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Thermomechanical and flexural properties of chopped silk fiber-reinforced poly(butylene succinate) green composites: effect of electron beam treatment of worm silk

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The effect of electron beam treatment on the thermomechanical and flexural properties of chopped silk fiber-reinforced poly(butylene succinate) (PBS) green composites was studied for the first time in this work. The surface topological changes in worm silk fibers before and after the electron beam irradiation at various doses (5–100 kGy) were observed. Dynamic mechanical and flexural properties and thermal expansion behavior of neat PBS and silk/PBS green composites were investigated by means of dynamic mechanical analysis, three-point flexural test, and thermomechanical analysis. The irradiated silk/PBS composite result was compared with neat PBS and un-irradiated silk/PBS counterparts. It was concluded that use of electron beam irradiation at an appropriate dosage may contribute to an enhancement of the dynamic mechanical and flexural properties as well as to the thermodimensional stability of silk-based green composites. The result revealed that the property enhancement was most profound at the electron beam absorption dose of 20 kGy.

Keywords: electron beam irradiation; worm silk fibers; poly(butylene succinate); green composites; thermomechanical properties; mechanical properties

1. Introduction

During the past years, green composites consisting of biodegradable polymers and biodegradable reinforcements have attracted more and more attentions owing to their potential in environmentally friendly reinforced plastics applications.[1–3]

A number of academia and industries are interested in some biodegradable polymers such poly(lactic acid) (PLA), poly(butylene succinate) (PBS), and poly(ε-carprolactone) since 2000.[4–6] In addition, many studies on green composites or biocomposites have focused on such biodegradable polymer resins.[7–10] PBS, which is thermoplastic aliphatic polyester, has excellent biodegradability in nature like in soil, lake, sea, and compost.[11] It also has comparable mechanical properties with polyethylene. It has been reported that PBS can be used as matrix resin of a composite, particularly in a biocomposite system.[7,12,13] PBS can also be processed in film, fiber, or pellet. In general, PBS has better processability and toughness, and elongation than PLA, but it has worse mechanical and thermal properties. Therefore, the property improvement of neat PBS is

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frequently necessary for extended applications. One of the easiest ways to access the property improvement of neat polymer resin is an incorporation of environmentally benign and biodegradable reinforcements into the matrix, in accordance with a biodegradable polymer matrix. Natural fibers are reasonable for the purpose. Most of natural fibers used for the reinforcement of a polymer matrix in a biocomposite system have been plant-based or cellulose-based natural fibers such as kenaf, jute, hemp, flax, bamboo, etc.[14–19] However, it has been noticed that animal-based or protein-based natural fibers, such as worm silk and wool, are also promising as candidate reinforcing fibers.[7,20–22] Compared with plant-based natural fibers, animal-based silk fibers have superb mechanical and elastic properties and relatively uniform topography. They are tough and commercially available in a continuous form.

A useful approach to further increase the properties of a natural fiber-reinforced polymer green composite is treating natural fiber surfaces by means of chemical or physical treatment methods. There are a large number of papers dealing with fiber surface treatment or modification of cellulose-based natural fibers through chemical approaches like alkali treatment, silane treatment, acetylation, benzylation, etc.[23–28] Such chemical methods may not be quite beneficial with animal-based (or protein-based) natural fibers to be studied here.

There have been a number of research efforts demonstrating some positive effect of electron beam irradiation on the property improvement of cellulose-based natural fiber-reinforced polymer composites.[16,29–31] The positive effect gave us some research motivation on extending electron beam technology to animal-based natural fibers. Consequently, this study has been focused on how the electron beam irradiation of worm silk fibers influences the properties of silk/PBS green composites. In the present work, a bundle of worm silk fibers were irradiated with various electron beam absorption doses in the range of 5–100 kGy at ambient temperature prior to composite fabrication. The effect of silk fibers irradiated with electron beam on the properties of silk/PBS green composites was investigated using dynamic mechanical analysis, thermomechanical analysis, flexural test, thermogravimetric analysis, and scanning electron microscopy. The ultimate objective of the present study is to increase the storage modulus, flexural modulus and strength, and thermodimensional stability by incorporating worm silk fibers into neat PBS and also to further enhance the properties of silk/PBS green composites through fiber surface treatment by means of electron beam irradiation technique.

