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Effects of E-beam treatment on the interfacial and mechanical properties of henequen/polypropylene composites

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Abstract—In the present study, chopped henequen natural fibers without and with surface modification by electron beam (E-beam) treatment were incorporated into a polypropylene matrix. Prior to composite fabrication, a bundle of raw henequen fibers were treated at various E-beam intensities from 10 kGy to 500 kGy. The effect of E-beam intensity on the interfacial, mechanical and thermal properties of randomly oriented henequen/polypropylene composites with the fiber contents of 40 vol% was investigated focusing on the interfacial shear strength, flexural and tensile properties, dynamic mechanical properties, thermal stability, and fracture behavior. Each characteristic of the material strongly depended on the E-beam intensity irradiated, showing an increasing or decreasing effect. The present study demonstrates that henequen fiber surfaces can be modified successfully with an appropriate dosage of electron beam and use of a low E-beam intensity of 10 kGy results in the improvement of the interfacial properties, flexural properties, tensile properties, dynamic mechanical properties and thermal stability of henequen/polypropylene composites.

Keywords: Natural fiber-reinforced green composites; henequen; electron beam treatment; interfacial shear strength; mechanical properties; thermal stability.

1. INTRODUCTION

Cellulose-based natural fibers have been widely used as reinforcing fibers in natural fiber composites or green composites due to their advantages in lightness, cost

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effectiveness, environmental friendliness, carbon dioxide reduction in nature, etc., over conventional glass fibers. Green composites are now being utilized in many countries, especially in automotive, building, commodity and other applications [1–3]. Among many cellulose-based natural fibers like jute, kenaf, hemp, flax, sisal, henequen and banana, sisal and henequen fibers are attracting more attention for manufacturing low-cost and lightweight materials [4, 5]. Henequen (*Agave fourcroydes*), which is a similar family to sisal, is a straight, hard and strong fiber obtained from the 60–120 cm long leaves of agave plants, which is native to Yucatan, Mexico. In general, henequen fiber is composed of 77% cellulose, 4–8% hemicellulose, 13% lignin and 2–6% pectin and waxes [2]. It consists of a large number of hollow-type cells in a fiber, having a tubular structure, which is good for thermal and acoustic insulation. The natural fibers have been used extensively to make twines, ropes, carpets and cordages for a long period of time [6].

Polypropylene (PP) has been most frequently used as thermoplastic resin in conventional glass fiber-reinforced plastics (GFRPs). This is due to its cost effectiveness, good mechanical properties, easy processibility, versatile applications, etc. PP has also been widely used in natural fiber-reinforced plastics (NFRPs) or green composite systems. Recently, NFRP has increasingly attracted attention as a promising alternative material to conventional GFRP with its advantages above-described [7–9].

In fiber-reinforced polymer composites the mechanical properties, in general, depend on various factors like fiber and matrix types, fiber–matrix adhesion, fiber content, fiber aspect ratio, fiber orientation, fiber modification, and composite processing method as well as stress transfer efficiency at interfaces [10–12]. The fiber–matrix adhesion is critically important especially in composite systems using natural fibers as reinforcement [2]. The improvement in the interfacial adhesion between hydrophilic natural fibers and a hydrophobic polymer matrix through the surface modification of the natural fibers may significantly contribute to an increase of the mechanical properties and performances of composites. Therefore a number of chemical and physical surface modification studies have been devoted to understand and improve the interfacial and mechanical properties of various composite systems with different natural fibers and polymer resins [13–21].

There are two main methods of natural fiber surface modification to improve the interfacial adhesion between the natural fibers and the resin in a green composite. 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 [2, 13–17]. The other is physical modification by means of plasma and electron beam treatments [18–21]. 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 [22]. 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.

Consequently, the aim of the present study is to investigate the effect of electron beam (E-beam) intensity on the interfacial and mechanical properties of henequen/PP composites. In this work, the interfacial shear strength and quasi-static and dynamic mechanical properties of composites fabricated with chopped henequen fibers surface-treated at different E-beam intensities and a PP resin have been explored by means of single fiber microbonding tests using a PP resin microdroplet formed on a single henequen fiber, flexural and tensile tests, dynamic mechanical analysis and scanning electron microscopic observations, respectively. The result has been discussed focusing on the effect of E-beam on the interfacial shear strength, flexural strength and modulus, tensile strength and modulus, storage modulus and tan δ, and fracture surfaces of randomly oriented henequen/PP composites.

2. EXPERIMENTAL

2.1. Materials

Bundles of straight henequen (HQ) fibers in the 60–70 cm long filament form that originated from Yucatan, Mexico were kindly supplied from the Composite Materials and Structures Center at Michigan State University, USA. The average density was about 1.45 g/cm^3. The fiber diameter was about 150–200 μm. Polypropylene (P-4203 PP Fiber, Kolon Glotech Co., Korea) in the irregularly entangled woolly fiber form was used throughout this work. The denier and tenacity of the PP fibers were 10 and 1.5–4.5 g/denier, respectively. The PP fiber length was 76 mm in average and the fiber diameter was about 20–50 μm. Prior to composite fabrication, henequen fibers were irradiated with various E-beam intensities of 10, 30, 50, 70, 100, 150, 200 and 500 kGy, respectively. The E-beam treatments were conducted at ambient temperature in air using ELV-4 type equipment at EB-Tech Co. Ltd., Korea. Raw or 'as-received' henequen fibers were also used without E-beam treatment (0 kGy) for comparison. The E-beam treated fibers were kept clean and sealed until utilized. Upon use, the fibers were fully dried to remove possible moisture therein.

2.2. Single henequen fiber/PP microdroplet formation

A single filament of PP was taken out from PP fibers. Then, the single PP filament was placed perpendicularly across a single henequen fiber on a hot plate of about 200°C. The henequen fiber was lifted up as soon as the PP filament was melted again. On this occasion, a tiny amount of the PP resin was covered over the single henequen fiber surface and the resin about the fiber axis was rotated with re-melting by holding both ends in order to make the PP resin microdroplet uniform; then it

