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Effect of Electron Beam Irradiation on the Interfacial and Thermal Properties of Henequen/Phenolic Biocomposites

Yansong Pang, Sung Bong Yoon, Jeong Min Seo, Seong Ok Han[1], and Donghwan Cho†

Polymer/Bio Composites Research Lab, Department of Polymer Science and Engineering, Kumoh National Institute of Technology, Gumi, Gyungbuk 730-701, Korea
[1]Functional Materials Research Center, Korea Institute of Energy Research, Daejeon 305-343, Korea

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Abstract: Natural fiber/phenolic biocomposites with chopped henequen fibers treated at various levels of electron beam irradiation (EBI) were made by means of a matched-die compression molding method. The interfacial property was explored in terms of interfacial shear strength measured by a single fiber microbonding test. The thermal properties were studied in terms of storage modulus, tan δ, thermal expansion and thermal stability measured by dynamic mechanical analysis, thermomechanical analysis and thermogravimetric analysis, respectively. The result showed that the interfacial and thermal properties depend on the treatment level of EBI done to the henequen fiber surfaces. The present result also demonstrates that 10 kGy EBI is most preferable to physically modify the henequen fiber surfaces and then to improve the interfacial property of the biocomposite, supporting earlier results studied with henequen/poly (butylene succinate) and henequen/unsaturated polyester biocomposites.

Keywords: *biocomposites, natural fiber, electron beam irradiation, interfacial property, thermal property*

1. Introduction

Biocomposites or natural fiber composites are defined as composite materials composed of biodegradable natural fibers as reinforcement and biodegradable or non-biodegradable polymers as matrix[1]. Eco-friendly biocomposites using plant-derived fibers may be novel materials of the twenty-first century not only to reduce the growing environmental threat but also to alleviate the uncertainty of petroleum supply[2]. Advantages of natural fibers over conventional glass fiber reinforcement are low cost, low density, high toughness, acceptable specific strength, enhanced energy recovery, recyclability, carbon dioxide reduction in nature, biodegradability, etc.[3,4]. Recently a number of studies have extensively focused on natural fibers such as kenaf, flax, jute, hemp, sisal, and henequen as green alternatives to conventional glass reinforcements and also on the biocomposites as attractive materials with abundant natural resources and environmental acceptability[5,6].

Not only in conventional polymer composites but also in biocomposites, the interfacial adhesion between the fibers and the matrix is important to achieve the best performance of the materials. The main drawback of natural fibers is its hydrophilic nature that lowers the interfacial adhesion with a comparatively hydrophobic polymer matrix. There are several approaches of fiber surface modification to improve the interfacial adhesion of the biocomposite. One is chemical modification of natural fiber surfaces by means of dewaxing, alkalization, grafting, cyanoethylation, acetylation, bleaching, and sizing with silane or other coupling agents[7-9]. The other is physical modification by means of plasma and electron beam treatments[10,11].

Electron beam irradiation (EBI) techniques have been increasingly utilized for surface modification and property enhancement of polymer materials like fibers, films, plastics and composites for many years[12]. EBI may effectively remove the surface impurities and generate functional groups on the fiber surfaces with an optimal treatment. Electron beam processing is a dry, clean and cold method with advantages such as energy-saving, high speed, uniform irradiation and environmental friendliness.

Henequen (*Agave fourcroydes*), which is a similar family with sisal, is long, hard, and strong fiber obtained from the 60 ~ 120 cm long leaves of agave plants, which

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† Corresponding author: e-mail: dcho@kumoh.ac.kr

is native to Yucatan, Mexico. It has been used traditionally to make twines, ropes, carpets and cordages for a long period of time[13,14]. Phenolic resin has been frequently used as general-purpose thermosetting resin in a variety of commodity and industrial applications for several decades. It is inexpensive, thermally stable, flame-resistant, thermally and electrically insulative, easily processible for composites, and has good mechanical properties[15,16]. However, reports on the biocomposite system with henequen natural fibers and phenolic resin are rarely found.

