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Interfacial Shear Strength and Thermal Properties of Electron Beam-Treated Henequen Fibers Reinforced Unsaturated Polyester Composites

Yansong Pang and Donghwan Cho*

Polymer/Bio Composites Research Lab., Department of Polymer Science and Engineering, Kumoh National Institute of Technology, Gumi, Gyungbuk 730-701, Korea

Seong Ok Han

Functional Materials Research Center, Korea Institute of Energy Research, Daejeon 305-343, Korea

Won Ho Park

Department of Textile Engineering, Chungnam National University, Daejeon 305-764, Korea

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Abstract: Natural fiber henequen/unsaturated polyester (UPE) composites were fabricated by means of a compression molding technique using chopped henequen fibers treated at various electron beam (EB) dosages. The interfacial shear strength (IFSS), dynamic mechanical properties, and thermal expansion behavior were investigated through a single fiber microbonding test, fractographic observation, dynamic mechanical analysis, and thermomechanical analysis, respectively. The results indicated that the interfacial and dynamic mechanical properties significantly depended on the level of the EB treatment irradiated onto the henequen fiber surfaces. The effect of EB treatment on the IFSS, storage modulus and fracture surface of the henequen/UPE composites agreed with each other. The results of this study also suggested that the modification of henequen fiber surfaces at 10 kGy EB is the most effective for improving the interfacial properties of the henequen/UPE composites.

Keywords: natural fiber composites, henequen, electron beam treatment, interfacial shear strength, dynamic mechanical properties.

Introduction

Natural fiber composites, often referred to as biocomposites, have increasingly attracted attention because they have potential not only as a novel material for natural resource, eco-friendliness, sustainability, lightness, CO_2 reduction in nature and cost-effectiveness, but also as an alternative to conventional glass fiber polymer composites.[1,2] Natural fiber composites are now being used especially in automotive, building, commodity, and other applications.

The properties of a fiber-reinforced polymer composite material significantly depend on many factors like fiber and matrix type, fiber-matrix adhesion, fiber content, fiber aspect ratio, fiber orientation, fiber modification, and composite processing method.[3] Ligno-cellulose fibers like jute, hemp, flax, sisal, henequen, coir and kenaf fibers have been frequently used as natural fiber reinforcement.[4] Of them, henequen fibers are attracting more attention due to relatively low cost and density.[5]

Henequen(*Agave fourcroydes*), which is a similar family with sisal, is long, hard, and strong fiber obtained from the 2-4 foot long leaves of agave plants, which is native to Yucatan, Mexico. The natural fibers have been used to make twins, ropes, carpets and cordages for a long period of time.[6] Thermosetting resins are frequently used as matrix in natural fiber composites because they have easy composite proccessibility, and better properties and performances in comparison with general-purpose thermoplastic polymers. Unsaturated polyester (UPE) resins are the most widely used thermosetting matrix in natural fiber composites as well as in conventional composite industries.[7-12]

The interfacial adhesion between natural fibers and a polymer matrix has often been issued in many natural fiber composite systems. A strong bond in the interfacial region is essential for achieving high mechanical performances of a composite. Therefore, a number of surface modification studies have been devoted to understand and improve the interfacial characteristics of natural fiber composites. How-

*Corresponding Author. E-mail: dcho@kumoh.ac.kr

ever, most of the earlier studies were focused on chemical modifications such as alkalization, acetylation, silanes coupling, and so on.[13-16] There have been some papers[17,18] dealing with natural fibers physically surface-treated with plasma to improve the interfacial adhesion between the fibers and the matrix of biocomposites. A study on physical modification of natural fiber surface using electron beam (EB) has been rarely found. Recently, Cho *et al.*[19] reported that the EB treatment significantly influences the interfacial properties of henequen/poly(butylene succinate) biocomposites. No paper has been reported on a henequen/UPE composite system with EB treatment yet.

An electron beam irradiation (EBI) technique has been increasingly utilized for surface modification and property 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.[20] Consequently, the objective of the present study is to explore the effect of EB treatment on the interfacial shear strength and thermal properties of UPE composites fabricated with henequen fibers modified at different EB dosages by means of a single fiber microbonding test using a resin microdroplet formed on a single henequen fiber, dynamic mechanical analysis (DMA), thermomechanical analysis (TMA), and scanning electron microscopy (SEM).