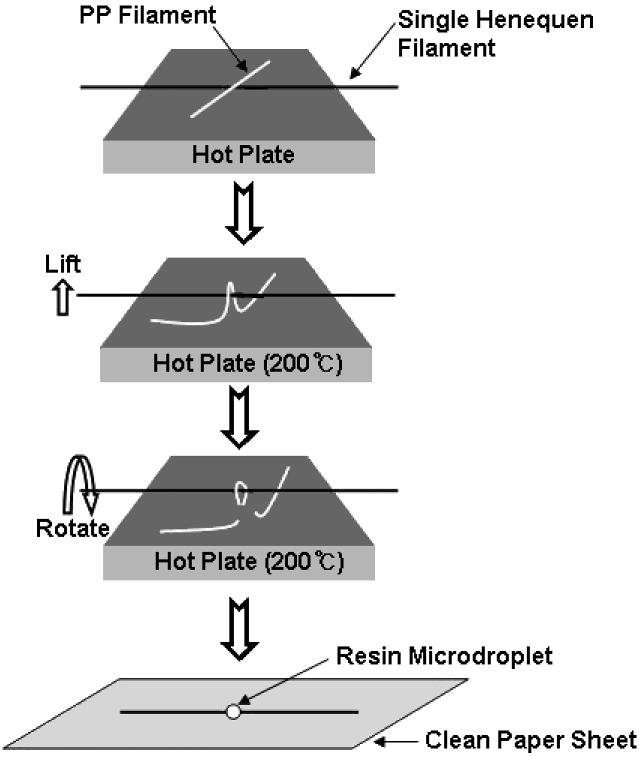


Figure 1. Schematic of the experimental procedure forming a PP microdroplet around a single henequen fiber.

was cooled down to ambient temperature to consolidate. Finally the thermoplastic PP microdroplet was uniformly formed around the single henequen fiber embedded. Figure 1 displays schematically the procedure forming a PP resin microdroplet on a single henequen fiber.

The procedure for forming a resin microdroplet on a single henequen fiber treated with varying the E-beam intensity was repeated to prepare a sufficient number of henequen/PP composite model specimens for single fiber microbonding tests. The formation of the henequen/PP microdroplets was observed with an optical microscope (Nikon ECLIPSE, E200).

2.3. Composite processing

Henequen fiber bundles and PP fibers were dried at 80°C for 12 h in a vacuum oven before use. The henequen fibers were chopped to a length of about 10 mm long on average. The variance of the length was about ±2 mm. Prior to composite fabrication, the PP fibers and the chopped henequen fibers were uniformly mixed. The mixed fibers were placed in a stainless steel mould and then heated to 175°C for 30 min, holding at 1000 psi for 10 min using a hot-press. During processing, the PP fibers were melted enough to flow into the henequen fibers and then to encapsulate them. A pressure of 1000 psi was retained until the mould was naturally cooled down to ambient temperature. Finally, a set of randomly oriented henequen/PP composites reinforced with henequen fibers treated at different E-beam intensities were prepared. The dimensions of the obtained composite plaques were 85 × 85 mm^2. The thickness was varied according to the requirement of each analytical method to be utilized. It seems that the henequen fibers in the composite were not thermally degraded by the temperature and duration used during the processing, retaining their original color. No distinguishable pores and voids were observed from the composite specimens but a lot of micropores (cells) consisting of the henequen were found in the composite. Therefore, it was assumed that each composite sample contains a corresponding number of the cells on average as long as the composite has the same fiber contents. The fiber contents of each composite were fixed to be 40 vol%.

2.4. 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, in general, have different fiber diameters in micrometer scale, depending on the fiber locations due to the irregular fiber surfaces. A universal testing machine (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 micro-vise grip distance was 20 mm. Figure 2 illustrates the single fiber microbonding

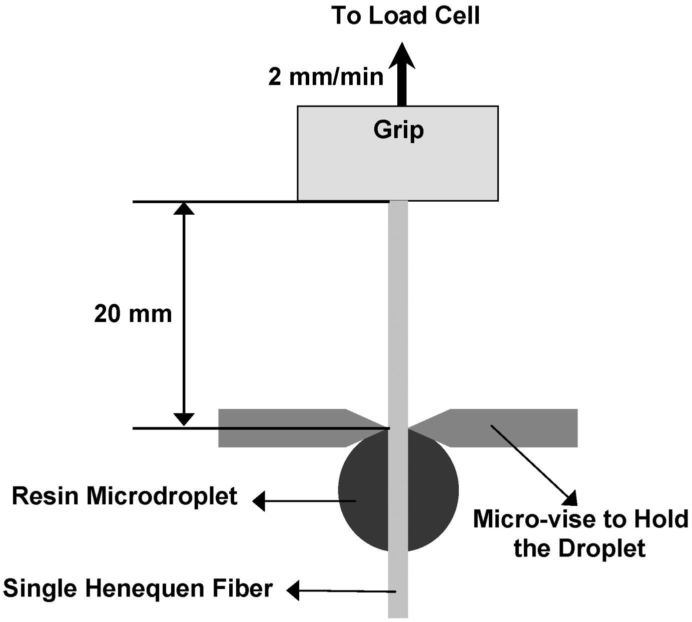


Figure 2. Brief illustration of a single fiber microbonding test method.

test using a single henequen fiber/PP composite model specimen. Each test was performed with about 30 specimens. The average value of the interfacial shear strength for each composite specimen was measured from all the values obtained using the following equation:

$$\tau = F/(\pi \cdot D_{\mathrm{f}} \cdot L_{\mathrm{e}}).$$

Here, τ is the interfacial shear strength (IFSS). F is the force required for debonding the resin microdroplet from the single henequen filament while tensile loads are applied. π is the circular constant, 3.1416. D_{f} is the diameter of the measuring fiber and L_{e} is the fiber length embedded in the resin microdroplet.

2.5. Three-point flexural test

The flexural properties of henequen/PP composites with various E-beam intensities were measured using a three-point bending test method according to ASTM D790M-86 using a universal testing machine (Instron 4467). The specimen dimensions were 50 × 25 × 2 mm^3. The span-to-depth ratio was 16. A load cell of 30 kN was used. A crosshead speed of 0.85 mm/min was used. The average values of flexural strength and modulus of each composite were obtained from ten test specimens.

2.6. Tensile test

The tensile properties of henequen/PP composites were measured according to DIN 53455 using a universal testing machine (Instron 4467). The specimen dimensions were 150 × 15 × 5 mm^3 and the gauge length was 100 mm. A load cell of 30 kN was used. A crosshead speed of 10 mm/min was used. The average values of tensile strength and modulus of each composite were obtained from ten test specimens.

2.7. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA Q800, TA Instruments) was carried out to study the storage modulus and tan δ of each composite with the fiber surfaces treated at different E-beam intensities. A single cantilever bending mode was used. A fixed frequency of 1 Hz and the oscillation amplitude of 20 μm were used throughout this work. A heating rate of 5°C/min was used purging a nitrogen gas. Before each measurement, the instrument was calibrated to have correct clamp position and clamp compliance. The specimen dimensions were 35 × 12 × 2 mm^3.