Consequently, the objective of this work is to examine the effect of fiber surface modification by EBI on the interfacial and thermal properties of henequen/phenolic biocomposites. The interfacial shear strength of various biocomposites fabricated using henequen fibers treated at different levels of EBI was investigated with a phenolic resin microdroplet formed on a single henequen fiber using a single-fiber microbonding test. Their thermal properties have also been studied using dynamic mechanical analysis (DMA), thermomechanical analysis (TMA), and thermogravimetric analysis (TGA).

2. Experimental

2.1. Materials

Henequen (HQ) fiber bundles in the 60~70 cm long filament form were supplied from Yucatan, Mexico. To modify the surfaces, henequen fibers were irradiated at various EBI dosages of 0, 10, 30, 50, 70, 100, 150, 200, and 500 kGy, respectively. The EBI treatments were kindly conducted at EB-Tech Co., Korea. A resol-type phenolic resin (KC4100B) kindly supplied from Kangnam Chemical Co., Korea was used as matrix.

2.2. Microdroplet Formation

A very tiny amount of resol-type phenolic resin was dropped on a single henequen fiber. The phenolic resin microdroplet covered around the henequen fiber surface was cured at 90°C for 1 h in a conventional oven. The procedures forming a resin microdroplet on a single henequen fiber treated at different EBI doses were repeated to prepare a sufficient number of single fiber microbonding specimens.

2.3. Biocomposite Fabrication

All the untreated and treated henequen fibers were sufficiently impregnated with phenolic resin one by one and then dried at 70°C for 1 h in a conventional oven in order to prepare henequen/phenolic molding compounds with the B-stage resin. The towpreg-type molding compounds were uniformly chopped to 6.4 mm in average length. The chopped molding compounds were placed in a stainless steel matched-die mold and then molded in a compression manner using a hot-press (Carver 2518). Figure 1 illustrates a schematic procedure of henequen/phenolic biocomposite fabrication. The molding compounds in the mold were pre-heated from ambient temperature to 70°C for 1 h. Then, the molding temperature was increased to 110°C for 1 h with a pressure of 1000 psi and subsequently heated to 140°C for 30 min. Finally, the mold was naturally cooled down to ambient temperature without removing the applied pressure. Figure 2 represents a time-temperature-pressure profile for processing henequen/phenolic biocomposites. The mold dimensions were 50 mm × 50 mm. The thickness of the obtained biocomposites was accommodated according to the specimen requirement for each analytical method. The fiber content of henequen/phenolic biocomposites with random fiber distribution was 20% by weight. The henequen fibers were untreated or treated at various EBI

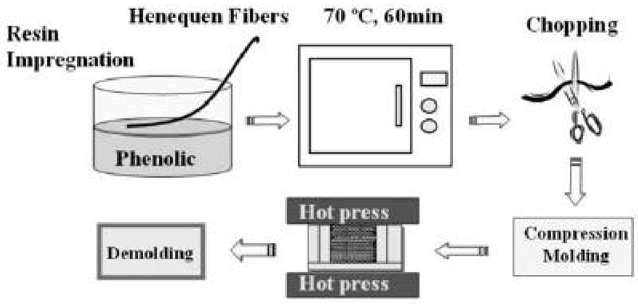

Figure 1. Experimental procedure to fabricate henequen/phenolic biocomposites.

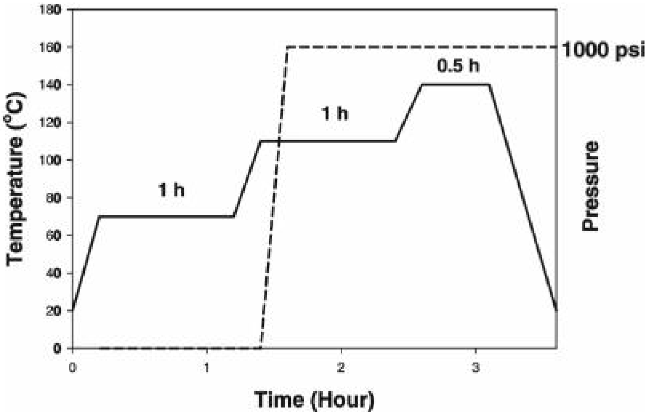

Figure 2. A time-temperature-pressure profile for fabricating henequen/phenolic biocomposites with randomly oriented chopped henequen fibers.

