EBI

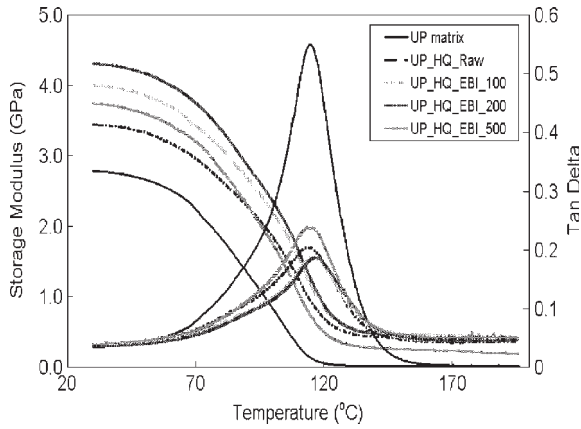

Figure 8.
Storage modulus of UP, untreated and EBI treated henequen/UP biocomposites.

dosages, respectively. The highest performance of biocomposite was obtained from the biocomposite reinforced with 200 kGy EBI treated henequen fiber. The glass transition temperature of UP was measured at 115 °C and this temperature was not changed for the biocomposites. However, the tan δ peak height, which is related to damping and impact properties of a material, was greatly reduced by incorporation of the chopped henequen fibers. The height of tan δ peak showed the lowest for the biocomposite treated with 200 kGy resulting from the least participating polymer chains in the transition, which can be explained as the best adhesion between UP matrix and henequen fiber.

The highest performance of biocomposites with treated henequen fiber at 200 kGy can be explained that the internal crosslinking between the cellulose structures may be formed by electron beam irradiation of high energy. For the formation of crosslinked bonds, the presence of two radicals on adjacent chains in a polymer is required. Their subsequent recombination results in the chemical bond between two polymeric chains. Thus, the crosslinking reaction can take place with higher popularity at a high dose than at a low dose of EBI. The combination of the internal crosslinking between cellulose structures and the surface modification contributed to the highest performance of biocomposite with treated henequen fibers at 200 kGy. At such an excessive dose of EBI such as 500 kGy, the henequen fiber surface microstructure was critically changed and it was expected that there must be serious chain scissions of the cellulose fiber. At this stage, the henequen fiber was chemically degraded, accordingly, it may cause some deterioration of the storage modulus of henequen/UP biocomposite.[16]

Figure 9 compares the storage modulus of UP, untreated and alkali treated henequen/UP biocomposites. The storage modulus of all alkali-treated henequen/UP biocomposites was increased in comparison with that of the untreated henequen/UP biocomposite at 30 °C. The storage modulus of biocomposites made of henequen fiber treated with 2, 5 and 10 wt% NaOH solution showed 17.6%, 26.5% and 14.7% increase, respectively, comparing to the untreated kenaf fiber (3.4 GPa). For the tan δ peak, there was no temperature shift with the different concentrations of alkali solution, however, the height of tan δ peak showed the lowest for the biocomposite treated with 5 wt% NaOH solution resulting from the least participating polymer chains in the transition, which can be explained as the best adhesion between UP matrix and henequen fiber.

Figure 10 shows the fracture surfaces of henequen/UP biocomposites fabricated using the chopped henequen fibers treated

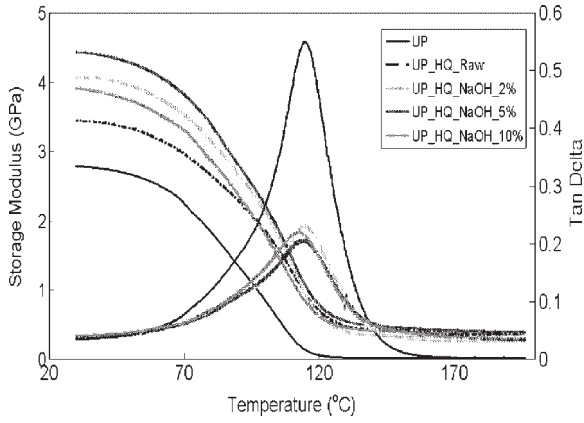

Figure 9.
Storage modulus of UP, untreated and alkali treated henequen/UP biocomposites.

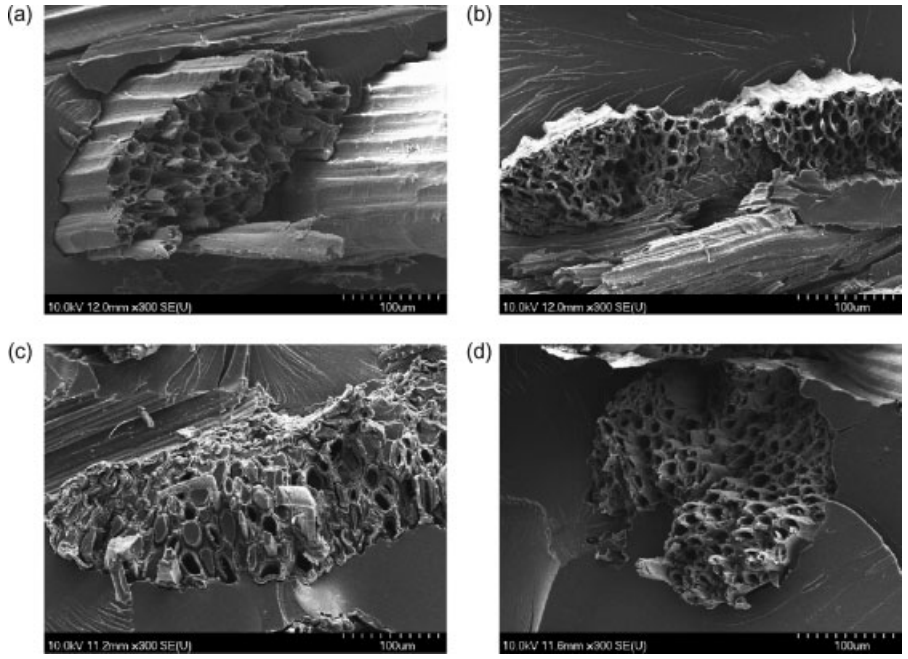

Figure 10.
Fracture surfaces of EBI treated henequen/UP biocomposites. (a) Untreated, (b) 100 kGy, (c) 200 kGy, and (d) 500 kGy.