Experimental

Materials. Henequen (HQ) fiber reinforcement in the 60~70 cm long filament form was originated from Yucatan, Mexico. It has been found from scanning electron micrographic observations that the average diameter of a single henequen fiber was in the range of 250 to 350 μm. It was measured that the tensile strength of a single henequen fiber was about 130 MPa. Henequen fibers were irradiated with various EB dosages of 0, 10, 30, 50, 70, 100, 150, and 200 kGy, respectively. The EBI processing was successfully conducted at EB-Tech Co., Korea. Unsaturated polyester (UPE) resin containing a 35 wt% styrene monomer as crosslinking agent and also diluent was purchased from Sewon Chemical Co., Korea. Methyl ethyl ketone peroxide (MEKP) was used as catalyst. Figure 1 shows the chemical structure of the ortho-type UPE resin used in this work.

Microdroplet Formation. To make a henequen/UPE microdroplet, a very tiny amount of uncured unsaturated polyester resin containing 0.2 wt% MEKP was dropped on a single henequen fiber of about 80 mm long. The UP resin microdroplet uniformly covered over the surface of the single henequen fiber was fully cured at 70 °C for 2 h in a conventional oven. The procedures for forming a resin microdroplet on a single henequen fiber treated with various EB dosages were repeated to prepare a sufficient number of henequen/UPE composite specimens for single fiber microbonding tests.

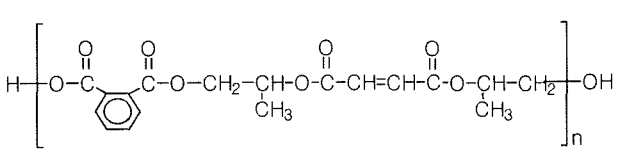

Figure 1. Chemical structure of unsaturated polyester (UPE) resin.

Composite Fabrication. The henequen fibers pre-treated with various EB dosages were uniformly chopped to 6.4 mm (1/4 inch) long. The chopped henequen fibers were well mixed with the UPE resin containing the MEKP. After mechanically mixed the chopped fibers with the UPE resin, the mixture was poured in a disposable mold made of glass plates with the dimensions of 30 mm×70 mm×20 mm. The henequen/UPE mixture was primarily cured at 25 °C for 15 h and then fully cured at 70 °C for 2 h in a conventional oven. Finally, the cured henequen/UPE composite was demolded after naturally cooled down to ambient temperature. The thickness of the obtained natural fiber composites was accommodated according to the specimen requirement for each analytical method. The content of chopped henequen fibers in the henequen/UPE composites fabricated was 10 wt%.

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 2 shows a schematic illustration of a single fiber microbonding test including a thermosetting resin microdroplet formed on a

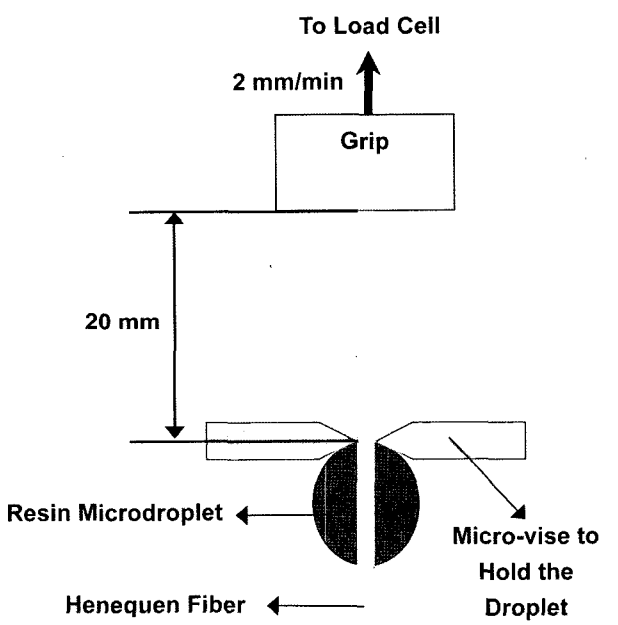

Figure 2. Schematic illustration of a single fiber microbonding test.

single henequen fiber. Prior to resin microdroplet formation, henequen fibers with a relatively uniform fiber diameter around 300 μm were selected because cellulose-based natural fibers including henequen may, in general, have variable fiber diameters at different locations due to the 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.

$$\tau = F/(\pi \cdot D_f \cdot L_e) \quad (1)$$

Here τ is the 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.