2. Experimental

2.1. Materials

Worm silk fibers (*Bombyx mori*) used in this work, which were kindly supplied from Korea Silk Research Institute, Jinju, Korea, consisted of dual filaments of 42 deniers. Each filament was of 21 deniers. Each filament was spun out from silkworm cocoon. The silk fibers were used as received without desericination process but with chopping to be 10 mm long in average. The as-received silk fibers were light gray in color. Poly (butylene succinate) pellets (PBS: Enpol™ G4560 J), a thermoplastic aliphatic polyester, was purchased from IRe Chemical Ltd., Korea. The melting temperature was 115 °C. The density was 1.26 g/cm^3. The melt flow index (g/10 min, 210 °C/2.16 kg) was in the range of 20–30. The average molecular weight of PBS used here was in the range of 140,000–160,000.

2.2. Electron beam irradiation process

Prior to electron beam processing, chopped silk fibers were dried at 60 °C for more than 24 h in a convection oven, and then, they were placed and uniformly spread in a polyethylene bag by a manual manner. The thickness of the polyethylene bag containing chopped silk fibers was less than 5 mm in average so that the electron beam uniformly went through the thickness direction of each bag. The electron beam irradiation processing was performed at ambient temperature at EB Tech., Daejeon, Korea. An electron accelerator (ELV-8) was used. The electron beam energy of 1.14 MeV was applied for pretreating chopped silk fibers prior to composite fabrication. In the case of 5 kGy dose, the electron beam current of 3.6 mA was used, whereas the current of 7.2 mA was used for 10, 20, 30, 50, and 100 kGy. The irradiation was done in the electron beam channel, at which the samples to be irradiated were placed in a conveying cart moving 10 m per minute. The electron beam absorption doses were controlled by the total exposed number of each sample in the irradiation channel. Prior to composite fabrication, all the irradiated silk fibers were sufficiently dried in an oven and stored at ambient temperature until used. The color of silk fibers used was not changed even after irradiating and drying.

2.3. Composite fabrication

Random-type chopped silk fiber/PBS green composites with the silk fiber content of 30% by weight were fabricated by a film stacking and compression molding method. The composites are simply referred to as silk/PBS composites hereinafter. The chopped silk fiber length was about 10 mm in average. With commercial PBS pellets, a number of PBS films were prepared in between the smooth metal plates by using a hot-press. The pressing temperature was 150 °C, and the holding time was 3 min at 150 °C. The pressure was 1000 psi. PBS films of about 200 μm thick were obtained. The chopped silk fibers were placed in between multiple PBS films in a stainless steel mold and then compressed. The molding temperature was 150 °C, and the temperature was maintained for 15 min for successful melting of PBS films in the mold. And then, the molding pressure of 500 psi was applied for 3 min. The dimensions of silk/PBS green composites processed were $85 \times 85 \times 2$ mm. For comparison, neat PBS plaque was prepared under the same processing conditions.

2.4. Characterization

Scanning electron microscopy (SEM, JSM 6380, JEOL, Japan) was performed to observe the surface topography of the irradiated silk fibers and also to examine the fracture surfaces of each green composite. Each fiber and composite sample was fractured in a liquid nitrogen bath for microscopic observations. All the samples were uniformly coated with platinum for 3 min by a sputtering method.

Dynamic mechanical analysis (DMA, Q800, TA Instruments, USA) was used to measure the storage modulus and tan δ of neat PBS plaque and silk/PBS green composite. A tension mode was applied throughout the DMA measurement. Each DMA measurement was performed from -50 to 80 °C with the heating rate of 2 °C/min. The oscillation amplitude was 0.1 mm, and the sinusoidally oscillating frequency was 1 Hz. The dimensions of each specimen were $40 \times 10 \times 2$ mm.

Thermomechanical analysis (TMA 2940, TA Instruments, USA) was used to examine the thermal expansion behavior of neat PBS plaque and silk/PBS green composites. An expansion probe was used throughout the work. A load of the probe was 0.05 N. The measurement was carried out purging a nitrogen gas of 50 mL/min. The measuring temperature range was 30–100 °C, and the heating rate was 5 °C/min. The thickness (the original length for the CLTE measurement) of each sample was 3 mm. The coefficients of linear thermal expansion (CLTE) of each sample were obtained from the slope of each TMA curve in the temperature range of 40–70 °C and 70–100 °C, respectively.

