Mechanical and Thermal Properties of Waste Silk Fiber-Reinforced Poly(butylene succinate) Biocomposites

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Received 16 May 2005; accepted 28 September 2005
DOI 10.1002/app.23300
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This article reports the mechanical and thermal properties of poly(butylene succinate) (PBS) biocomposites reinforced with industrially available waste silk fibers, fabricated with varying fiber contents and lengths. The result indicates that use of waste silk fibers may be a potential as reinforcement for effectively improving the static and dynamic mechanical properties of a biodegradable polymer matrix resin, depending on the waste silk fiber content and length in the present biocomposite system. The "as-separated" waste silk/PBS biocomposites showed the maximum tensile and flexural properties at a fiber loading of 40 wt %, and the "chopped" waste silk/PBS biocomposites showed the optimal strength and modulus with waste silk fibers of 12.7 mm length. The chopped waste silk fibers play a more contributing role in improving the mechanical properties of waste silk/PBS biocomposites than the as-separated waste silk fibers at a fixed fiber loading. Above the glass transition temperature, the storage modulus of waste silk/PBS biocomposites was significantly greater than that of PBS resin, especially in the higher temperature region. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4972–4980, 2006

Key words: biocomposites; waste silk fibers; poly(butylene succinate); mechanical properties; dynamic mechanical properties; thermal stability

INTRODUCTION

Recently, researches on biocomposites or natural fiber composites, using renewable resources like natural fibers as an alternative for glass fiber reinforcement of conventional glass fiber/polymer composites, have been considerably increasing because of many advantages, such as their low density, low cost, acceptable specific mechanical strength, recyclability, environmental friendliness, etc.[1–10]

There are two main categories of natural fiber reinforcements for producing biocomposite materials, based on their natural sources. One is plant-based and the other is animal-based. In general, plant-based natural fibers are ligno-cellulosic and are mainly composed of cellulose, hemicellulose, and lignin, whereas animal-based natural fibers are composed of proteins. Plant-based natural fibers such as flax, jute, hemp, kenaf, and sisal have been more frequently used and extensively studied because of their natural abundance, cost effectiveness, high annual production and a wide range of properties depending on the plant source. Most of the published articles about biocomposites have been focused on these plant-based natural fibers.[8–14] On the other hand, only a few papers on biocomposites utilizing animal-based natural fibers like silk have been reported.[15,16]

Most recently we reported some fundamental results on a variety of properties of novel silk-reinforced biodegradable polymer matrix biocomposites.[16,17] It has been found that raw silk fibers (*Bombyx mori*) play an effective role as reinforcement in greatly improving the mechanical and thermomechanical properties of unreinforced poly(butylene succinate) (PBS). The reports stressed that the tensile and flexural properties of the biocomposites fabricated using the raw silk fibers are comparable to those of the biocomposites with plant-based natural fibers, suggesting that the use of silk fibers as reinforcement may be a potential candidate for enhancing the properties and performances of biodegradable polymer matrix resins.

Silk fibers have advantages over plant-based natural fibers, such as uniform fiber properties, continuous fiber type, high toughness, high crystallinity, and high tensile strength.[18] However, *Bombyx mori* raw silk fibers spun out from silkworm cocoons are relatively expensive. Therefore, they would not be cost-effective compared with plant-based natural fibers. However, waste silk fibers or scrap silk fibers, originated from *B. mori*, can be industrially available at extremely low

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Contract grant sponsor: Ministry of Commerce, Industry and Energy; contract grant number: 2003-T-0060.

cost. A large volume of the fibers may be discarded as scrap at the later stage of manufacturing process of silk fabrics.[19] Such scrap fibers may be considered as industrial waste. Therefore, they have also been increasingly challenged as recyclable resource.

PBS, which is a thermoplastic aliphatic polyester, has excellent biodegradability in soil, lake, sea, and compost.[20] It also has mechanical properties comparable with those of general-purpose thermoplastics such as polyethylene, polypropylene, and polystyrene. It is recyclable and can be processed by injection, extrusion, compression, and lamination molding techniques.[21] It is commercially available at lower cost than poly(3-hydroxybutyrate) and poly(lactic acid), which have often been studied as potential biodegradable polymers in a biocomposite system. Therefore, PBS can be utilized as a promising matrix polymer for biocomposite materials.

The mechanical characteristics like tensile and flexural properties in a fiber-reinforced polymer composite system play an important role in understanding performances and potential applications of the material. The static and dynamic mechanical properties of biocomposites strongly depend on the reinforcing natural fiber loading as well as the fiber length. The overall research objective is ultimately to elucidate the performance and potential application of waste silk/PBS biocomposites. The goals of the present work are primarily to fabricate waste silk fiber-reinforced PBS biocomposites and to explore the effect of waste silk fiber content and length on the mechanical and thermal properties of the biocomposites. Here, we report fundamental results on the properties of a biodegradable polymer matrix biocomposite reinforced with industrial waste silk fibers of varying fiber content and length. The results will be discussed in terms of tensile and flexural properties, dynamic mechanical properties, and thermal stability.

EXPERIMENTAL

Materials

The waste silk or silk scrap used in the present study was kindly supplied from the Korea Silk Research Institute manufacturing silk fabrics in Jinju, Korea. The silk scraps were obtained by cutting from both ends of the silk fabric during the weaving process. The "as-received" waste silk contains a number of silk fibers loosely connected with a poly(ethylene terephthalate) thread. Each filament of the silk fibers used in this work was originally spun out from silkworm cocoons (*B. mori*). The as-received waste silk used here consists of the fibroin inner layer only, because the sericin outer layer was removed from the raw silk fibers.