Scanning Electron Microscopic Observation. Scanning electron microscopy (SEM, Hitachi, S-570) was used to observe the henequen fiber surfaces and the composite fracture surfaces with different EB surface treatments.

Dynamic Mechanical Analysis. Dynamic mechanical analysis (DMA 983, TA Instruments) was used to study the dynamic mechanical thermal properties of each composite fabricated with the fibers treated at various EB dosages. 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 the correct clamp position and clamp compliance. The specimen dimensions were 30 mm × 10 mm × 3 mm.

Thermomechanical Analysis. Thermomechanical analysis (TMA 2940, TA Instruments) was used to study the thermomechanical stability and thermal expansion behavior of each composite treated with various EB dosages. 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.

Results and Discussion

It has been investigated that the effect of interfacial strength on the mechanical and thermal properties of chopped natural fiber/polymer composite materials importantly depends on fiber content and fiber length used.[21-23] The interfacial adhesion between the fiber and the resin in a natural fiber composite is strongly influenced by surface modification of hydrophilic natural fibers because the polymer matrix resin is usually of hydrophobic character. And, the interfacial property of a composite material can be closely related with the microscopic topography of the modified fiber surfaces and the composite fracture surfaces and with the thermal and mechanical properties. Therefore, it is worthy to examine the interfacial characteristics of a natural fiber composite through combined characterization techniques.

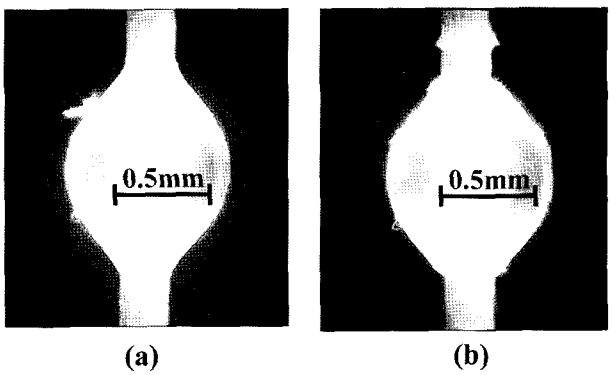

Figure 3. Optical microscopic photos showing the UPE resin microdroplet formed on a single henequen fiber before (a) and after (b) the single fiber microbonding test (× 10).

Interfacial Shear Strength (IFSS). Figure 3 shows the optical microscopic photos observed with the henequen/UPE composite specimens before and after the single fiber microbonding test. It represents a model specimen to mimic the henequen-reinforced unsaturated polyester composite. It is shown that the single henequen fiber was embedded in the UPE microdroplet of the ellipsoidal shape formed during the specimen preparation. The ellipsoidal microdroplet indicates that there was good wettability between the natural fiber and the UPE resin. It was observed that the henequen fiber was debonded from the resin and slightly deformed by the applied load during the microbonding test.

Figure 4 shows the IFSS result obtained for untreated

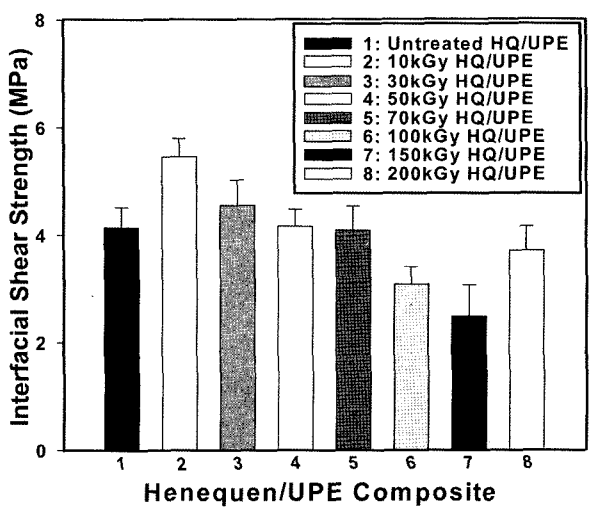

Figure 4. A comparison of interfacial shear strength of henequen/UPE composites fabricated using henequen (HQ) fibers treated at various EB dosages.