Thermogravimetric analysis (TGA Q500, TA Instruments, USA) was used to investigate the thermal stability of neat PBS plaque and the composites. A can-type alumina sample pan with the depth of 10 mm was used. Each measurement was carried out from 30 to 600 °C purging a nitrogen gas. The heating rate was 20 °C/min.

Three-point flexural tests were performed using a universal testing machine (UTM, Shimadzu JP/AG-50kNX, Japan) with neat PBS plaque and silk/PBS green composites according to ASTM D790M-86. The span-to-depth ratio was 16:1. The load cell of 50 kN was used and the crosshead speed was 0.85 mm/min. The averaged flexural strength and modulus were obtained from ten specimens.

3. Results and discussion

Figure 1 displays scanning electron micrographs of worm silk fibers without (A) and with (B–G) irradiation at various absorption doses. As similarly found in our earlier study [7], each thread of raw silk fibers was physically combined with several silk filaments with lengthwise striations, having a diameter of 50–60 μm in average. It was found that some impurities and un-identified low–molecular–weight substances were existed on the fiber surfaces. It seems that electron beam irradiation changed the fiber surface topography meaningfully, depending on the absorption dose applied. After irradiation, the longitudinal striations of silk fiber surfaces became clearer. At 5 and 10 kGy, the surface substances were partially removed, and some impurities were still found. At 20 and 30 kGy, it was likely that the surfaces were cleaned, indicating the surface substances removed and also leaving the more detailed surface topography behind. It was found that at 30 kGy each filament was more or less disintegrated, compared with that at 20 kGy. The silk fibers irradiated at 50 and 100 kGy were damaged to some extent, showing the disintegration of the filaments. The result implies that the silk fiber surfaces changed by the irradiation may influence the characteristics of green composite with the fibers.

Figure 2 shows the variations of the storage modulus of neat PBS and silk/PBS green composites as a function of temperature according to electron beam absorption dose applied. The effect of electron beam irradiation of silk on the storage modulus of the green composites was greatest at 20 kGy. The storage modulus (9.82 GPa at the maximum) of the composite with the silk fibers irradiated at 30 kGy was lower than that (9.99 GPa at the maximum) at 20 kGy but higher than the others (8.62–9.16 GPa at the maximum). The modulus of neat PBS was greatly increased in the silk/PBS green composites due to a reinforcing effect of silk fibers, particularly above the glass transition region near the tan δ peak temperature. Below the glass transition region, the storage modulus of the green composites with the silk fibers irradiated at lower than 10 kGy or higher than 50 kGy was similar to that of neat PBS plaque or even less. The reasons for the lower value are that 5 or 10 kGy was too low to remove the surface impurity