at different EB dosages. Each photo represents the interfacial region between the henequen fiber and the UP matrix. There is the gap or interstice between henequen fiber and UP matrix for the untreated henequen/UP specimen. The interfacial adhesion between the henequen fiber and the matrix was apparently improved when treated with EBI, reflecting the higher storage modulus than the untreated henequen/UP specimen. Especially, the best adhesion between henequen fiber and UP matrix can be found for the biocomposite reinforced with 200 kGy EBI treated henequen fiber. This result is coincident with the result of storage modulus of biocomposites, which shows the highest performance of 200 kGy EBI treated henequen/UP biocomposite. Also, the pore structure of henequen fiber can be maintained in the biocomposite and UP, thermosetting polymer, cannot penetrate into the pores of the henequen fiber.

Figure 11 displays the fracture surfaces of henequen/UP composites fabricated using the chopped henequen fibers treated at different alkali solutions. The apparently improved interfacial adhesion between henequen fiber and matrix can be found with the NaOH treatment, especially, 5 wt% NaOH. These results are agreed with the results of dynamic mechanical properties of biocomposite treated with different NaOH concentrations. For alkali treated henequen fiber the pore structure was disappeared resulting from swelling and contracting of henequen fiber during alkali solution treatment and drying process.

From these results we can conclude that the improved dynamic mechanical performances of henequen/UP biocomposites can be obtained with the optimum treatment of henequen fiber with either EBI or alkali solution resulting in the better adhesion between henequen fiber and UP matrix. Also, EBI can be used as an environmentally friendly process for treatment of natural fibers to develop eco-friendly biocomposites.

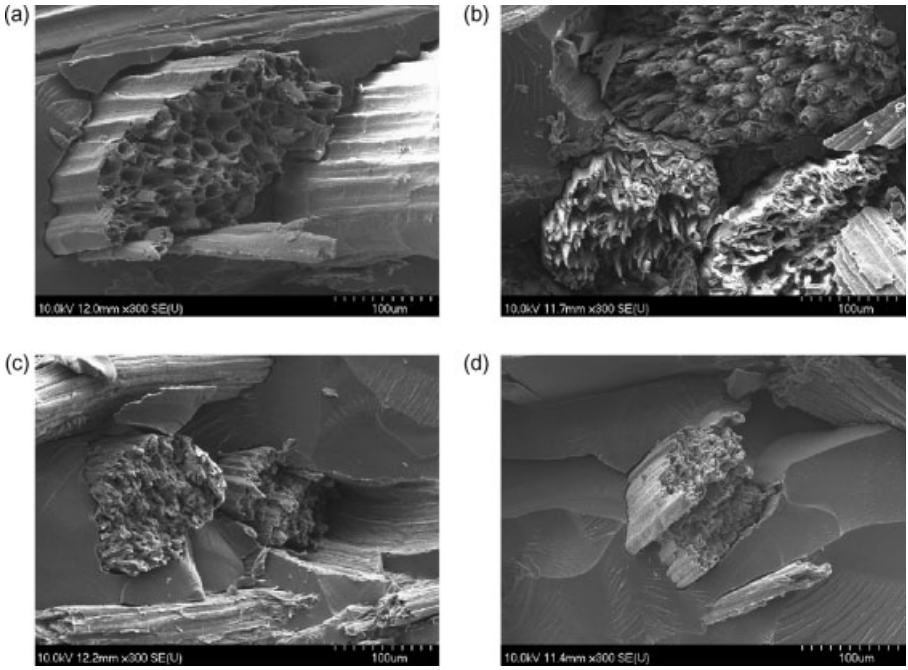

Figure 11.
Fracture surfaces of alkali treated henequen/UP biocomposites. (a) Untreated, (b) NaOH 2wt%, (c) NaOH 5wt%, and (d) NaOH 10wt%.

Conclusions

Electron beam irradiation and alkali treatment effects on both the henequen fiber and its biocomposites were investigated to develop the environmentally friendly biocomposites and its manufacturing process. Electron beam irradiation on the henequen fibers lowered the maximum thermal decomposition temperature of cellulose, and little change of the functional groups for the henequen fibers. On the contrary, these results were very different from those of the henequen fiber treated with alkali solution. Alkali treatment on henequen fibers showed no change of the maximum decomposition peak of cellulose. Also, the glycoside bonding formation and the removal of hemicellulose were induced by alkali treatment. The henequen/UP biocomposites were manufactured and the effects of EB or alkali treatments of henequen fiber on the thermal, dynamic mechanical and interfacial properties of henequen fiber/UP biocomposites were analyzed. The reinforcing effects of henequen fibers resulted in the higher storage modulus than UP matrix itself by increasing of 159%, 150%, respectively 5wt% NaOH solution, 200 kGy EB treatment. Also, the kenaf fiber treatment by EB or NaOH solution improved the dynamic mechanical properties of henequen/UP biocomposite.

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