2.8. Thermogravimetric analysis

Thermogravimetric analysis (TGA Q500, TA Instruments) was carried out to study the thermal stability of each composite. A heating rate of 20°C/min was used purging a nitrogen gas. Derivative thermogravimetric (DTG) curves were also recorded for inspecting the noticeable weight change as a function of temperature.

2.9. Scanning electron microscopic observation

Scanning electron microscopy (SEM, JSM-6380) was used to observe the fracture surfaces of each composite with the henequen fibers treated at different E-beam intensities. All the specimens were gold-coated before observation. The acceleration voltage used was 10 kV.

3. RESULTS AND DISCUSSION

3.1. Interfacial shear strength

Figure 3 presents the variation of the interfacial shear strength (IFSS) measured from a large number of the single fiber microbonding tests performed with various henequen/PP composite model specimens prepared using henequen fibers treated at different E-beam intensities. The IFSS value of raw (0 kGy) henequen/PP composite was significantly increased about 36% from 3.9 MPa to 5.3 MPa by the treatment of a low E-beam intensity (10 kGy) on the henequen fiber surfaces. However, it was gradually decreased with an increase in the beam intensity up to 100 kGy, showing a lower IFSS value than the raw henequen/PP specimen. At 100 kGy, the IFSS value was the lowest (about 2.5 MPa). Above 100 kGy, the IFSS was largely increased again and the composite specimen prepared at 200 kGy had a similar value as the specimen at 10 kGy. With an excessive irradiation of E-beam at 500 kGy, the IFSS was obviously decreased.

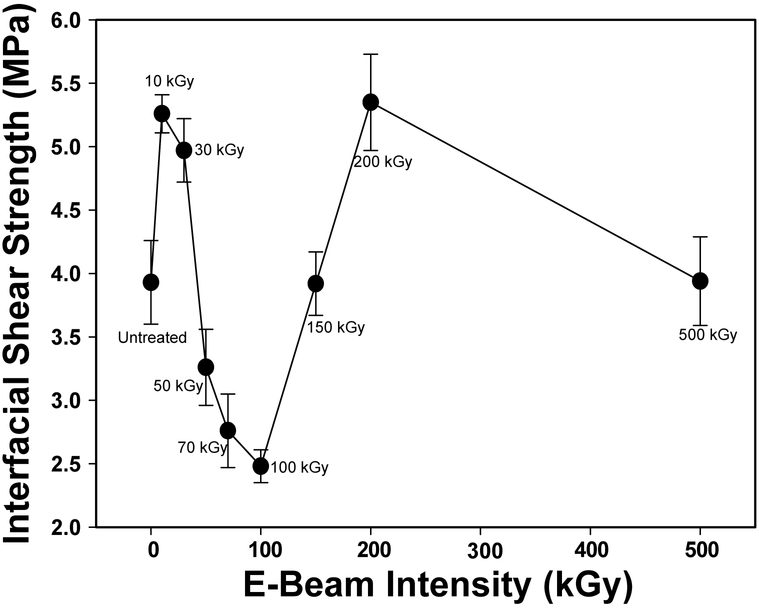


Figure 3. Variation of the interfacial shear strengths of henequen/PP composites as a function of E-beam intensity.

This study demonstrates that the intensity of E-beam irradiated on the henequen fibers strongly influenced the interfacial adhesion between the henequen and the PP resin of the composite. The variation of the IFSS as a function of E-beam intensity shown in Fig. 3 agreed well with the results found from henequen/poly(butylene succinate) [21], henequen/unsaturated polyester [20] and henequen/phenolic [6] composites previously. It is noted that the natural fiber surfaces have been modified effectively and an appropriate E-beam intensity should be applied to improve the interfacial property of a green composite. Based on the microbonding test, it may be said that the effect of E-beam on the interfacial strength of the composite may be primarily governed by the irradiated henequen fiber surfaces than with the resin matrix type. Although the tendency of the IFSS variation was similar regardless of the thermoplastic or thermosetting matrix resin studied, the relative values of the IFSS varied with the resin type.

3.2. Quasi-static mechanical properties

Figure 4 depicts the variation of the flexural modulus (top) and strength (bottom) measured from three-point flexural tests for various random-type henequen/PP composites prepared using the chopped henequen fibers treated at different E-beam intensities. The overall variation of the flexural modulus as a function of E-beam intensity was similar to the behavior of the IFSS shown in Fig. 3. The single data point on the far left in Fig. 4 is for PP control in the absence of the chopped henequen fibers. The flexural modulus of PP was greatly improved by about 27% by adding the untreated henequen fibers of 40 vol%. The flexural modulus of raw (0 kGy) henequen/PP composite was increased about 9% from 737 MPa to 800 MPa by the E-beam treatment of 10 kGy applied to the henequen fiber surfaces. However, the modulus was gradually decreased with increasing the intensity up to 100 kGy, having a lower value than the raw henequen/PP specimen. At 100 kGy, the flexural modulus was the lowest (about 673 MPa). Above 100 kGy, the modulus was largely increased again and the composite specimen prepared with the fibers treated at 200 kGy showed the greatest values (about 862 MPa) among the intensities used. With an excessive irradiation of E-beam at 500 kGy, the flexural modulus was significantly decreased.

This variation against the E-beam intensity was quite consistent with the variation of the IFSS described in Fig. 3. This supports that the intensity of E-beam irradiated on the henequen fibers strongly affects not only the interfacial adhesion between the fibers and the PP resin in the composite but also the flexural modulus. On the other hand, the flexural strength in the bottom of Fig. 4 was gradually decreased with increasing of the E-beam intensity even though there was a slight increase of the strength with the fiber treatment at a low intensity of 10 kGy. The flexural strength of the untreated and treated henequen/PP composites was lower than that of PP control. The fiber strength becomes weakened with the increased E-beam intensity. Nevertheless, it is noted that the flexural strength of raw henequen/PP composite can be more or less increased by treating the fiber surfaces at the lowest