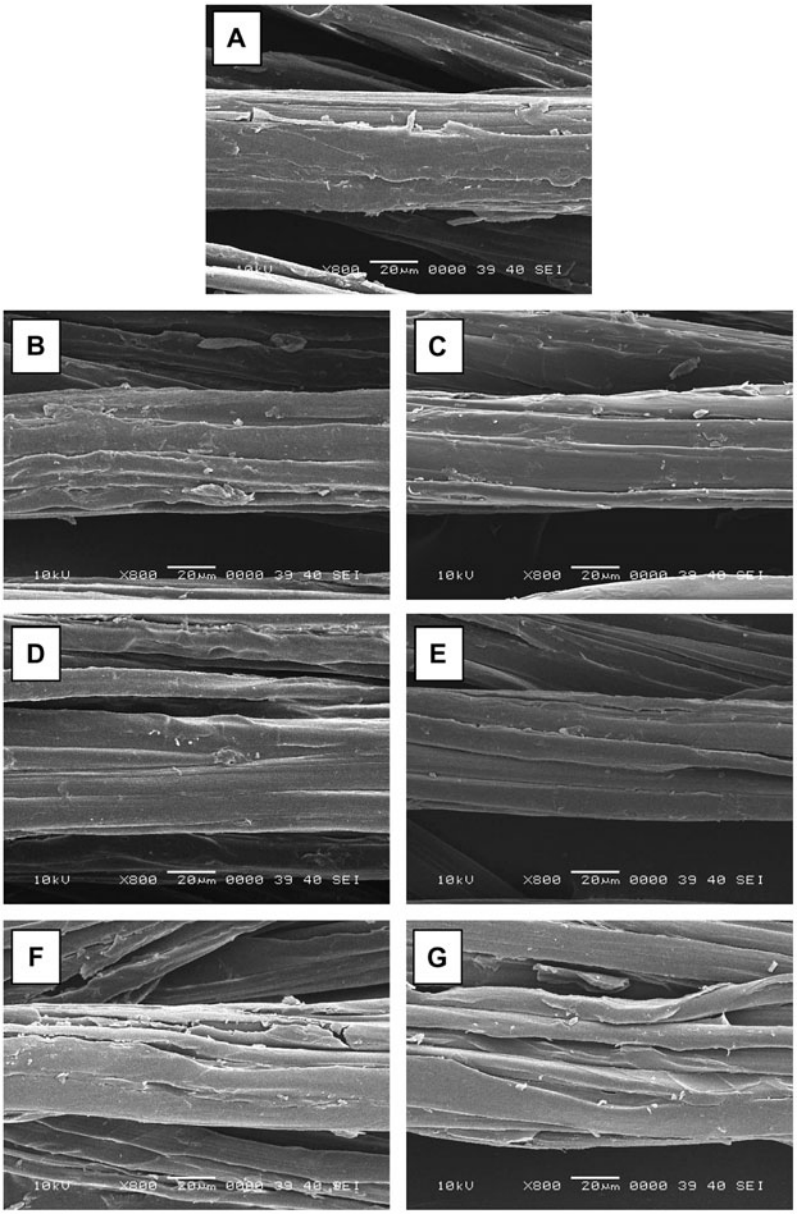

Figure 1. SEM micrographs of worm silk fibers irradiated at various absorption doses: (A) 0 kGy, (B) 5 kGy, (C) 10 kGy, (D) 20 kGy, (E) 30 kGy, (F) 50 kGy, (G) 100 kGy.

and substance leading to a weak surface boundary in the composite and that 50 or 100 kGy was too high, giving rise to some fiber damage and disintegration, resulting in a negative effect on the storage modulus. It was noted that incorporation of chopped silk fibers to neat PBS played a considerable role in reinforcing PBS in the temperature region of 0–80 °C. Comparing at 25 °C, the storage modulus of silk/PBS green composite was markedly increased from 1.51 to 3.79 GPa, indicating an improvement of about 150%.

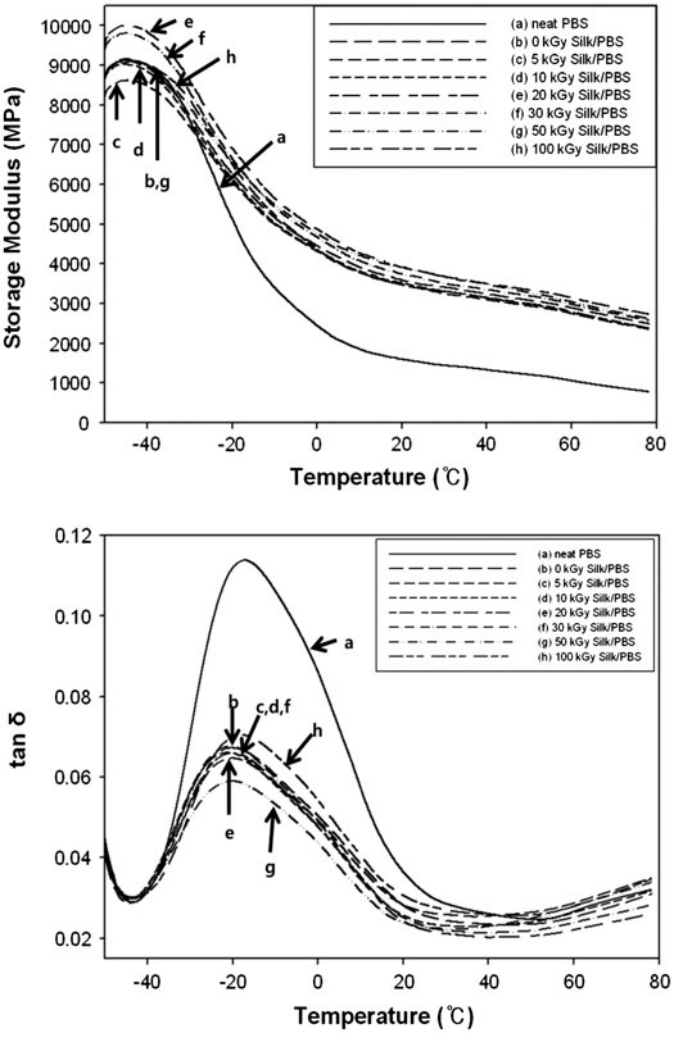

Figure 2. Variations of storage modulus and tan δ of neat PBS and various silk/PBS green composites depending on the absorption dose.