A number of loosely connected short silk fibers were individually separated by manually removing the poly(ethylene terephthalate) thread from the as-received waste silk. The average length of the separated fibers is approximately in the range of 35–70 mm. In this article, the term "as-separated waste silk fibers" indicates the short fibers manually separated from the waste silk or silk scrap. Each thread of the waste silk fibers was physically combined with multiple filaments with lengthwise striations, as reported earlier.[16] The average diameter of each filament was in the range of about 7–8 m, as shown in Figure 1. The waste silk fibers were in light ivory and were used as reinforcement without further surface modification.

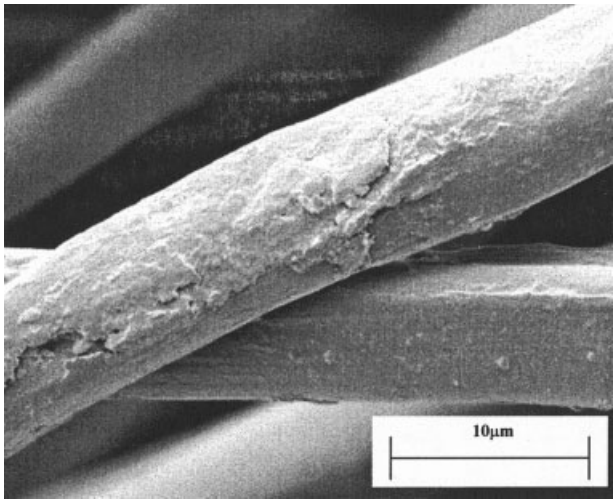

Figure 1 Scanning electron micrograph of single filaments in waste silk fibers used in this work.

To investigate the waste silk fiber length effect, the as-separated waste silk fibers were chopped to approximately 25.4 mm (1 in.), 12.7 mm (1/2 in.), 6.4 mm (1/4 in.), and 3.2 mm (1/8 in.) in average length, using a manually operating lab-scale fodder chopper. Here, the obtained fibers are referred to as "chopped waste silk fibers" throughout this article. The fiber contents used are 0, 20, 30, 40, and 50% by weight.

PBS (EnPol G-5100) was kindly supplied by IRe Chemical, Korea. The as-received PBS pellets were finely pulverized using a mechanical mixer to facilitate mixing them with chopped waste silk fibers. Figure 2 depicts the chemical structure of PBS used in the present study. The melting temperature of the PBS is about 120°C, and the density is 1220 kg/m^3. The melt flow index is 25 g/10 min at 190°C.

Biocomposite fabrication

All the waste silk fibers and PBS pellets used were dried at 100°C for 2 h in a conventional oven and at 80°C for 5 h in a vacuum oven before use, respectively. Prior to biocomposite fabrication, two different molding procedures were used. To prepare the biocompos-

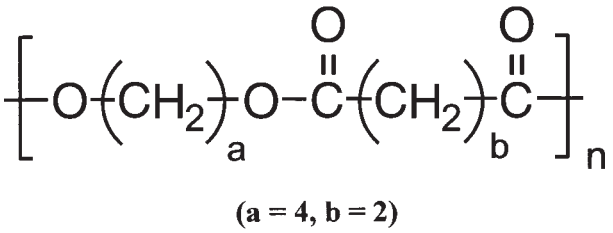

Figure 2 Chemical structure of poly(butylene succinate) used in the present study.

ites for examining the fiber content effect, the as-separated waste silk fibers were uniformly distributed in a steel mold according to scheduled fiber loadings, and then, the pulverized PBS powder was evenly spread over the fibers before molding. In this case, the as-separated waste silk fibers ranging from 35 to 70 mm were used without chopping. In addition, to prepare the biocomposites for examining the fiber length effect, the chopped waste silk fibers were mechanically mixed with the pulverized PBS powder using a kitchen blender. The mixing procedure did not significantly influence the given average length of waste silk fibers. The chopped waste silk/PBS molding compound was uniformly placed in a steel mold. In this case, the fiber content of 30 wt % was fixed.

The biocomposite molding was performed by compression method using a hot-press (Carver 2518). Two steel molds with different cavity dimensions (50 × 50 mm^2 and 100 × 150 mm^2) were used. The thickness of the obtained biocomposites was varied depending on the specimen requirement for each analysis. To fabricate all waste silk/PBS biocomposites, the molding compound was softened sufficiently to flow at 135°C for 10 min (for 50 × 50 mm^2 sized biocomposites) and also at 150°C for 15 min (for 100 × 150 mm^2 sized biocomposites). A pressure of 6.9 MPa was applied after 10 min at 135°C and retained until the mold was cooled down to ambient temperature.

Analysis

Tensile test

The tensile properties of waste silk/PBS biocomposites and PBS control were measured according to DIN 53,455 using a universal testing machine (Instron 4467). The specimen dimensions were 150 × 15 × 5 mm^3, and the gauge length was 100 mm. A 30 kN load cell was used with a crosshead speed of 10 mm/min. The average values of tensile strength and modulus were obtained from 10 specimens.