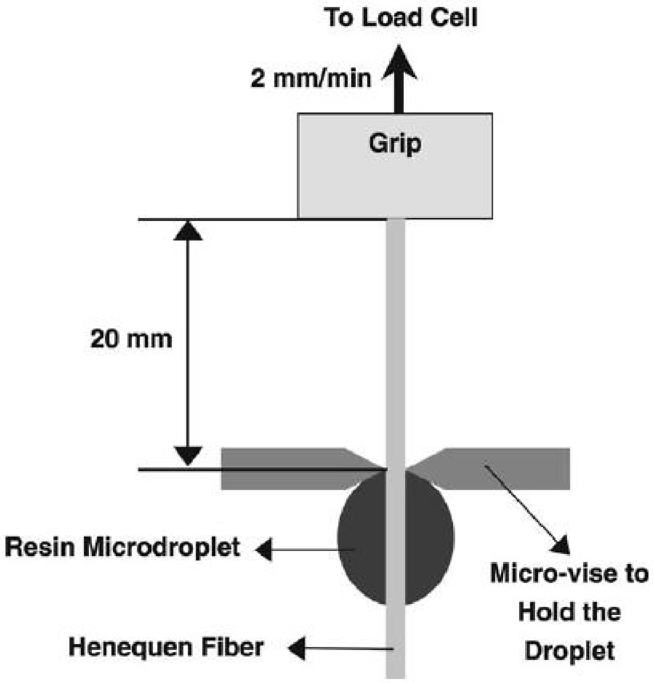

Figure 3. Schematic illustration of a single fiber microbonding test.

levels of 0, 10, 30, 50, 70, 100, 150, and 200 kGy before biocomposite fabrication, respectively.

2.4. Single Fiber Microbonding Test

A universal testing machine (UTM, Instron 4467) was used for a single fiber microbonding test. The load cell was 100 N and the crosshead speed was 2 mm/min. The grip distance was 20 mm and the micro-vise grip distance was 0.4 mm. Figure 3 shows a schematic illustration of a single fiber microbonding test. Prior to resin microdroplet formation, henequen fibers with a relatively uniform fiber diameter were selected for the single fiber microbonding test because cellulose natural fibers including henequen may generally have different fiber diameters at different locations in the micrometer scale due to irregular fiber surface.

Each test was performed with about 30 specimens. The average value of the interfacial shear strength (IFSS) for each composite specimen was obtained from all the test results, using the following equation.

$$\tau = F/(\pi \cdot D_f \cdot L_e)$$

Here τ is the interfacial shear strength (IFSS). F is the force required for debonding the resin microdroplet from the single henequen fiber filament while tensile loads are applied. D_f is the diameter of the measuring fiber. And L_e is the fiber length embedded in the resin microdroplet.

2.5. Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA 983, TA Instruments) was used to study the dynamic mechanical thermal properties of each biocomposite with the fiber surface of different EBI treatments. A fixed frequency of 1 Hz and the oscillation amplitude of 0.2 mm were used throughout this work. A heating rate of 3°C/min was used. The temperature range was from ambient temperature to 250°C with flowing N_2 gas of 50 cc/min. Before each measurement, the instrument was calibrated to have correct clamp position and clamp compliance. The specimen dimensions were 30 mm × 10 mm × 3 mm.

2.6. Thermomechanical Analysis

Thermomechanical analysis (TMA 2940, TA Instruments) was used to study the thermomechanical stability and thermal expansion behavior of each biocomposite with different EBI surface treatments. The temperature range from ambient temperature to 110°C and the heating rate of 2°C/min were used with purging N_2 gas (50 cc/min). The expansion mode to monitor the thermal expansion was used. The specimen dimensions were 5 mm × 5 mm × 3 mm.

2.7. Thermogravimetric Analysis

Thermogravimetric analysis (TGA 951, Du Pont) was used to study the thermal stability of the biocomposites composed of the resin matrix and the henequen fibers treated at different EBI doses. The measuring temperature range from ambient temperature to 500°C and the heating rate of 10°C/min were used with purging N_2 gas (80 cc/min). Each sample weight was about 20 mg.