As can be seen, the tan δ peak temperature of neat PBS found at about $-17\,^{\circ}C$ is related to the glass transition temperature. The peak temperature was not significantly changed with the electron beam absorption dose done to the silk fiber surfaces. The tan δ peak height, relating with a property of material's damping, was considerably decreased in the presence of chopped silk fibers due to a reinforcing effect.

Figure 3 represents the linear thermal expansion behavior of neat PBS and silk/PBS green composites as a function of temperature according to the absorption dose irradiated to the silk fibers. Each TMA data exhibited a slight curvature so that the CLTE were determined from the slope in the temperature range of 40–70 °C and 70–100 °C, respectively. Table 1 summarizes the CLTE values. Neat PBS exhibited the highest CLTE value (0.820 μm/°C between 40 and 70 °C and 1.602 μm/°C between 70 and 100 °C). The thermal expansion was considerably reduced in the presence of chopped

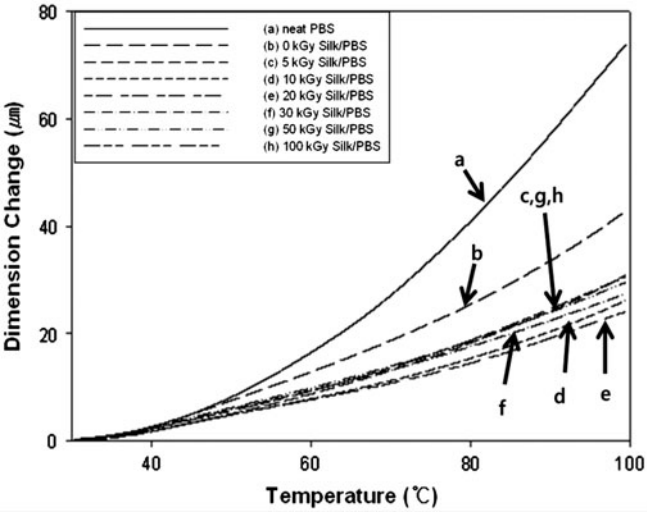

Figure 3. Variations of the linear thermal expansion of neat PBS and various silk/PBS green composites depending on the absorption dose.

Table 1. CLTE measured with neat PBS and various silk/PBS green composites with silk irradiated at different absorption doses.

Sample	40–70 °C ($\times 10^4$/°C)	70–100 °C ($\times 10^4$/°C)
Neat PBS	2.73	5.34
0 kGy Silk/PBS	1.79	2.72
5 kGy Silk/PBS	1.25	2.01
10 kGy Silk/PBS	1.03	1.67
20 kGy Silk/PBS	0.97	1.54
30 kGy Silk/PBS	1.21	1.62
50 kGy Silk/PBS	1.26	1.78
100 kGy Silk/PBS	1.25	1.94

silk fibers in the PBS matrix. The thermal expansion of irradiated silk/PBS green composites was much lower than that of un-irradiated counterpart. The lowest CLTE value (0.291 μm/°C between 40 and 70 °C and 0.461 μm/°C between 70 and 100 °C), reflecting the greatest thermodimensional stability as well, was found with the silk/PBS composites with silk fibers irradiated at 20 kGy. Among the irradiated silk/PBS composites, the highest expansion was occurred with the fibers irradiated at 5 kGy, which was the lowest intensity of electron beam applied. The higher CLTE values at 50 and 10 kGy can be ascribed to the irradiated silk fibers damaged and disintegrated somewhat at such the relatively high intensity of electron beam. The TMA result indicates that incorporation of silk fibers was effective to enhance the thermodimensional stability of neat PBS and also the electron beam intensity between 10 and 30 kGy may be useful for further reducing the thermal expansion of silk/PBS green composites.