Flexural test

The flexural properties of waste silk/PBS biocomposites and PBS control were measured using a three-point bending method according to ASTM D 790M-86, using a universal testing machine (Instron 4467). The specimen dimensions were 50 × 25 × 2 mm^3, and the span-to-depth ratio was 16. A crosshead speed of 0.85 mm/min was used. The average values of flexural strength and modulus were obtained from 10 specimens.

Dynamic mechanical analysis

The storage modulus and tan δ were measured from −70 to 110°C with purging liquid nitrogen, using a dynamic mechanical analyzer (DMA 983, TA Instruments). The specimen dimensions were 30 × 10 × 2.7 mm^3. A heating rate of 2°C/min was used to allow thermal equilibrium to be achieved in each specimen in the furnace. The biocomposite specimen was deformed in a single cantilever bending mode at a fixed frequency of 1 Hz. The oscillation amplitude used was 0.2 mm.

Thermogravimetric analysis

The thermal stability of PBS, waste silk, and waste silk/PBS biocomposites was examined up to 500°C with a purging N_2 gas stream of 80 cm^3/min using a thermogravimetric analyzer (TGA 951, DuPont). A heating rate of 10°C/min was used. About 20 mg of each specimen was loaded for each measurement. The derivative thermogravimetry (DTG) curves were also recorded.

RESULTS AND DISCUSSION

Tensile properties

Figure 3 shows the tensile strength and modulus measured for PBS and four as-separated waste silk/PBS biocomposites with various fiber loadings. The tensile strength was gradually increased with the increase in the waste silk fiber loading up to 40 wt %, compared with that of the unreinforced PBS control. The decrease of the tensile strength in 50 wt % waste silk/PBS biocomposite is due to insufficient filling of melted PBS matrix resin into waste silk fibers during biocomposite processing at such a high fiber loading. In the earlier report[16] on the study of PBS biocomposites reinforced with "as-spun" chopped raw silk fibers of 12.7 mm in average length, such insufficient filling was found at a 60 wt % fiber loading or higher. In the present study using as-separated waste silk fibers of 35–70 mm in length, such incomplete filling was found in the fiber content of 50 wt %. It is noted that the tensile strength of PBS resin was increased about 27% by incorporating as-separated waste silk fibers of 40 wt % into the matrix. The presence of the waste silk fibers in the PBS matrix contributes more effectively to

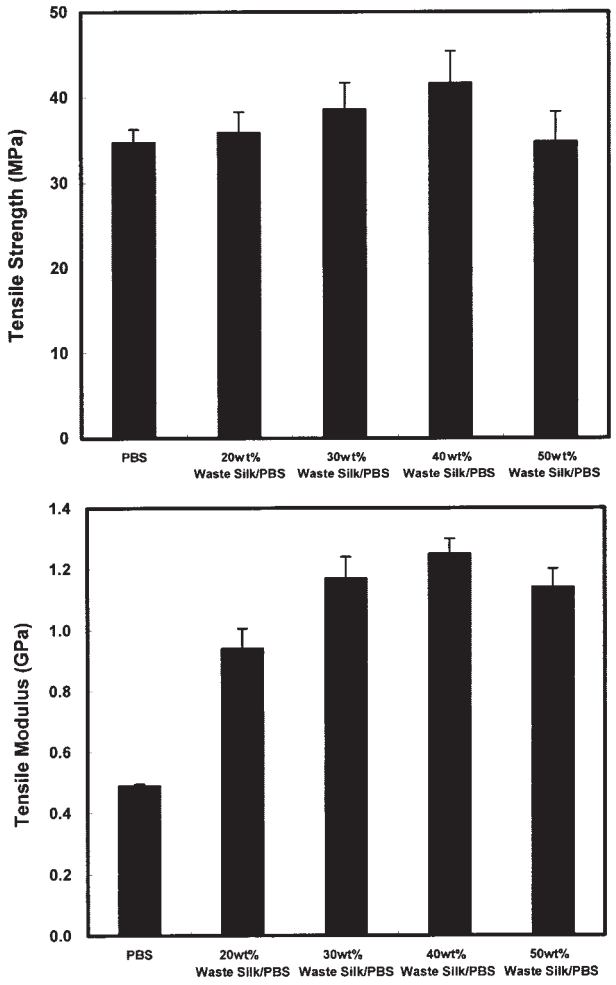

Figure 3 Tensile strength and modulus of PBS and as-separated waste silk/PBS biocomposites with different silk fiber contents.

enhancing the tensile modulus of PBS than to enhancing the strength. Even at a fiber loading of 20 wt %, the modulus of PBS was increased about 90%, as found with a raw silk/PBS biocomposite system in the previous study.[16] The maximum tensile modulus was obtained with the 40 wt % waste silk/PBS biocomposite, and the improvement was about 160% compared with that of the PBS control. The modulus at a 50 wt % waste silk fiber loading was decreased because of the incomplete filling effect, as described.