3. Results and Discussion

Figure 4 depicts the single fiber microbonding test result for untreated and surface-treated henequen/phenolic biocomposites. The interfacial shear strength (about 4.3 MPa) of untreated henequen/phenolic specimen was slightly higher than that of untreated henequen/unsaturated polyester (UPE) composite reported earlier[11]. The interfacial shear strength (IFSS) values measured for treated henequen/ phenolic composite specimens were greater than those measured for the henequen/UPE composite prepared at the same dosage of EBI treatment, as reported earlier[11]. This indicates that the EBI treatment on the henequen fiber more effectively contributes to enhancing the inter-

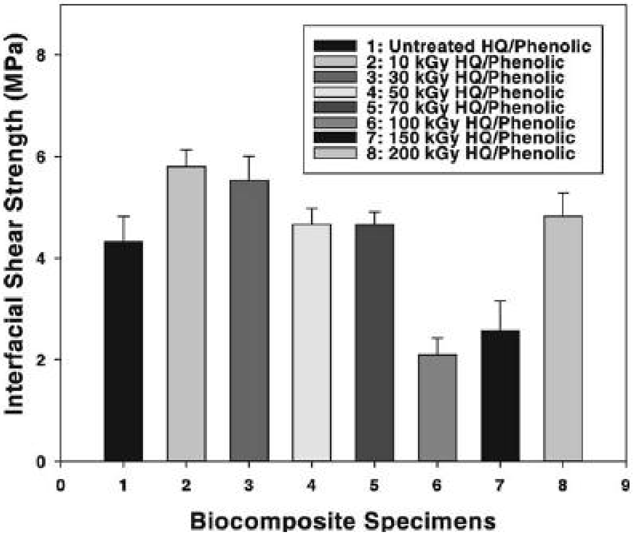

Figure 4. A comparison of the interfacial shear strengths obtained for henequen (HQ)/phenolic biocomposites fabricated using henequen fibers treated at various EBI levels.

facial adhesion of henequen/phenolic biocomposites than henequen/UPE cases. This may be due to the presence of high number of hydroxyl groups, which can interact with hydroxyl groups on the natural fiber surface to form intermolecular hydrogen bonds. Based on the earlier founding[17], most of the weak boundary components like impurities and waxes existing on the henequen fiber surfaces were removed at the early stage of EBI and the surface more or less became undulated with the treatment. The variation of the IFSS value with the EBI doses in the henequen/phenolic biocomposites was almost similar to the varying tendency found in the henequen/UPE composite earlier. The treatment higher than 70 kGy resulted in the decrease of the IFSS value to a lower value than the untreated one. The decreased IFSS was increased by the EB treatment at 200 kGy. This is due probably to the surface damage by a high intensity of EB, leading to an increased surface area of the natural fiber. This agrees with the result found from henequen/UPE and henequen/poly(butylene succinate) biocomposite systems[11,17].

The interfacial shear strength result suggests that the optimal treatment level of EBI on the henequen fibers may be 10 kGy in the present biocomposite system. Also, this work indicates that the irradiation of electron beam to natural fibers significantly affects the interfacial adhesion between the fibers and the polymer matrix, depending on the surface modification by EBI.

Figure 5 shows the variation of the storage modulus as a function of temperature for various henequen/phenolic biocomposites fabricated with 6.4 cm long chopped henequen fibers surface-treated at different EBI levels. The fiber content was fixed to 20% by weight. The storage modulus of each henequen/phenolic specimen was greater than that of the corresponding henequen/UPE composite. This is because the storage modulus of phenolic resin is greater than that of UPE resin only. The storage modulus of phenolic resin was further enhanced by incorporating the chopped henequen fibers depending on the surface treatment done. The greatest storage modulus value was obtained from 50 kGy henequen/phenolic specimens. The