Figure 4 shows the TGA (top) and Derivative thermogravimetric (DTG) (bottom) curves measured with neat PBS and various silk/PBS green composites with silk fibers irradiated at different absorption doses. DTG curves provide useful information on the

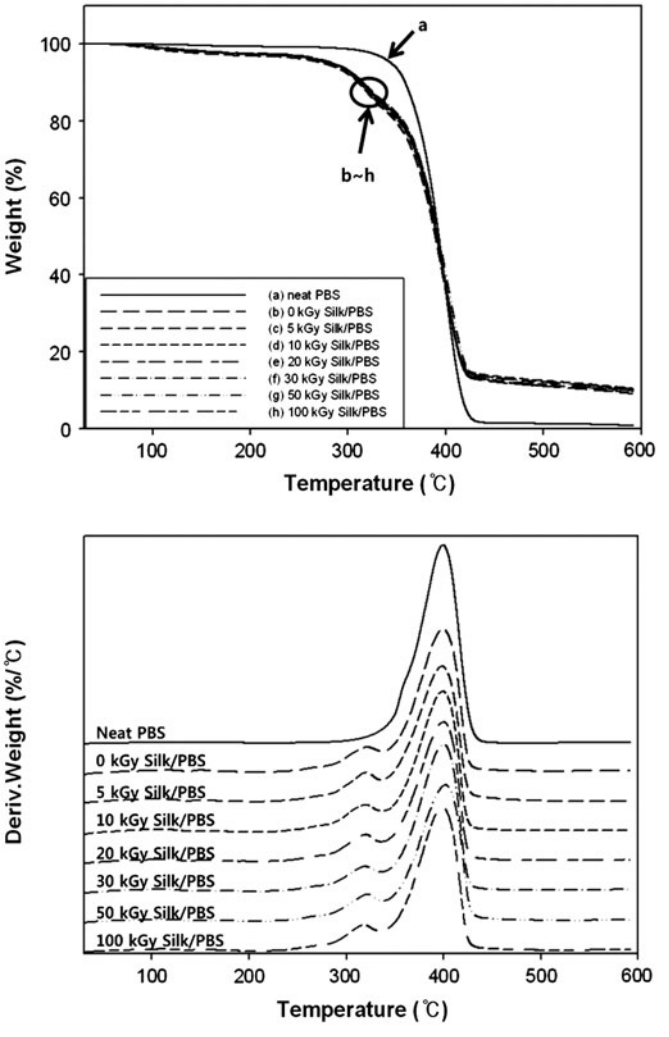

Figure 4. TGA and DTG traces measured with neat PBS and various silk/PBS green composites with silk fibers irradiated at various absorption doses.

component and the mutual effect of the components in a composite.[32] It was obvious that the thermal stability of the composites below about 400 °C was lower than that of neat PBS. This is due surely to lower thermal stability of worm silk than PBS, as similarly found earlier.[7,33] The higher residual weight in the composite specimens than neat PBS was greater residual weight of silk than PBS at above 400 °C. The DTG curves show two distinguishable peaks. The primary peak occurred at about 315 °C was due to the weight loss resulting from the thermal degradation of as-received worm silk and the secondary peak at about 400 °C was due mainly to the thermal degradation of PBS in the composite. The silk fibers began to slowly lose the weight from about 220 °C. The initial weight loss starting below 100 °C may be due to the absorbed moisture therein even after drying. It has been studied that chemical changes in the *B. mori* silk

fiber gradually start near 190 °C. As seen in Figure 4, all the composite specimens displayed very similar TGA and DTG curve patterns, reflecting that the chopped silk fiber contents incorporated in the PBS matrix were quite constant. The result also revealed that the electron beam irradiation doses to the silk fibers did not influence significantly the thermal stability of resulting green composites.

Figure 5 compares the flexural strength and modulus of neat PBS and silk/PBS green composites with chopped silk fibers irradiated at different absorption doses. Neat PBS exhibited the lowest flexural strength and modulus, as expected. All the composite specimens had higher flexural properties than neat PBS without silk fibers, particularly showing much improvement in the modulus. Among the silk/PBS green composites, the flexural strength was slightly higher in the cases of 10–50 kGy than of 0, 5, and 100 kGy. It was noticeable that the flexural strength was increased with the incorporation