(raw) and EB-treated henequen/UPE composites. The standard deviation bars obtained from 30 specimens of each model composite are denoted in each plot. The relative IFSS value (about 4.1 MPa) of untreated henequen/UPE composite is 64% greater than that (about 2.5 MPa) of untreated henequen/poly(butylene succinate) (PBS) composite studied previously.[24] The single fiber microbonding test method is useful for evaluating the interfacial strength between the fiber and the matrix of a composite regardless of the fiber content because the fiber content does not have to be considered in such a model composite system. The higher IFSS value of henequen/UPE composite than henequen/PBS composite is because thermosetting UPE resin has the higher mechanical property and the better wettability to the natural fiber surface than thermoplastic PBS resin. However, the effect of the EB treatment condition on the IFSS of each henequen/UPE composite exhibited an almost similar tendency to the result found in the henequen/PBS biocomposites earlier. The IFSS of untreated henequen/UPE specimen was increased about 32% by an introduction of low EB intensity (10 kGy) to the henequen fiber surfaces. It was gradually decreased with increasing EB dosage up to 150 kGy. The treatment of EB intensity higher than 70 kGy resulted in the IFSS of henequen/UPE specimen lower than the raw henequen/UPE counterpart without EB treatment. The decreased IFSS value was enhanced by the EB treatment at 200 kGy, which is consistent with the result of the henequen/PBS composite above-mentioned.

The effect of EB treatment on the IFSS in the present work can also be explained by the earlier result[24] of morphological observation and X-ray photoelectron spectroscopy (XPS) of untreated and EB-treated henequen fiber surfaces. Based on the founding, it can be said that most of the weak boundary components such as impurities and waxes existing on the fiber surfaces were apparently removed at the initial stage of EB treatment and the surface more or less became undulated with the treatment. The oxygen/carbon ratio of the fibers treated at 10 kGy was relatively smaller than that of the corresponding fibers treated at other EB treatment levels, indicating the less hydrophilic character of the henequen fiber and the greater interfacial adhesion between the fibers and the resin. The oxygen-containing functional groups on the fiber surfaces were more or less increased with the EB treatment level up to 150 kGy, reflecting the more hydrophilicity of the fiber and the lower IFSS than at 10 kGy. The oxygen/carbon ratio of the henequen fibers was decreased again due to possible internal crosslinking between the cellulosic structures at high EB energy. Consequently, it may be addressed that the change of the functional groups on the henequen fiber surfaces due to EB treatment mainly contributes to improving the IFSS of the henequen composites.

The mechanical and thermal properties of a natural fiber composite can be effectively improved by use of optimal fiber content and length, giving rise to good fiber dispersion and composite processing. The properties can be achieved by an optimal treatment of natural fibers. The interfacial shear strength result demonstrates that the optimal treatment of EB on the henequen fibers may be 10 kGy in the present system. The present result also stresses that the exposure of electron beam to henequen fibers strongly influences the interfacial property of the natural fiber composite, reflecting that the fiber surfaces can be modified effectively.

Figure 5 displays the fracture surfaces of henequen/UPE composites fabricated using the chopped henequen fibers treated at different EB dosages. Each photo represents the interfacial region between the henequen fiber and the UPE matrix. There are some debonded areas in the untreated henequen/UPE specimen. With the treatment at 10 kGy EB, the interfacial adhesion between the natural fiber and the matrix was apparently improved, reflecting the higher interfacial shear strength than other specimens. The poorest interfacial adhesion was found in the case of 150 kGy henequen/UPE composite, resulting in the lowest IFSS value. It seems that the interfacial adhesion of henequen/UPE composite was enhanced with the EB treatment at 200 kGy, as expected from the microbonding test result.