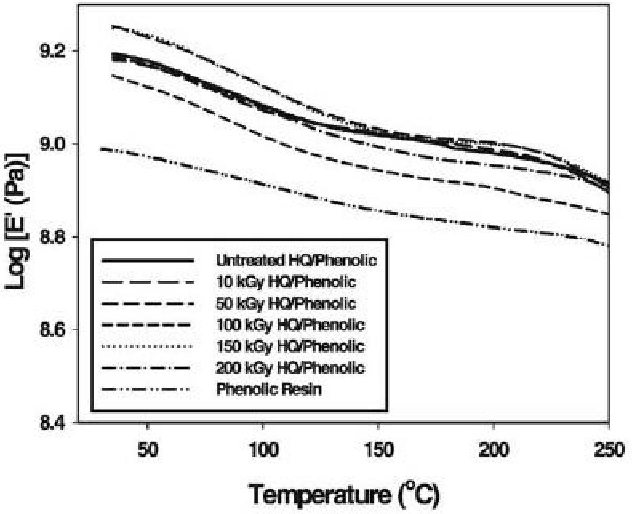

Figure 5. Variations of the storage modulus as a function of temperature for henequen (HQ)/phenolic biocomposites with different EBI treatments of henequen fibers.

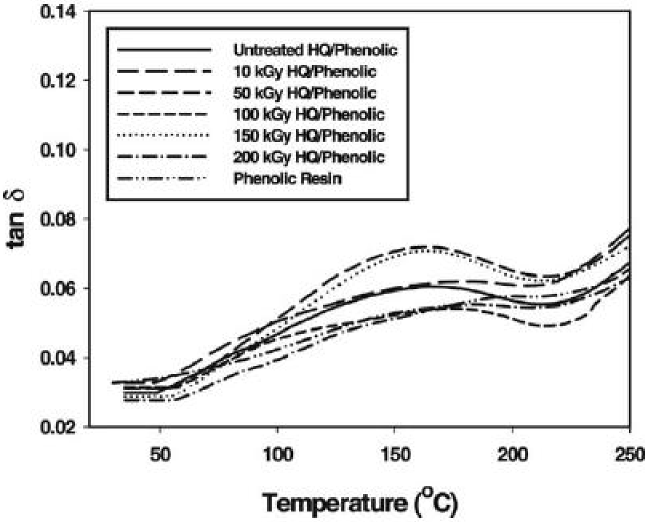

Figure 6. Variations of the tan δ as a function of temperature for henequen (HQ)/phenolic biocomposites with different EBI treatments.

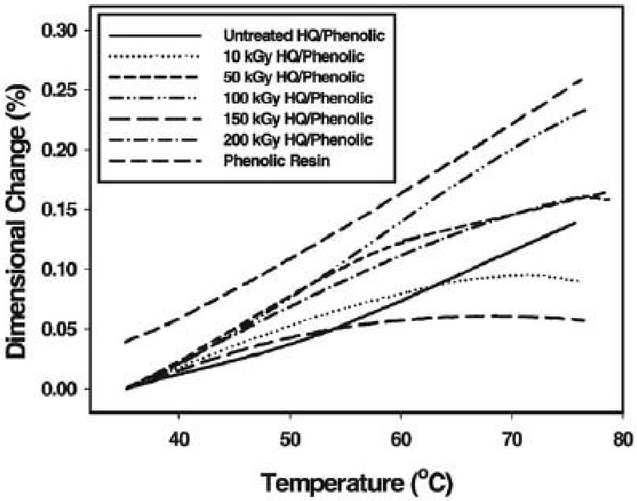

Figure 7. TMA thermograms as a function of temperature for phenolic resin and henequen (HQ)/phenolic biocomposites with different EBI treatments of henequen fibers.

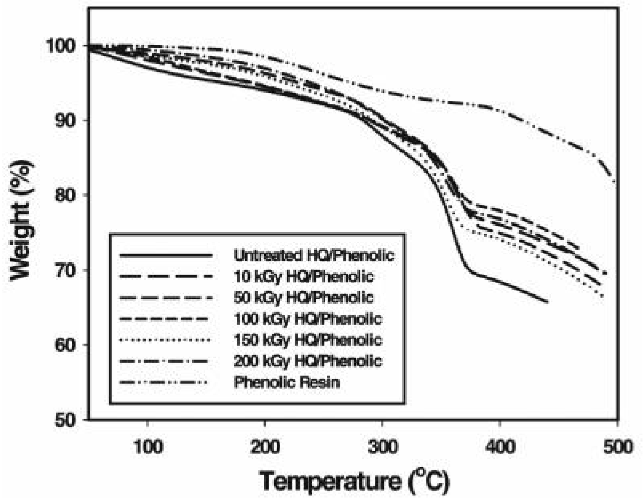

Figure 8. Changes in the thermal stability for henequen (HQ)/phenolic biocomposites with different EBI treatments of henequen fibers, measured in N_2.