Figure 4 depicts the tensile strength and modulus measured for PBS control, an as-separated waste silk/PBS biocomposite and four chopped waste silk/PBS biocomposites fabricated with varying waste silk fiber lengths. The fiber content was constant to be 30 wt %. As mentioned earlier, it is noted that the as-separated waste silk fibers have various lengths between 35 and 70 mm. The tensile strength of PBS was increased because of a reinforcement effect by the waste silk fibers used here. The greatest tensile strength was obtained with the biocomposites reinforced with chopped waste silk fibers of 12.7 mm length, whereas the greatest modulus was obtained with chopped waste silk fibers of 25.4 mm length. It shows that there may be the optimal fiber length and content required to enhance the tensile properties. It has been suggested that here the optimal fiber length may be between 12.7 and 25.4 mm, and the optimal fiber content is about 40 wt %. As observed with varying the fiber content, the incorporation of chopped waste silk fibers with different fiber lengths in the PBS matrix contributes more effectively to the tensile modulus than to the strength. At a fixed fiber loading of 30 wt %, the tensile modulus of PBS was markedly increased about 94%, whereas the strength of PBS was slightly increased about 8%. The greatest improvement in the tensile modulus was about 160% by reinforcing with chopped waste silk fibers of 24.5 mm length. This may be because the longer the reinforcing silk fiber, the greater the fiber alignment, leading to an increase in the modulus. It is generally known that the tensile modulus of a fiber-reinforced composite material

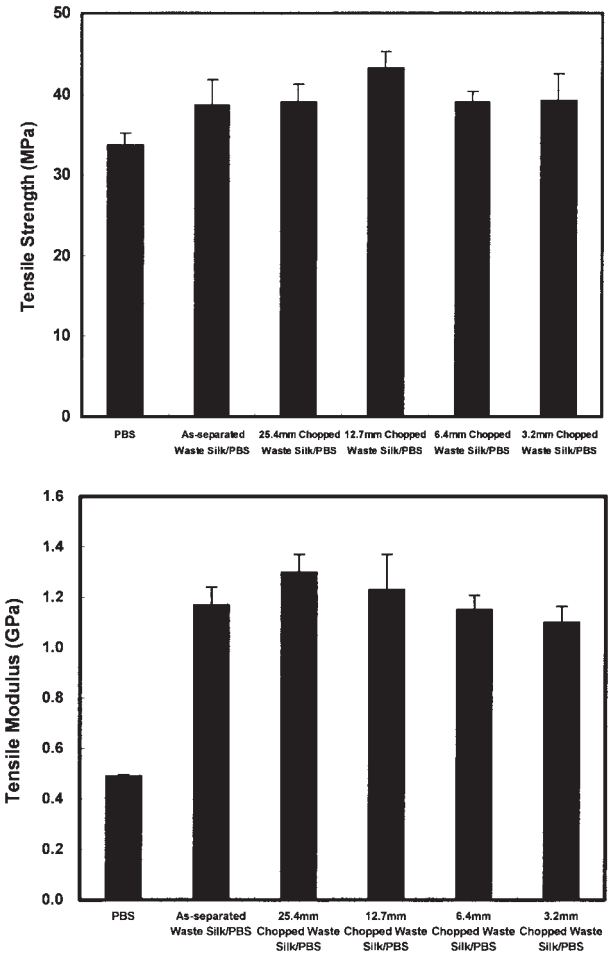

Figure 4 Tensile strength and modulus of PBS, as-separated waste silk/PBS biocomposite, and chopped waste silk/PBS biocomposites with different fiber lengths. The fiber content was 30 wt %.

strongly depends on the reinforcing fiber alignment in the polymer matrix. Although the chopped silk fibers were randomly distributed at a fixed loading of 30 wt % in the confined mold, it is expected that the longer fibers may be aligned with higher population and with greater local anisotropy of the crystalline structure in comparison with the shorter fibers.

The reason for the higher tensile strength in the 12.7-mm long chopped waste silk/PBS specimen than in the 25.4-mm long waste silk/PBS one is that the shorter fiber may be more uniformly distributed with the PBS matrix resin than the longer fiber during biocomposite processing in the confined mold. Use of the chopped waste silk fibers shorter than 6.4 mm also increases the tensile strength and modulus of PBS, but the improvement is lower than in the case of 12.7-mm long waste silk fibers.

The tensile properties of the as-separated waste silk/PBS biocomposites are slightly lower than those of chopped one fabricated at the same fiber content, even though the as-separated waste silk fiber length is roughly longer than the chopped fiber length. This may be explained by that the as-separated fibers may not be more uniformly distributed into the PBS matrix than the chopped fibers.

Flexural properties

Figure 5 shows the flexural strength and modulus of PBS and four as-separated waste silk/PBS biocomposites processed with varying silk fiber loadings. The flexural properties were gradually increased with the fiber loading up to 40 wt %. With the addition of 50 wt % waste silk fibers, the flexural properties were somewhat decreased. This is due to the insufficient filling of the melted PBS resin into the reinforcing natural fibers during composite processing, as described. The greatest flexural properties of the biocomposite were also obtained with the waste silk fibers of 40 wt %. The flexural strength and modulus were improved by 26 and 54%, respectively, in the 40 wt % waste silk/PBS biocomposites, compared with those of the PBS control, showing the greater improvement in the flexural modulus.

The flexural strength and modulus of PBS, an as-separated waste silk/PBS biocomposite, and four chopped waste silk/PBS biocomposites fabricated with varying fiber lengths at the fixed fiber content of 30 wt % are shown in Figure 6. The flexural properties of PBS were significantly increased with an introduction of chopped waste silk fibers, regardless of the average fiber length. The 12.7-mm long waste silk/PBS biocomposite exhibited the greatest flexural modulus. The flexural strength and modulus of the PBS control were improved by 34 and 50%, respectively, in the 12.7-mm long waste silk/PBS specimen. The flexural result also indicates that the strength of the biocomposites does not significantly depend on the variation of chopped waste silk fiber length, whereas the modulus is more or less greater than that reinforced with as-separated waste silk without chopping.