Dynamic Mechanical Properties. Figure 6 shows the variation of the storage modulus as a function of temperature for henequen/UPE composites fabricated with the henequen fibers treated at various EB dosages. Table I lists the values of the storage modulus measured at 40, 60, 80, and 100 °C. As shown, the storage moduli measured for UPE resin at 40 and 60 °C are greater than those for untreated henequen/UPE specimen and lower than those for EB-treated henequen/UPE composites with an exception of the 150 kGy one. This implies that in the untreated henequen/UPE composite the fiber surfaces need to be modified with an appropriate EB intensity to improve the storage modulus as well as the interfacial shear strength.

The storage modulus of untreated henequen/UPE composite was largely increased by about 76% with an application of 10 kGy EB, having the greater value than UPE control and the greatest value among the specimens. The higher storage modulus of the treated composite is due to the greater interfacial adhesion and bond strength between the henequen fibers and the matrix, as reported using different surface modification methods for different natural fibers by other authors.[11,25-27] The henequen/UPE specimen treated at 150 kGy had the lowest storage modulus at each temperature measured and at 200 kGy the storage modulus was increased again. This is quite consistent with the IFSS result shown in the interfacial study above-described. The result demonstrates that the EB treatment level done on the natural fibers significantly influences not only the interfacial behavior, but also dynamic mechanical properties of the henequen/UPE composite. In addition, the EB treatment more greatly increased the storage modulus at temperatures higher than 60 °C.

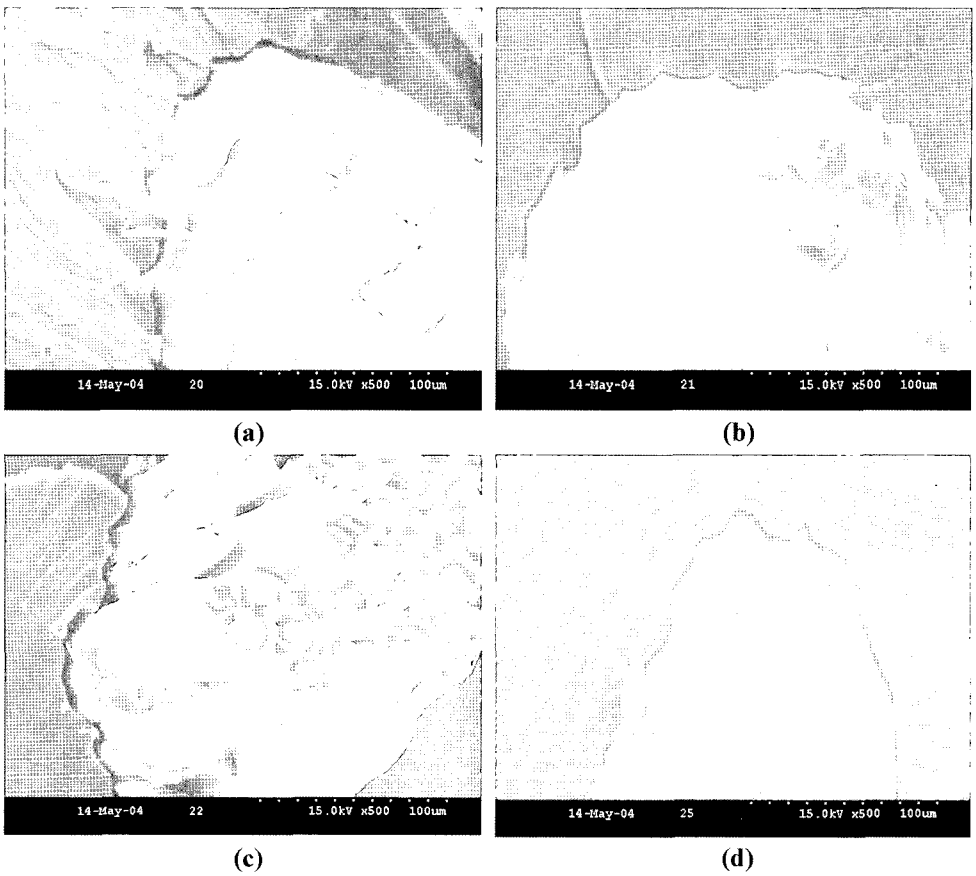

Figure 5. SEM micrographs showing the interfacial region between the henequen fiber and the matrix upon fracture of henequen/UPE composites with different EB treatments: (a) untreated, (b) 10 kGy, (c) 150 kGy, and (d) 200 kGy.