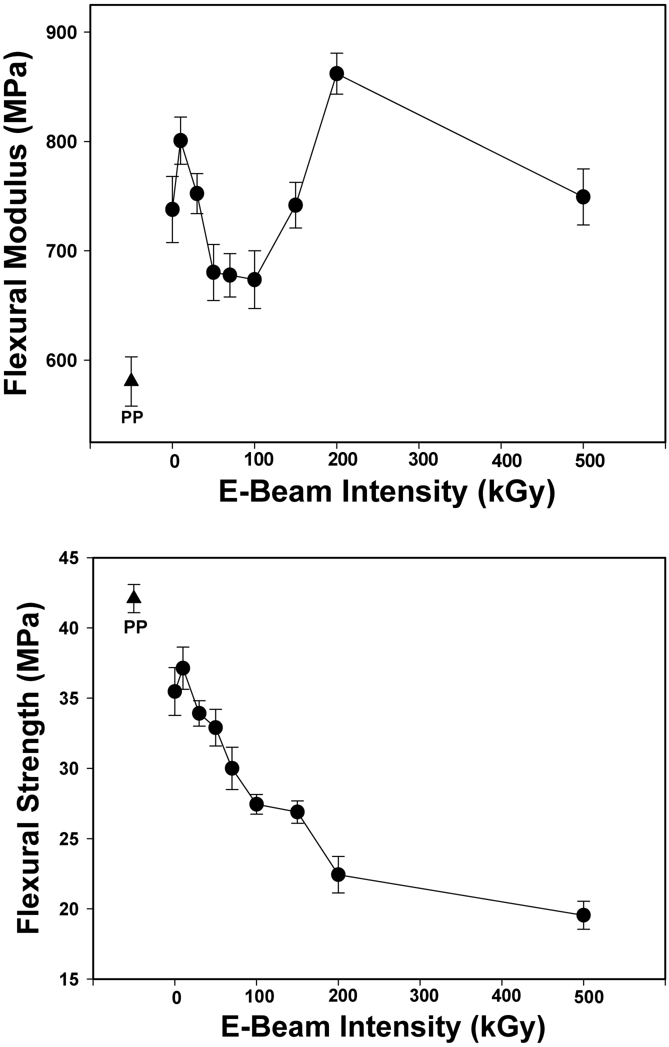


Figure 4. Variation of the flexural modulus (top) and strength (bottom) of PP and henequen/PP composites as a function of E-beam intensity.

E-beam intensity used. It is also reported that use of the E-beam greater than 30 kGy may not be recommended to use in terms of the mechanical strength even though the flexural modulus was somewhat recovered in the specimens treated at a high intensity of 200 kGy.

Figure 5 shows the variation of the tensile modulus (top) and strength (bottom) measured for various henequen/PP composites processed using the chopped henequen fibers treated at different E-beam intensities. The tensile modulus (0.91 GPa) of PP was slightly increased by incorporating the chopped henequen fibers. The tensile modulus of raw henequen/PP composite was increased about 24% from about 0.98 GPa to about 1.22 GPa by the E-beam treatment of 10 kGy.

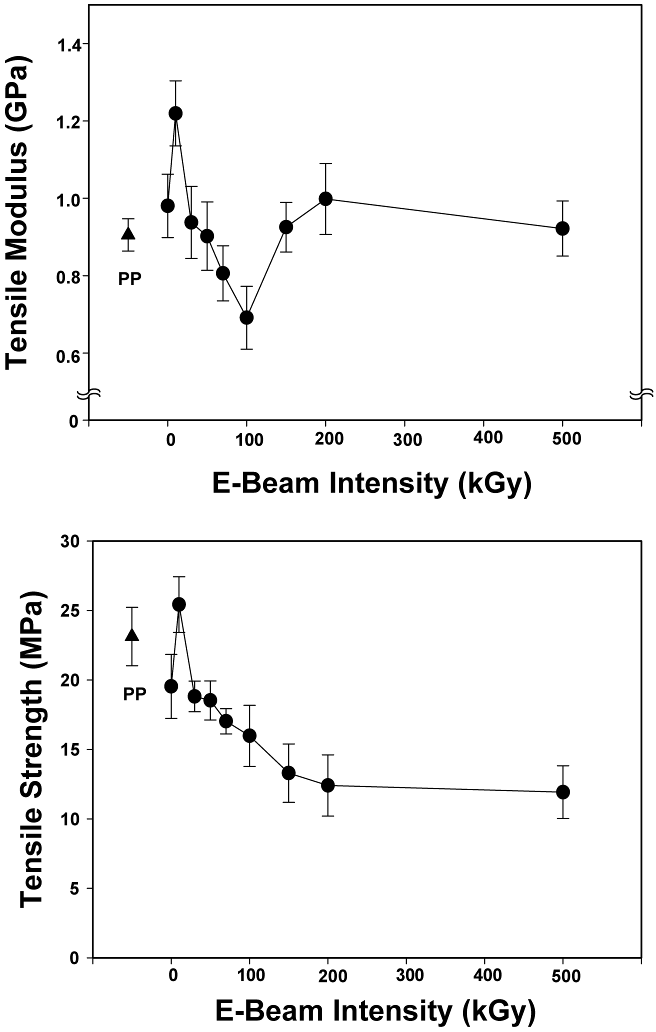


Figure 5. Variation of the tensile modulus (top) and strength (bottom) of PP and henequen/PP composites as a function of E-beam intensity.

However, the modulus was gradually decreased with increasing the intensity up to 100 kGy, giving a lower value than the raw henequen/PP composite and the PP control. At 100 kGy, the tensile modulus was the lowest (about 0.69 GPa). Above 100 kGy, although the tensile modulus was increased again, it was lower than that of the henequen/PP composite at 10 kGy. At 500 kGy, the flexural modulus was somewhat decreased, as found from the microbonding and flexural tests above-described.

This result demonstrates that the tensile properties as well as the flexural properties of random-type henequen/PP composites strongly depended on the E-beam intensity used for the henequen fiber modification. As similarly found in the flexural study, the tensile strength of raw henequen/PP composite was slightly lower than that of the PP control but it was improved about 30% by using the henequen fibers treated at 10 kGy, showing a greatest value (25.4 MPa) of the tensile strength among the tested specimens. The composite specimens treated at the intensity greater than 10 kGy exhibited the lower tensile strength than the PP control, as similarly found in the flexural result. The static mechanical result indicates that the E-beam treatment performed at a low intensity of 10 kGy to the henequen was more or less effective to improve the tensile properties of raw henequen/PP composite in comparison with the flexural properties. This is probably because the tensile properties of the composite may be more influenced by the modified surfaces of the henequen fibers than the flexural properties. Substantially in a fiber-reinforced polymer matrix composite, the tensile properties are sensitive to the aligned fibers and the morphological change of the modified fiber surfaces, whereas the flexural properties are more influenced by the matrix resin through the thickness of the specimen than the tensile properties.