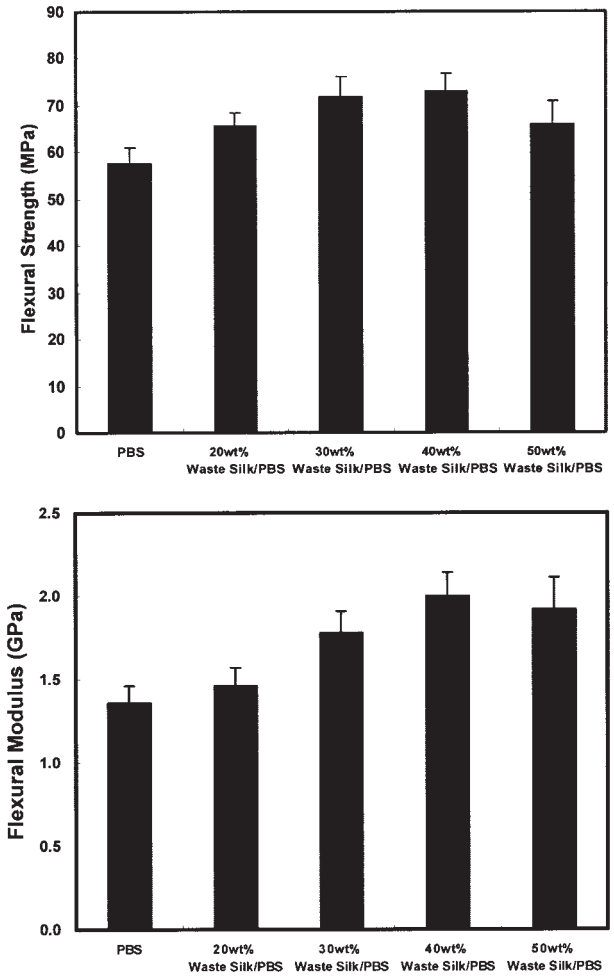

Figure 5 Flexural strength and modulus of PBS and as-separated waste silk/PBS biocomposites with different fiber contents.

Combining the mechanical test results, it is concluded that the tensile and flexural moduli are increased greatly with increasing the content and length of reinforcing waste silk fibers, exhibiting the greater percent improvement than that is seen in their strength. It is suggested that the optimum loading of as-separated waste silk fibers for successfully fabricating a waste silk/PBS biocomposite using the present processing technique and also for obtaining the highest mechanical properties is 40% by weight. Also, the use of chopped waste silk fibers with a uniform length is more desirable as reinforcement for improving the mechanical properties of the waste silk/PBS biocomposite than use of as-separated waste silk fibers. As a result, it is noticeable that waste silk fibers play a contributing role in improving the mechanical properties of PBS resin in the present material system,

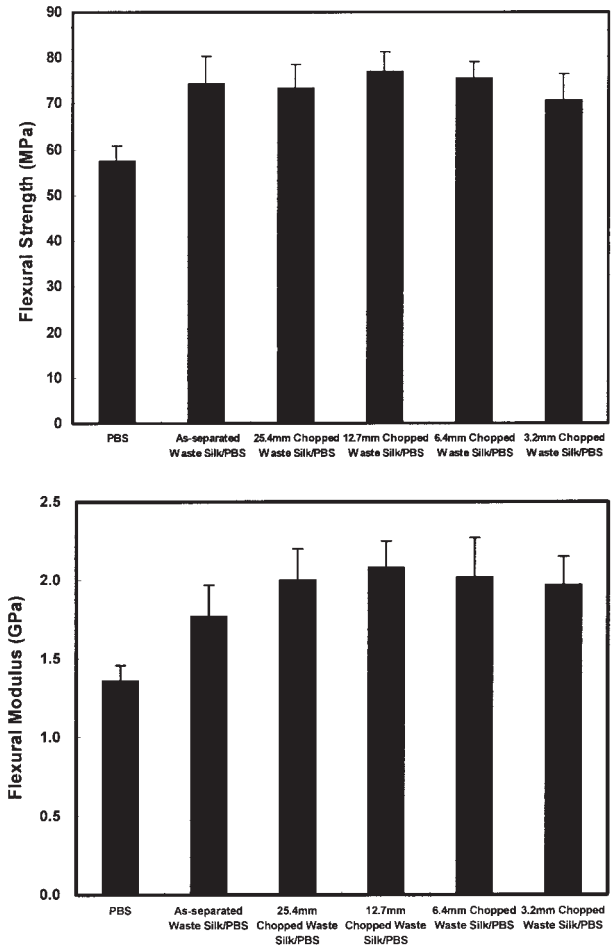

Figure 6 Flexural strength and modulus of PBS and as-separated waste silk/PBS biocomposite and chopped waste silk/PBS biocomposites with different fiber lengths. The fiber content was 30 wt %.

although the waste silk fibers have been used without surface modification in the present study.