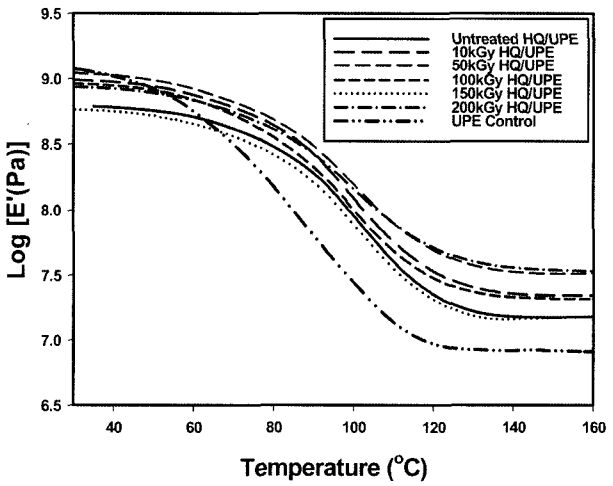

Figure 6. Variation of the storage modulus as a function of temperature for henequen/UPE composites fabricated using henequen (HQ) fibers treated at various EB dosages.

Table I. The Effect of Fiber Surface Modification at Various EB Treatment Levels on the Storage Modulus of Henequen (HQ)/UPE Composites

Specimen	E' (MPa) at 40 °C	E' (MPa) at 60 °C	E' (MPa) at 80 °C	E' (MPa) at 100 °C
UPE control	1022	517	151	26
Untreated HQ/UPE	599	508	297	91
10 kGy Treated HQ/UPE	1056	824	484	119
50 kGy Treated HQ/UPE	941	748	437	116
100 kGy Treated HQ/UPE	881	687	349	99
150 kGy Treated HQ/UPE	558	448	260	76
200 kGy Treated HQ/UPE	833	680	402	141

Figure 7 compares the tan δ among the UPE resin and the henequen/UP composites. The tan δ peak height, which is related to damping and impact properties of a material, was greatly reduced by incorporation of henequen fibers. This is because the fibers restrict the movement of polymer mole-

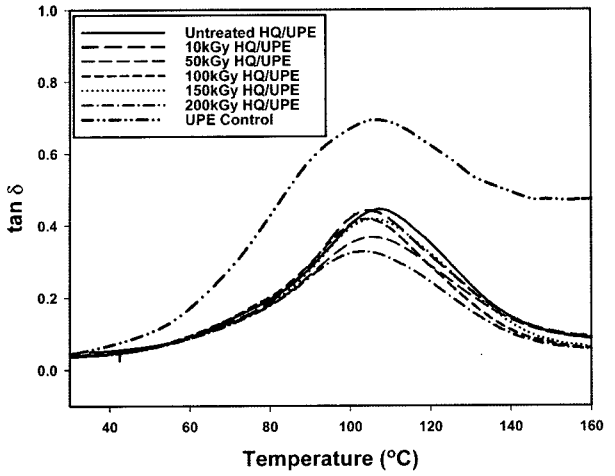

Figure 7. Variation of the tan δ as a function of temperature for henequen/UPE composites fabricated using henequen (HQ) fibers treated at various EB dosages.

cules.[26] The peak height of EB-treated henequen/UPE composites was quite lower than that of untreated counterpart. This turns out that the henequen fibers played a role as reinforcement and the interfacial adhesion between the fibers and the resin was enhanced by the EB treatment.