3.3. Dynamic mechanical properties

In a composite material, the dynamic mechanical properties are influenced not only by the fiber and matrix types, fiber loading, fiber length and fiber distribution but also by the fiber–matrix adhesion. Figure 6 shows the variation of the storage modulus as a function of temperature for PP control and various random-type henequen/PP composites reinforced with the chopped henequen fibers untreated and treated at different E-beam intensities. The storage modulus of PP control was

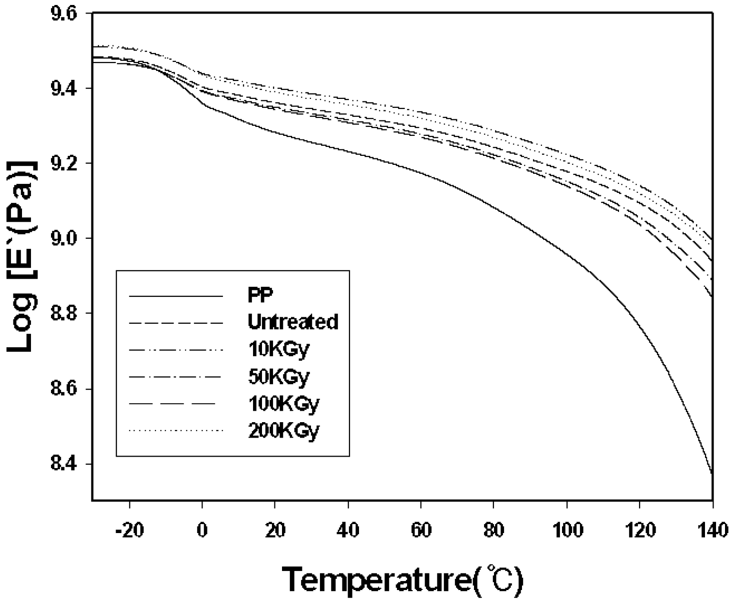


Figure 6. Variation of the logarithmic storage modulus as a function of temperature for PP and untreated and E-beam treated henequen/PP composites.

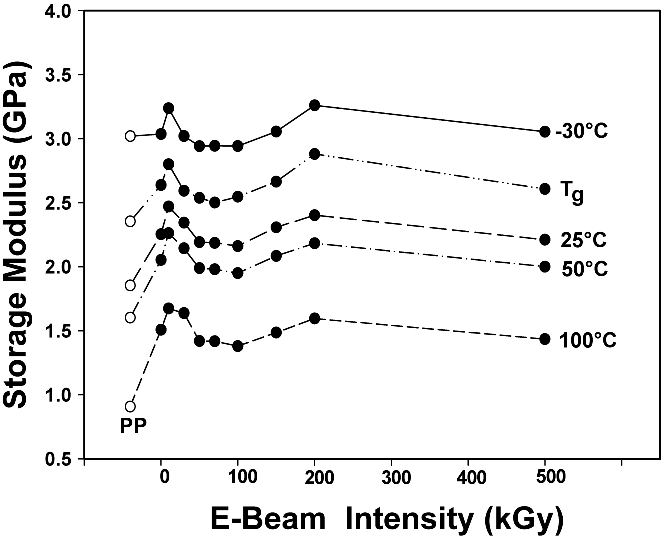


Figure 7. Plots of the storage modulus measured at specified measuring temperatures as a function of E-beam intensity.

greatly increased by incorporating the chopped fibers of 40 vol% over the measuring temperature range, especially above the glass transition region. The glass transition temperature (T_g) of PP was −1°C . For instance, at 25°C and 50°C it was increased by approximately 22% and 28%, respectively. It seems that the storage modulus of the untreated henequen/PP composite was increased about 10% by the fiber surface treatment at 10 kGy and 200 kGy, indicating that it obviously depended on the E-beam intensity used.

In order to inspect more clearly the variation, the storage moduli obtained at specified measuring temperatures (−30°C, T_g, 25°C, 50°C and 100°C) were plotted as a function of E-beam intensity, as shown in Fig. 7. Here the open circles indicate the storage modulus of PP at each measuring temperature and the closed circles indicate that of henequen/PP composites with different E-beam intensities observed at each measuring temperature. The reason for selecting such specified temperatures is as follows: −30°C at the glassy region, T_g at the glass transition temperature, 25°C at room temperature and also at above the glass transition, and 50°C and 100°C at possible use temperatures. As similarly studied from the interfacial and static mechanical results, the storage modulus of PP was significantly improved in the henequen/PP composites, especially at the glass transition temperature or higher. This is due to a reinforcing henequen fiber effect. Below T_g, the storage modulus of the untreated composite was similar to that of the PP because the dynamic mechanical behavior critically relies on the thermal motion of a brittle polymer matrix frozen in the glassy state. It is clear that the modulus was gradually decreased with increasing the measuring temperature.