Dynamic mechanical properties

Figure 7 shows the variation in the storage modulus (top) and the tan δ (bottom) observed for the PBS control and as-separated waste silk/PBS biocomposites with different fiber loadings as a function of temperature. The glass transition temperatures (T_g) of the PBS control and the waste silk/PBS biocomposites are approximately in the range of −12°C to −9°C, as found from raw silk fiber-reinforced PBS biocomposites previously.[16] Beyond the glass transition region, the storage modulus in the logarithmic scale is much greater than that of the PBS control. The E' value was significantly increased by gradually adding the as-separated waste silk fibers. The storage modulus was largely enhanced with an incorporation of 30 wt % waste silk, and then, it was slightly increased with an additional loading of the fibers up to 50 wt %. This is ascribed to the reinforcing effect imparted by the waste silk fibers that allows stress transfer from the PBS matrix to the waste silk.

Below the T_g, any significant change in the storage modulus was not observed with varying the fiber loading, indicating that there was no obvious fiber reinforcement effect. This is probably because the PBS matrix below the T_g, at which the molecular motion of polymer chains themselves is largely restricted, may contribute to the modulus of each biocomposite more importantly. Table I summarizes the values of the storage modulus measured at the tan δ peak (glass transition region) at 50°C (near rubbery plateau region) and at 100°C (before melting region) for PBS and as-separated waste silk/PBS biocomposites fabricated with various fiber contents. The change in storage modulus in each temperature region shows an increasing tendency with the increase in the waste fiber loading. At 100°C, the storage modulus of PBS control was greatly improved by the waste fiber reinforcement. The percent improvement of the storage mod-

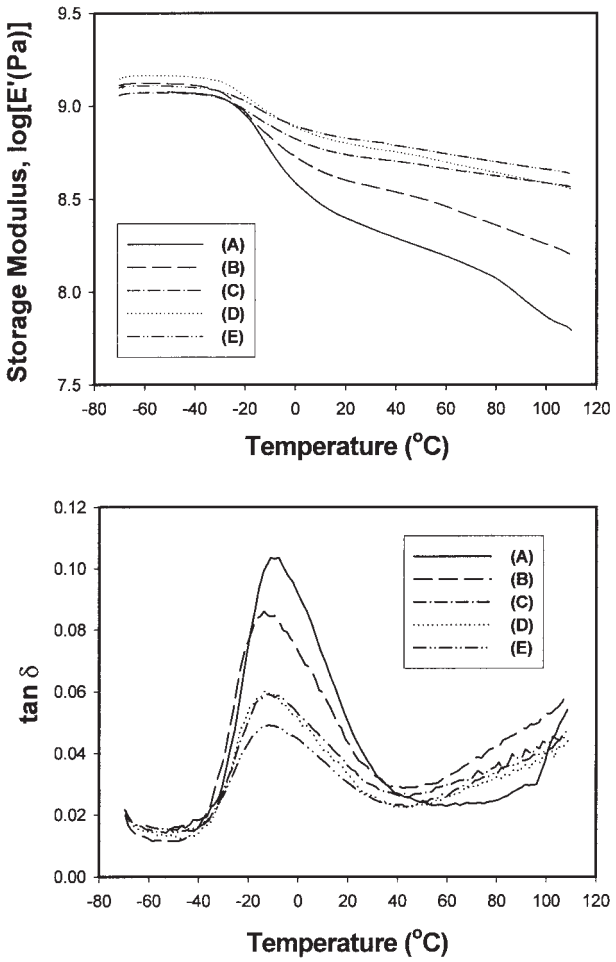

Figure 7 Variation in the storage modulus and tan δ of PBS and as-separated waste silk/PBS biocomposites with various fiber contents: (A) PBS, (B) 20 wt %, (C) 30 wt %, (D) 40 wt %, and (E) 50 wt %.

TABLE I
The Storage Moduli (E') Obtained at the Tan δ Peak, and 50 and 100°C for PBS Control and As-Separated Waste Silk/PBS Biocomposites with Different Waste Silk Fiber Contents

Specimen	E' (MPa) at tan δ peak	E' (MPa) at 50°C	E' (MPa) at 100°C
PBS control	553	174	74
Waste Silk (wt %)/ PBS			
20	721	318	180
30	776	484	385
40	953	535	385
50	908	583	457

ulus of the PBS control was about 72% at T_g, 207% at 50°C, and 420% at 100°C in the 40 wt % waste silk/PBS biocomposite. Therefore, it is concluded that the incorporation of as-separated waste silk fibers into the PBS matrix resin significantly increases the storage modulus in the temperature region far above the tan δ; peak.

From the variation of the tan δ; peak in the bottom of Figure 7, it is seen that the incorporation of the waste silk fibers into the PBS resin decreases the tan δ peak height with increasing the fiber content, indicating a lower damping characteristic. The result demonstrates that a waste silk fiber-reinforced biocomposite material may potentially have a structural damping property, as found with raw silk fiber-reinforced biocomposite materials earlier.[16] However, it is likely that the fiber loading did not influence the peak temperature of the biocomposites. This implies that the interaction between the waste silk and the PBS resin did not seem very strong. Such an interaction may be achieved by improving the interfacial adhesion between the natural silk fibers and the biodegradable polymer matrix, as studied in other biocomposite systems.[22–24]

Figure 8 illustrates the variation of the storage modulus (top) and the tan δ (bottom) as a function of temperature measured for PBS, an as-separated waste silk/PBS biocomposite and four chopped waste silk/PBS biocomposites fabricated with varying fiber lengths. A summary of the storage moduli measured at the tan δ peak, at 50°C, and 100°C is given in Table II. At a fixed waste silk fiber loading of 30 wt %, the storage modulus of PBS control was greatly increased with incorporation of the waste silk fiber into the resin, regardless of the fiber length. This is attributed to the reinforcing effect imparted by the waste silk fibers. In particular, the incorporation of chopped waste silk more greatly increased the storage modulus of the PBS than that of as-separated waste silk in the temperature region far above the T_g. Above the T_g, the E' values of as-separated waste silk/PBS biocomposite were lower than those of chopped waste silk/PBS counterparts, with better dispersion at the same fiber loading.