Thermomechanical Properties. Figure 8 shows the dimensional change as a function of temperature for cured UPE control and henequen/UPE composites with various EB treatments. The linear coefficient of thermal expansion (CTE) of each specimen was determined form the slope of each TMA thermogram in the range of 35~80 °C, where there was no weight loss observed by TGA. The values are listed in Table II. As compared, the CTE of UPE resin is greater than that of henequen/UPE composites. The EB-

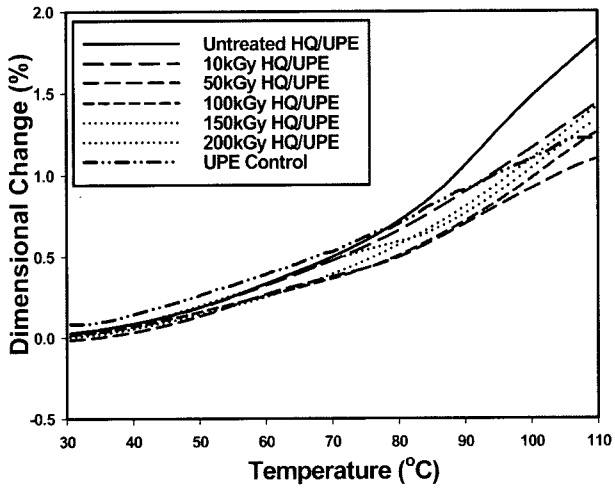

Figure 8. Variation of the dimensional change as a function of temperature for henequen/UPE composites fabricated using henequen (HQ) fibers treated at various EB dosages.

Table II. Coefficients of Thermal Expansion (CTE) of Henequen/UPE Composites with Henequen Fibers (HQ) Treated at Various EB Dosages

Specimen	CTE (μm/m/°C) 35~80 °C
UPE Control	146
Untreated HQ/UPE	139
10 kGy Treated HQ/UPE	131
50 kGy Treated HQ/UPE	113
100 kGy Treated HQ/UPE	99
150 kGy Treated HQ/UPE	104
200 kGy Treated HQ/UPE	129

treated henequen/UPE composites have the lower CTE value than the untreated counterpart. It is likely that the improved interfacial and dynamic mechanical properties due to EB treatment might somewhat contribute to decreasing the thermal expansion. However, it is unlikely that the EB treatment level correspondingly influences the variation of the CTE value, as in the IFSS and the storage modulus. One of the reasons for making interpretation of the thermal expansion behavior ambiguous is that the uncured UPE resin with high fluidity at ambient temperature was more or less infiltrated into the accessible room of hollow-type henequen fiber cells by the capillary effect during the composite fabrication and subsequently cured at processing temperature, as observed from the fractured surface of the composite in Figure 5(c). It has been investigated that the hollow-type cells in the fiber can be generated as the henequen fibers are exposed to high EB irradiation during the EB processing.[24] Another reason is that the composites used here have a less, random distribution of the chopped henequen fibers in such a small-sized specimen for TMA measurement.

Conclusions

The present study stresses that the irradiation of electron beam on the henequen natural fiber strongly influences the interfacial shear strength and the storage modulus of henequen/unsaturated polyester composites, indicating that the natural fiber surfaces have been modified effectively with EB and the optimal dosage of EB should be used to improve the interfacial and dynamic mechanical properties of a natural fiber composite. The IFSS of untreated henequen/UPE composite was significantly increased by an introduction of a low intensity of 10 kGy EB to the henequen fiber surfaces. The fractographic result also agrees with the single fiber microbonding test result.

The variation of the storage modulus of henequen/UPE composites shows that all the composite specimens have the higher storage modulus than the cured UPE control over the

temperature range measured. The storage modulus of the EB-treated natural fiber composites was greater than that of the untreated one, depending on the EB dosages used. It is noted that the dynamic mechanical result also supports the interfacial result. The CTE of the UPE control is greater than that of henequen/UPE composites. The EB-treated henequen/UPE composites have a lower CTE value than the untreated counterpart.

The result informs that the optimum treatment of EB on the henequen fibers contributes to enhancing the interfacial shear strength and the storage modulus in a natural fiber composite system. It is concluded that the fiber surface treatment at 10 kGy EB may be most effective in the present work.

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