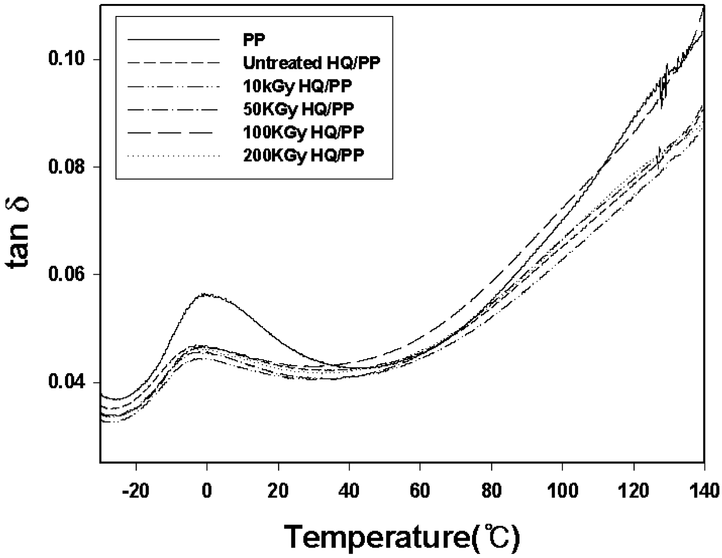


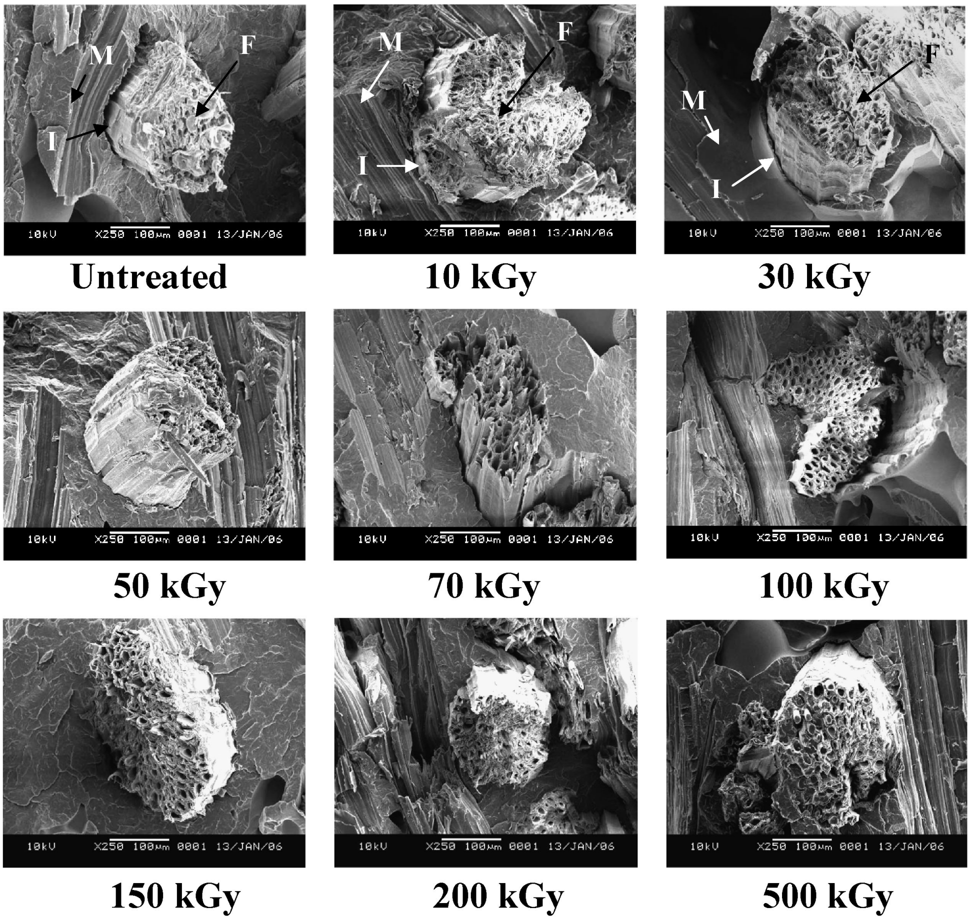
Figure 8. Variation of the tan δ as a function of temperature observed for henequen/PP composites.

At all the specified temperatures, the storage modulus of untreated henequen/PP composite was significantly increased by the fiber treatment with E-beam at 10 kGy. The E-beam irradiation greater than 10 kGy reduced the modulus, except for the case of 200 kGy. As indicated, an excessive irradiation of E-beam at 500 kGy deteriorated the dynamic mechanical property. The overall tendency of the modulus variation as a function of E-beam intensity was quite similar to the variation found from the interfacial and static mechanical studies described above. This implies that raw henequen fibers should be modified with E-beam at an appropriate intensity to improve the dynamic mechanical property of henequen/PP composites as well as their interfacial and static mechanical properties. Also, this dynamic mechanical study clarifies that the E-beam treatment given to the fibers influenced the storage modulus of the composite with a similar impact over all the temperature range below, at, and above the T_g. This result agrees with the report [21] that the henequen fiber itself irradiated with E-beam exhibited the decreased storage modulus with increasing the beam dosage.

Figure 8 presents the variation of tan δ as a function of temperature for PP and henequen/PP composites. It is obvious that the tan δ peak height, which is related to the damping property, was largely reduced with incorporation of the chopped henequen fibers. It was likely that the peak height of henequen/PP specimen at 10 kGy was somewhat lower than that of the untreated counterpart. As a matter of fact, the damping behavior was not clearly distinguishable among the specimens treated at other E-beam intensities. This is probably because the molecular chains exhibit flexibility around the glass transition temperature of the polymer matrix and the matrix is more responsible for the damping behavior of a composite than the loaded fiber. The glass transition temperature, which can be normally determined from the tan δ peak temperature, was observed to be around -5°C and it was not changed significantly by the E-beam treatment performed.

3.4. Fracture surfaces

As shown earlier, the increase and the decrease of static and dynamic mechanical properties were directly related to the increase and the decrease of interfacial shear strength between the henequen fibers and the PP matrix in the composites, respectively. The change of the interfacial shear strength in the henequen/PP composite model specimens, which were prepared for a single fiber microbonding test, may be qualitatively explained by observing the fracture surfaces of true henequen/PP composite plaques by means of a scanning electron microscopy (SEM). Figure 9 presents SEM micrographs of the fracture surfaces of the composites with the



Untreated

10 kGy

30 kGy

50 kGy

70 kGy

100 kGy

150 kGy

200 kGy

500 kGy

Figure 9. SEM micrographs showing the fracture surfaces for henequen/PP composites fabricated with the chopped henequen fibers treated at various E-beam intensities. (×250). M designates the matrix, F the fiber and I the interface, respectively.

chopped henequen fibers treated at various E-beam intensities. Each micrograph was just focused on a representative single henequen fiber surrounded with the PP matrix among a large number of henequen fibers. As observed earlier [21], the single fiber consisted of many cells and the fiber surfaces were undulated. The shape and diameter of the single fiber varied from fiber to fiber, as typically found in other cellulose-based natural fibers. In addition, how the fiber surfaces fractured depended on the E-beam irradiated. A detail description on the change of the henequen fiber topography according to the level of E-beam irradiation has been reported previously [21].

Close inspection of Fig. 9 shows that there was a gap or interstice between the henequen fiber and the PP matrix in the untreated (raw) composite. In the composite at 10 kGy, there was a close contact between them and the remaining fiber length pulled out after facture was relatively shorter than in other specimens. With increasing E-beam intensity, the interstice at the interface between the fiber and the matrix became profound and ultimately at 100 kGy a large portion of the fiber was pulled out, leaving the debonded fiber trace behind. At 150 kGy and higher, it was observed that the gap was reduced but the fiber surfaces and the cell structure were likely to be damaged by the E-beam irradiation. At 500 kGy, the small gap between the fiber and the matrix was found due probably to the loss of bonding ability with the degradation of henequen. The fractographic result supports the effect of E-beam intensity on the interfacial and mechanical behaviors of henequen/PP composites described earlier.

In addition to the description given in the present study on the result of interfacial and mechanical properties as a function of E-beam intensity, it is noticeable that the morphological and chemical changes in henequen fibers with variation in the E-beam intensity, as studied in the previous report [6, 21], also strongly support the result found in this work. Therefore, here it is worthwhile that an overall discussion be given to explain the similar behavior of the interfacial and mechanical properties dependence on the E-beam intensity obtained in the present study.