The greatest storage modulus of the chopped waste silk/PBS biocomposites was obtained with 12.7-mm long waste silk fibers, as described in the static mechanical test result earlier. The numerical improvement of the storage modulus of the PBS control by reinforcing with the 12.7-mm long waste silk fibers was about 43% at the tan δ peak, 256% at 50°C, and 523% at 100°C, respectively. As found in the tan δ result of the biocomposites with different as-separated waste silk fiber loadings, the peak height of the tan δ curve was largely decreased with the incorporation of chopped waste silk fibers. However, the peak height was not significantly affected with the fiber length. This was ascribed probably to the fixed loading of reinforcing waste silk fibers. The dynamic mechanical result also showed that the waste silk fiber content

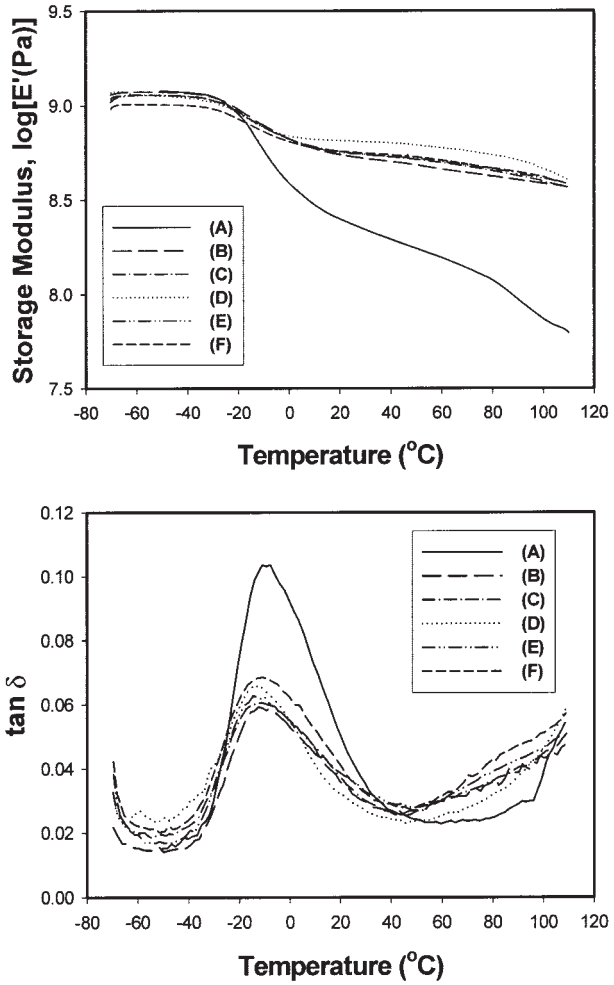

Figure 8 Variation in the storage modulus and tan δ of (A) PBS and (B) as-separated waste silk/PBS and (C–F) chopped waste silk/PBS biocomposites with various fiber lengths: (C) 25.4 mm, (D) 12.7 mm, (E) 6.4 mm, and (F) 3.2 mm. The fiber content was 30 wt %.

TABLE II
The Storage Moduli Obtained at the Tan δ Peak, and 50 and 100°C for PBS Control and Chopped Waste Silk/PBS Biocomposites with Different Waste Silk Fiber Lengths[a]

Specimen	E' (MPa) at tan δ peak	E' (MPa) at 50°C	E' (MPa) at 100°C
PBS Control	553	174	74
As-separated Waste Silk/PBS	776	484	385
Chopped Waste Silk (mm)/PBS			
25.4	778	516	393
12.7	791	619	461
6.4	788	523	410
3.2	748	533	418

[a] The fiber content was 30 wt %.

affects more greatly on the composite reinforcement than the fiber length, considering the variation of the storage modulus and the tan δ peak height of the biocomposites.

Thermal stability

A thermogravimetric analysis including the derivative thermograms is very useful to determine quantitatively the degradation behavior and the composition of the fiber and the matrix in a polymer composite material, and also it informs the mutual effect of the composite components. Figure 9 depicts the thermal stability of PBS resin, waste silk fiber, and as-separated waste silk/PBS biocomposites with different fiber contents. It is shown that the initial degradation of PBS resin started from near 300°C. As found from the DTG curve, the fastest weight loss of PBS occurred at about 386°C. The waste silk fiber began to lose its weight significantly at about 230°C, exhibiting a peak temperature of weight loss at about 323°C. The initial weight loss may be ascribed to the evaporation of water in the waste silk fiber. There was no significant weight loss in the range of 100–200°C. It has been reported[25] that chemical changes in the *B. mori* silk fiber start gradually at about 190°C and there is a large endothermic reaction corresponding to a substantial weight loss starting near 280°C, which is due to the thermal decomposition of silk fibers. Further weight loss took place from 330 to 500°C at a lower rate.