Table 1. Coefficients of thermal expansion (CTE) (μm/m/°C) of henequen/phenolic biocomposites with different EBI treatments of henequen fibers

Specimen	35°C ~75°C
Untreated Henequen/Phenolic	34
10 kGy Henequen/Phenolic	25
50 kGy Henequen/Phenolic	38
100 kGy Henequen/Phenolic	39
150 kGy Henequen/Phenolic	25
200 kGy Henequen/Phenolic	41
Phenolic Resin	54

result indicates that the EBI treatment influences the dynamic mechanical property as well as the interfacial property.

By inspecting the result of tan δ as a function of temperature in Figure 6, it was found that phenolic resin exhibited a relatively low tan δ value, compared with other henequen/phenolic biocomposites. It may be due to brittleness of cured phenolic resin. It may be explained by that the brittle phenolic resin may become more ductile due to the presence of henequen natural fibers. As a result, the glass transition temperature of the phenolic resin without the natural fibers was decreased from about 200°C to about 160°C, as similarly found with a decreased tendency in both henequen/UPE and henequen/poly (butylene succinate) biocomposites earlier[11,17].

Figure 7 shows the thermomechanical change as a function of temperature for phenolic resin and various henequen/phenolic biocomposites with different EBI treatments. The linear coefficient of thermal expansion (CTE) value of each specimen was measured from the slope of each TMA thermogram in the range of 35°C ~ 75°C. The result is given in Table 1. The CTE of phenolic resin was decreased with incorporation of chopped henequen fibers. The result indicates that use of henequen fibers with phenolic matrix to make the biocomposite is likely to reduce its thermal expansion but the EBI treatment effect on the thermomechanical stability of the biocomposites may be ambiguous due to the hollow-type cellulosic structure of henequen fibers, which make the thermal expansion behavior more complex.

Figure 8 shows the TGA thermograms of phenolic resin and henequen/phenolic biocomposites. As similarly observed in henequen/UPE specimens[18], the thermal stability of phenolic resin was decreased because of the presence of henequen fibers in the biocomposite system, especially in the higher temperature region. The decreased stability of each composite specimen was significantly improved by EBI treatment done to the henequen fibers but it was still lower than that of phenolic resin only. The TGA thermogram of phenolic resin exhibited a typical behavior of thermal degradation of a resol-type phenolic resin, showing a multiple weight loss stage with temperature. Use of natural fiber henequen with a polymeric resin to make the composite more or less decreased with the thermal stability over the temperature range measured. Therefore, it is needed to find out experimental approaches for improving the thermal stability of the natural fibers and the related biocomposites to extend their processing, performance and application.

4. Conclusions

The interfacial shear strength of henequen/phenolic biocomposite prepared using henequen fibers treated with electron beam irradiation was greater than that of untreated henequen/phenolic counterpart, depending on the treatment level of EBI. In particular, the IFSS of untreated henequen/phenolic biocomposite was significantly increased by using a low EB intensity of 10 kGy to the henequen fiber surfaces. The higher intensity greater than 100 kGy decreased the interfacial strength between the natural fibers and the polymer matrix.

The storage modulus of phenolic resin was increased by incorporating the chopped henequen fibers depending on the surface treatment done, especially with the EB intensity lower than 50 kGy. The glass transition temperature of phenolic resin without henequen fibers was decreased due to the presence of ductile henequen fibers. The result indicates that the EBI treatment influences the dynamic mechanical property as well as the interfacial property of the biocomposite.

The thermomechanical result indicates that an introduction of henequen fibers to phenolic matrix is likely to reduce its thermal expansion but the EBI treatment effect on the thermal expansion behavior of the biocomposites was not clear due to the hollow-type cellulosic structure of henequen fibers.

The thermal stability of phenolic resin was decreased due to the incorporation of thermally less stable henequen fibers in the biocomposite system. However, the decreased stability was significantly improved by the EBI treatment done to the henequen fibers.

Acknowledgement

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