It has been known that there exist waxes and impurities on the surfaces of raw henequen fibers, which can result in a weak boundary layer once they bond with a polymeric matrix. In the presence of low E-beam irradiated, they can be removed and the fiber surface topography becomes more detailed, showing clear striations along with the fiber direction and some nodes along with the transverse direction [21]. It may significantly contribute to the enhancement of the interfacial adhesion between the henequen fibers and the PP matrix. With increase in the E-beam intensity up to 100 kGy, the fiber surfaces became weakened. At 200 kGy, the fiber exhibited the finer surfaces with detailed undulations and nodes. It provided greater surface roughness, resulting in the increased interfacial adhesion due to mechanical interlocking. However, it seemed that the fiber surfaces began to be damaged at such a high intensity. At 500 kGy, the fiber surfaces exhibited more damage and less undulation. It was likely that the original characteristic of the fiber surfaces was completely lost. In addition, there must be some serious chain scissions in the fiber molecules due to an excessive E-beam intensity, leading to the chemical degradation and physical deterioration of the fiber itself, as demonstrated from the DMA study [21]. This indicates the lowest storage modulus of the henequen fiber treated at 500 kGy among various E-beam intensities used and also the fiber breakage around 200°C during the DMA measurement.

The increase in the interfacial shear strength and the static and dynamic mechanical properties in the composite specimens at 200 kGy may be explained by taking into account the surface components present after the treatment. The amount of lignin and cellulose components affects the adhesion of a lignocellulose material to a polymer matrix [23]. Especially, the cellulose component contributes to the bonding with the matrix resin, whereas the lignin component restricts possible contacts of the cellulose with the matrix. Therefore the presence of lignin may reduce the bonding ability of the cellulose component with the polymer resin. It seemed that at 200 kGy the lignin component in henequen was removed to a greater extent than at the lower E-beam intensity, leaving the greater surface roughness behind, resulting in the greater adhesion between the henequen fibers and the PP matrix.

3.5. Thermal stability

Thermogravimetric analysis (TGA) is very useful for quantitatively understanding the degradation behavior and the composition of the fiber and the matrix in a composite. The magnitude and location of peaks found in the derivative thermogravimetric (DTG) curve also provide useful information on the components and the mutual effect of the composite components [24]. Figure 10 depicts the thermal stability of PP matrix, raw henequen fiber, and five henequen/PP composites. As can be seen from the DTG curve in the bottom, the PP matrix began to degrade at about 300°C showing the fastest weight loss with a peak temperature at 457°C. The raw henequen fiber exhibited the initial weight loss below 100°C due to the evolution of the intrinsically absorbed water molecules. This may be observed even after complete drying prior to the measurement. The primary weight loss of henequen was found at above 200°C, showing a peak temperature at about 309°C due to degradation of hemicellulose component therein. The secondary weight loss took place to a greater extent, showing a peak temperature at about 377°C due mainly to degradation of cellulose.

The thermal stability of henequen/PP composites was likely to be intermediate between the PP matrix and the henequen fiber, depending on the E-beam intensity used for the fiber surface treatment. In the DTG curves, there are three distinguishable peaks of weight loss in the composite specimens. These indicate that all the composites used here have three different decomposition stages depending on the components, as similarly reported with flax/poly(3-hydroxybutyrate) [25] and silk/poly(butylene succinate) [11, 12] biocomposites earlier. It is clear that the first and second stages were associated with degradation of henequen fiber and the third with the PP matrix. The three peak temperatures were slightly shifted to higher temperatures in the henequen/PP composites. However, the first and second peak

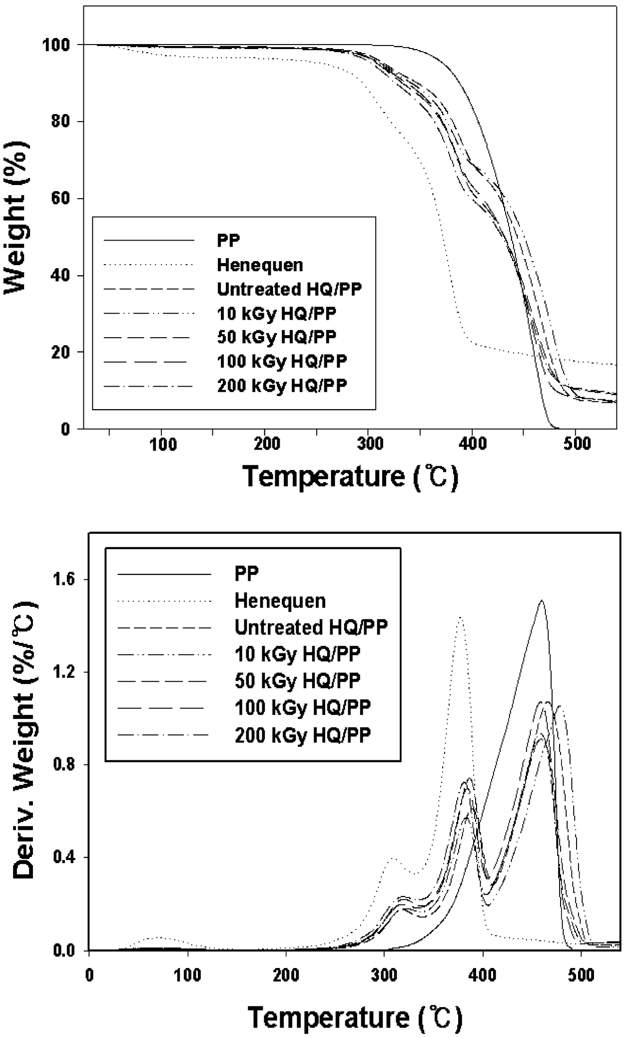


Figure 10. TGA (top) and DTG (bottom) thermograms measured for henequen/PP composites fabricated with the henequen fibers treated at various E-beam intensities.

temperatures of the untreated composite were not significantly changed in comparison with the treated composites. The third peak temperature was shifted to a higher temperature, especially in the case of 10 kGy. This is probably ascribed to the increased interfacial adhesion between the henequen fibers and the PP matrix in the composite, as described above.

As a result, it may be described that the PP matrix, which has greater thermal stability than the henequen over the temperature range measured, played a role in the thermal stability of the composites and also that the henequen fiber, which has greater thermal stability than the PP above about 450°C, played a role in the thermal stability. Therefore, it can be stressed that in the composite the less thermal stability of the natural fiber in the low temperature region may be compensated by the PP matrix incorporated, whereas the less thermal stability of the PP in the high temperature region may also be compensated by the henequen fibers embedded. However, the effect of E-beam treatment in the thermal stability was not as distinguishable as that in the interfacial and mechanical properties of the henequen/PP composites described above.

4. CONCLUSIONS

The present study demonstrates that henequen fiber surfaces can be modified successfully with an appropriate dosage of electron beam and the treatment of henequen fibers at a low E-beam intensity of 10 kGy before composite processing significantly contributes to improving the interfacial shear strength, the static and dynamic mechanical properties, and the thermal stability of untreated henequen/polypropylene composites.