The thermal stability of waste silk/PBS biocomposites is likely to be intermediate between the PBS matrix and the waste silk depending on the fiber loading. It is clearly seen from the DTG result that there are two distinguishable peak temperatures of weight loss in the biocomposites. The first peak temperature mainly due to the waste silk fiber therein was slightly increased about 2–4°C, whereas the second peak temperature mainly due to the PBS matrix surrounding the reinforcing waste silk fibers in the biocomposite was increased about 14–17°C. This result implies that in the biocomposite the less thermal stability of the waste silk fiber in the low temperature region below 400°C may be compensated by the PBS matrix, whereas the less thermal stability of the PBS in the high temperature region above 400°C may also be compensated by the reinforcing waste silk fibers. The thermal stability of the biocomposites reinforced with waste silk fibers chopped in different lengths was observed to be similar to the typical thermogram of as-separated waste silk/PBS biocomposites in Figure 9. However, the degradation behavior did not depend on the chopped waste silk fiber length because of the fixed fiber content.

CONCLUSIONS

Industrially available waste silk fiber-reinforced poly(butylene succinate) biocomposites have been fabri-

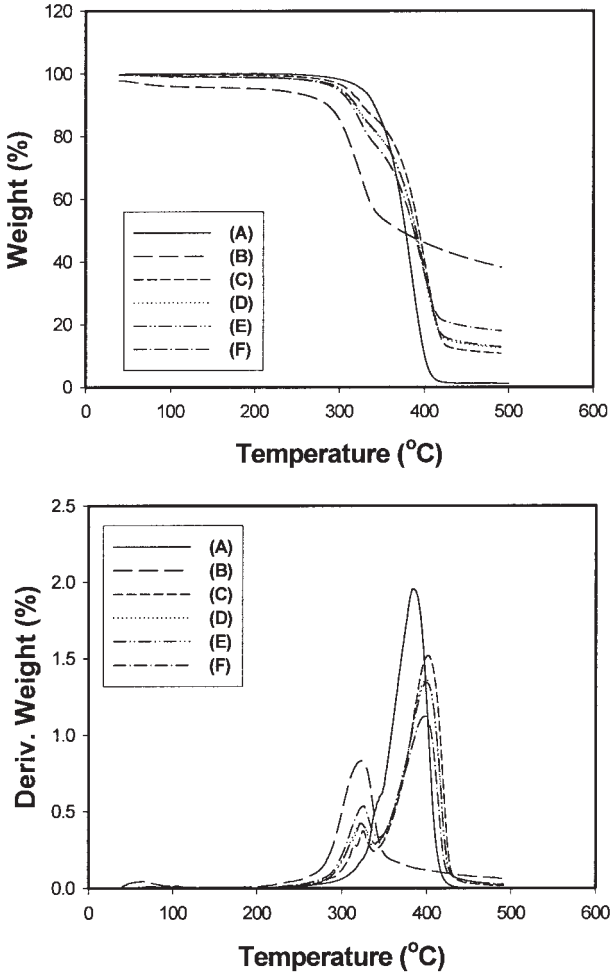

Figure 9 TGA (top) and DTG (bottom) thermograms showing the thermal stability of (A) PBS, (B) waste silk, and (C–F) as-separated silk/PBS biocomposites with different fiber contents: (C) 20 wt %, (D) 30 wt %, (E) 40 wt % and (F) 50 wt %.

cated with varying fiber contents and lengths. The investigation of their mechanical and thermal properties gives rise to the following conclusions.

The tensile and flexural properties of PBS control were significantly increased with increase in the waste silk fiber content in the biocomposite system, showing the maximum tensile strength and modulus at a 40 wt % loading of as-separated waste silk fibers and also with chopped waste silk fibers of 12.7 mm in average length. At a fiber loading of 40 wt %, the tensile strength and modulus of PBS control were improved by 27 and 160%, respectively. Its flexural strength and modulus were also improved by 26 and 54%, respectively, in the 40 wt % waste silk/PBS biocomposites.

Above the glass transition temperature, the storage modulus of all the waste silk fiber-reinforced PBS biocomposites studied was significantly greater than that of PBS resin, especially in the higher temperature region. The storage modulus of the biocomposites was increased with increase in the loading of waste silk fibers, and the greatest value was obtained with the chopped waste silk fibers of 12.7 mm length. The tan δ peak height of the biocomposites was decreased with increase in the waste silk fiber content, whereas it was not significantly influenced with the fiber length.

The thermal stability of waste silk/PBS biocomposites was observed to be intermediate between the PBS resin and the waste silk fiber depending on the fiber content. Below ~400°C, the thermal stability of the biocomposites was decreased with increasing waste silk fiber content, whereas above ~400°C, it was increased with increasing fiber content.

As concluding remarks, the present results suggest that the use of industrially available waste silk fibers, which have been considered as industrial waste, may be a potential as reinforcement for effectively improving the mechanical and thermal properties of a biodegradable polymer matrix resin, depending on fiber content and length in a biocomposite system. There may be an additional margin of the property improvement attainable by appropriate fiber surface modification, leading to better interfacial adhesion between the natural fiber and the biodegradable polymer matrix.

We thank the IRe Chemical Ltd. for kindly providing poly(butylene succinate) and also the Korea Silk Research Institute for kindly supplying waste silk fibers for this research.

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