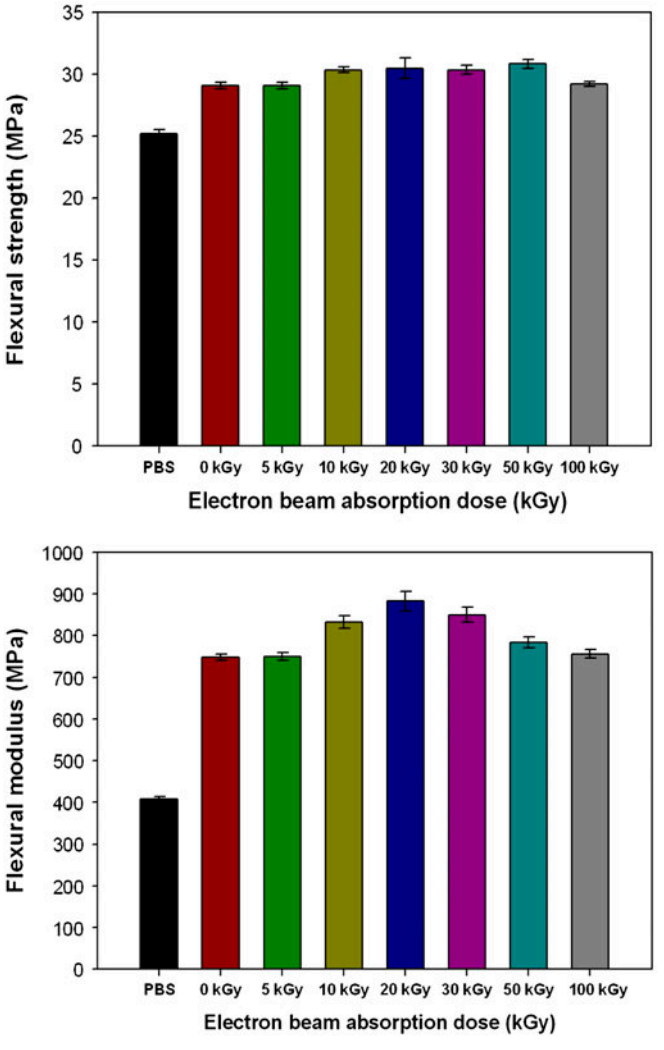

Figure 5. Flexural strength and modulus of neat PBS and various silk/PBS green composites depending on the absorption dose.

of animal-based natural fibers. It has often been found in biocomposite systems that the mechanical strength was decreased by introducing cellulose-based natural fibers in a polymer matrix.[18,25,34] It was also noted that the flexural modulus of neat PBS was greatly increased in the green composite reinforced with silk fibers, indicating the highest modulus at 20 kGy. The modulus of neat PBS was about 90% increased by the incorporation of chopped silk fibers and further increased about 20% by the electron beam treat-