It is concluded that the henequen fiber surfaces irradiated at 10 kGy among various E-beam intensities were most effective in improving the interfacial and mechanical properties of henequen/PP composites. The E-beam irradiation at the intensity higher than 10 kGy led to the reduction of the properties investigated. At 200 kGy, the interfacial and mechanical properties were increased to the level of the composite with the henequen fibers treated at 10 kGy but the fiber surfaces were likely to be damaged. At 500 kGy, which was expected to be an excessive radiation dose, the original characteristic of the henequen fiber surfaces was lost, leading to the chemical degradation and physical deterioration of the henequen/PP composite as well as the henequen fiber itself.

The result stresses that the optimum treatment of electron beam radiation not only to henequen fibers but also to other cellulose-based natural fibers significantly contributes to enhancing the interfacial adhesion between the reinforcing fibers and the polymer matrix and consequently the mechanical and thermal properties of a green composite system.

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REFERENCES

1. A. K. Mohanty, M. Misra and G. Hinrichsen, Biofibers, biodegradable polymers and biocomposites: an overview, *Macromol. Mater. Engng.* **276/277**, 1–24 (2000).
2. A. K. Mohanty, M. Misra and L. T. Drzal, Surface modifications of natural fibers and performance of the resulting biocomposites: an overview, *Composite Interfaces* **8**, 313–343 (2001).

3. A. Baillie, Eco-composites, *Compos. Sci. Technol.* **63**, 1223–1224 (2003).
4. M. Cazaurang-Martínez, P. Herrera-Franco, P. I. Gonzalez-Chi and M. Aguilar-Vega, Physical and mechanical properties of henequen fibers, *J. Appl. Polym. Sci.* **43**, 749–756 (1991).
5. K. Joseph, R. D. T. Filho, B. James, S. Thomas and L. H. de Carvalho, A review on sisal reinforced polymer composites, *Revista Brasileira de Engenharia Agricola e Ambiental* **3**, 367–379 (1999).
6. Y. Pang, Effect of electron beam irradiation on the interfacial and thermal properties of natural fiber henequen/polymer biocomposites, *MS Thesis*, Department of Polymer Science and Engineering, Kumoh National Institute of Technology, Gumi, Korea (2005).
7. A. Cho, S. G. Lee, W. H. Park and S. O. Han, Eco-friendly biocomposite materials using biofibers, *Polym. Sci. Technol.* **13**, 460–476 (2002).
8. S. V. Joshi, L. T. Drzal, A. K. Mohanty and S. Arora, Are natural fiber composites environmentally superior to glass fiber reinforced composites?, *Composites: Part A* **35**, 371–376 (2004).
9. R. Fisher, Natural fibers and green composites, *Compos. Manuf.* **March**, 20–23 (2006).
10. A. B. Strong, *Fundamentals of Composites Manufacturing: Materials, Methods, and Applications*. Society for Manufacturing Engineer, Dearborn, MI, USA (1989).
11. S. M. Lee, D. Cho, W. H. Park, S. G. Lee, S. O. Han and L. T. Drzal, Novel silk/poly(butylene succinate) biocomposites: the effect of short fiber content on their mechanical and thermal properties, *Compos. Sci. Technol.* **65**, 647–657 (2005).
12. S. M. Lee, S. O. Han, D. Cho, W. H. Park and S. G. Lee, Influence of chopped fiber length on the mechanical and thermal properties of silk fiber-reinforced poly(butylene succinate) biocomposites, *Polym. Polym. Compos.* **13**, 479–488 (2005).
13. L. Y. Mwaikambo and M. P. Ansell, The effect of chemical treatment on the properties of hemp, sisal, jute and kapok for composite reinforcement, *Die Angew. Makromol. Chem.* **272**, 108–116 (1999).
14. K. C. M. Nair, S. Thomas and G. Groeninckx, Thermal and dynamic mechanical analysis of polystyrene composites reinforced with short sisal fibers, *Compos. Sci. Technol.* **61**, 2519–2529 (2001).
15. S. Joseph, M. S. Sreekala, Z. Oommen, P. Koshy and S. Thomas, A comparison of the mechanical properties of phenol formaldehyde composites reinforced with banana fibers and glass fibers, *Compos. Sci. Technol.* **62**, 1857–1868 (2002).
16. I. van de Weyenberg, J. Ivens, A. de Coster, B. Kino, E. Baetens and I. Verpoest, Influence of processing and chemical treatment of flax fibers on their composites, *Compos. Sci. Technol.* **63**, 1241–1246 (2003).
17. P. Ganan, S. Garbizu, R. Llano-Ponte and I. Mondragon, Surface modification of sisal fibers: effects on the mechanical and thermal properties of their epoxy composites, *Polym. Compos.* **26**, 121–127 (2005).
18. S. G. Lee, S. S. Choi, W. H. Park and D. Cho, Characterization of surface modified flax fibers and their biocomposites with PHB, *Macromol. Symp.* **197**, 89–99 (2003).
19. A. Y. Chu, M. Y. Kwon, S. G. Lee, D. Cho, W. H. Park and S. O. Han, Interfacial adhesion of silk/PLA biocomposites by plasma surface treatment, *J. Soc. Adhes. Interf. Korea* **5**, 9–16 (2004).
20. Y. Pang, D. Cho, S. O. Han and W. H. Park, Interfacial shear strength and thermal properties of electron beam-treated henequen fibres reinforced unsaturated polyester composites, *Macromol. Res.* **13**, 453–459 (2005).
21. S. O. Han, D. Cho, W. H. Park and L. T. Drzal, Henequen/poly(butylene succinate) biocomposites: electron beam irradiation effects on henequen fibre and the interfacial properties of biocomposites, *Composite Interfaces* **12**, 231–247 (2006).
22. Available at www.eb-tech.com.

23. A. Albano, J. Reyes, M. Ichazo, J. Gonzalez and M. I. Chipara, Influence of gamma irradiation on the thermal stability of blends of PP with previous treated sisal fiber, *Polym. Degrad. Stab.* **73**, 225–235 (2001).
24. S. Renneckar, A. G. Zink-Sharp, T. C. Ward and W. G. Glasser, Compositional analysis of thermoplastic wood composites by TGA, *J. Appl. Polym. Sci.* **93**, 1484–1492 (2004).
25. S. Wong, R. Shangks and A. Hodzic, Interfacial improvements in poly(3-hydroxybutyrate)-flax fiber composites with hydrogen bonding additives, *Compos. Sci. Technol.* **64**, 1321–1330 (2004).