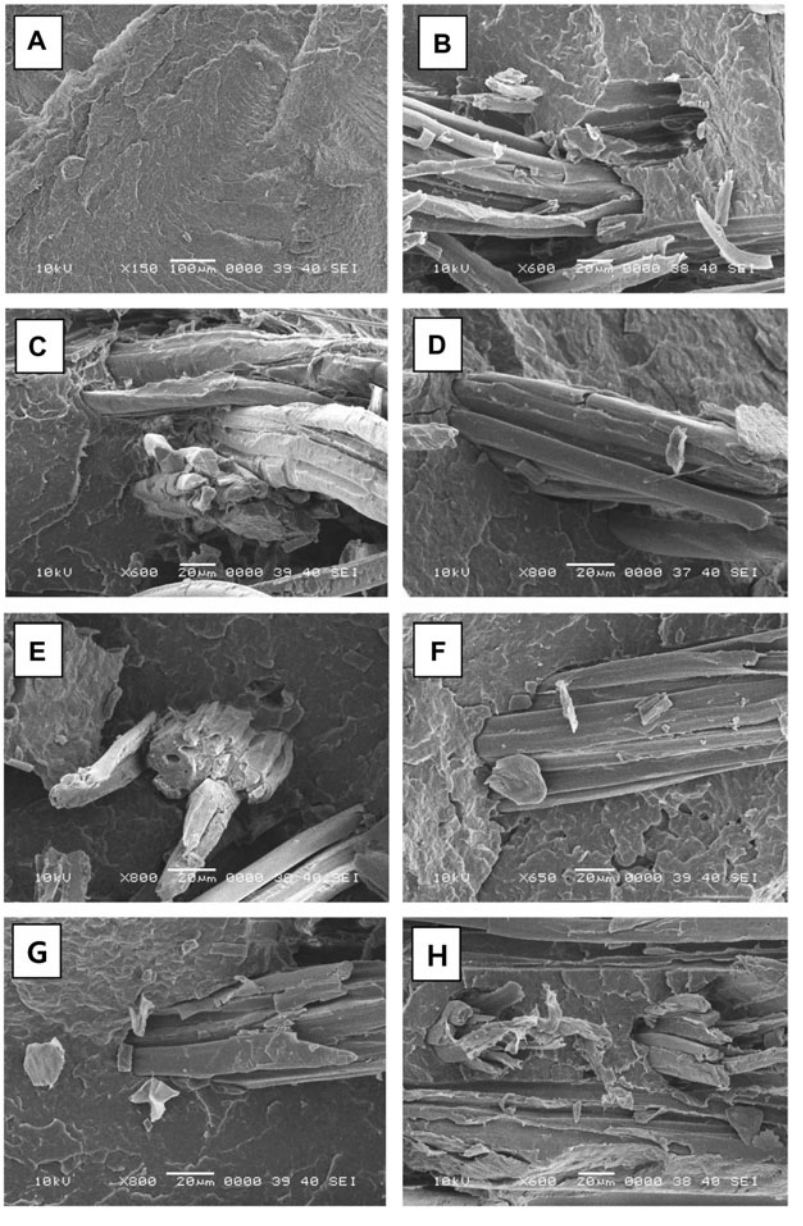

Figure 6. SEM micrographs of neat PBS and silk/PBS green composites reinforced with silk fibers irradiated at various absorption doses: (A) neat PBS, (B) 0 kGy, (C) 5 kGy, (D) 10 kGy, (E) 20 kGy, (F) 30 kGy, (G) 50 kGy, (H) 100 kGy.

ment of the silk fibers prior to composite fabrication. Among the composites, the low flexural modulus was found with the samples with silk fibers un-irradiated and irradiated at 5, 50, and 100 kGy. The result revealed that there was no benefit of electron beam irradiation on the flexural property enhancement once an irradiation absorption dose lower than 10 kGy or higher than 50 kGy was applied for treating worm silk fibers. As reported in our previous studies, [16,29] an electron beam irradiation of 10 kGy or less was preferable for enhancing the mechanical properties of cellulose-based natural fiber reinforced green composites.

Figure 6 represents the SEM micrographs showing the fractured surfaces of neat PBS (A) and various silk/PBS green composites with chopped worm silk fibers un-irradiated (B) and irradiated at different absorption doses (C–H). Neat PBS exhibited a typical ductile fracture pattern with surface roughness. In the presence of silk fibers incorporated into PBS matrix, the fracture pattern was varied. Some un-irradiated silk fibers in the composite were pulled out upon fracturing. The interfacial contacts between the silk fiber and the PBS matrix were relatively poor. At 5 and 10 kGy, the contacts were more or less enhanced but some fiber pull-out phenomenon was observed. In the case of 20 kGy, it seemed that there were good interfacial contacts between the fiber and the matrix. The length of pull-out fibers was shortened, indicating an increased interfacial bonding between them. This may contribute to increasing the mechanical properties as well as the thermodimensional stability. It was observed in the cases of 50 and 100 kGy that parts of the silk fibers in the fractured composite specimens were broken away and the fibers were easily disintegrated by the fracture load. Such the poor interfacial adhesion between the silk fibers and the matrix, which can be seen the fracture behavior of the composite, was responsible for the lowered mechanical and thermodimensional stabilities in the green composites.

4. Conclusions

The present paper reports the effect of electron beam treatment on the thermomechanical and flexural properties of animal-based natural fiber-reinforced green composites. As a result, the following conclusions were informed.

(1) The incorporation of animal-based worm silk fibers into neat PBS considerably enhanced the thermomechanical and flexural properties. Moreover, the surface treatment of silk fibers by electron beam irradiation under appropriate absorption dose conditions before fabricating silk/PBS green composites contributed not only to further enhancing the dynamic storage modulus and flexural modulus but also to increasing the thermodimensional stability of the composites.
(2) The property enhancement was most profound at the electron beam absorption dose of 20 kGy. It was stressed that the irradiation at 10 kGy or less was weak resulting in insufficient removal of impurities existing on the silk fiber surfaces and also the irradiation 50 kGy or higher was strong leading to some fiber damage and disintegration.
(3) This study suggests that electron beam technology may be a useful tool to increase the mechanical and thermal properties of animal-based natural fiber-reinforced green composites.

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