

MECHANICAL AND THERMAL PROPERTIES OF NOVEL SILK/POLY(BUTYLENE SUCCINATE) BIOCOMPOSITES

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ABSTRACT

In the present study, novel short silk fibre (*Bombix mori*) reinforced poly(butylene succinate) biocomposites have been fabricated with varying fibre contents by a compression molding method and their mechanical and thermal properties have been studied in terms of tensile and flexural properties, thermal stability, thermal expansion, dynamic mechanical properties, and microscopic observations. The results demonstrate that chopped silk fibres play an effective role as reinforcement for improving the mechanical properties of PBS in the present system although raw silk fibres are used without any surface modification in order to enhance the interfacial adhesion between the fibre and the matrix. The tensile and flexural properties of PBS matrix resin are markedly improved with increasing the short fibre content in the composites, showing a maximum value at 50w% of fibre loading. Also, the thermomechanical stability of PBS resin is greatly improved by incorporating reinforcing short silk fibres in the composite matrix, having much lower linear coefficient of thermal expansion values and higher storage modulus than PBS control, respectively. The thermal stability of silk/PBS biocomposites is likely to be intermediate between the PBS matrix and the silk fibre depending on the short fibre content. This work also suggests that animal-based natural silk fibres as reinforcement in a natural fibre composite system may be potential for effectively improving the properties and performances of biodegradable polymer matrix resins.

1. INTRODUCTION

With emphasis of environmental awareness, consciousness and legislation, academic and industrial needs for developing environmentally friendly composite materials have recently been increasing with considerable attraction, based on renewable resources like natural fibres as alternatives for glass fibre reinforcement in traditional glass fibre-reinforced polymer matrix composites.¹⁻⁵ Advantages of natural fibres over traditional reinforcing fibres such as glass and carbon fibres are low cost, low density, high toughness, acceptable specific strength, enhanced energy recovery, recyclability, biodegradability, etc.⁶ Therefore, natural fibres can serve as reinforcement by improving the strength and stiffness and reducing the weight of the resulting biocomposite materials although the properties of natural fibres vary with their sources and treatments.⁷⁻⁹

Biocomposites or natural fibre composites are defined as composite materials composed of biodegradable natural fibres as reinforcement and biodegradable or non-biodegradable polymers as matrix.¹⁰ Biocomposites derived from natural fibres and traditional synthetic thermoplastics or thermosets are not sufficiently environmentally benign because matrix resins are non-biodegradable. However, these biocomposites do maintain a balance between economic and environmental issues allowing them to be considered for a variety of industrial applications like automobile, construction, consumer products, and others.^{11,12}

Natural fibres are largely divided into two categories depending on their origin: plant-based and animal-based. In general, plant-based natural fibres are ligno-cellulosic in nature and are composed of cellulose, hemicellulose and lignin, whereas animal-based fibres are of proteins. Plant-based natural fibres like flax, jute, sisal and kenaf have been more frequently utilized and studied so far, due to their natural abundance, cost effectiveness, world annual production and a wide range of properties depending on the plant source. A large number of earlier papers have been reported on biocomposites based upon these plant-based natural

fibres.¹³⁻¹⁷ However, use of animal-based natural fibres like silk and wool in a biocomposite material has been rarely reported.

Silk fibres (*Bombyx mori*) spun out from silkworm cocoons are consisted of fibroin in the inner layer and sericin in the outer layer, all protein-based. Each raw silk thread has a lengthwise striation, consisting of two fibroin filaments of 10~14 μm each embedded in sericin or silk gum. The chemical compositions are in general as follows: silk fibroin of 75~83 %, sericin of 17~25 %, waxes of about 1.5 % and others of about 1.0 % by weight.¹⁸ Silk fibres are biodegradable, of well-aligned structure with high crystallinity, higher tensile strength than glass fibre or synthetic organic fibres, and good elasticity and resilience.¹⁹ They are normally stable up to 140°C and the thermal decomposition temperature is greater than 150°C. It is known that the densities are in the range of 1320~1400 kg/m^3 with sericin and 1300~1380 kg/m^3 without sericin, respectively. Silk fibres are also commercially available in a continuous fibre type.

A large number of studies on the biocomposite materials have focused on non-biodegradable polymers such as synthetic thermoplastics and thermosets as matrix.²⁰⁻²³ This may be due to some advantages of them over cost, material versatility and processibility without significant difficulties, which can be probably caused by an introduction of biodegradable polymers, in using traditional composite processing methods even though the insufficient biodegradability due to the polymer matrix is imparted. Poly(butylene succinate) (PBS), which is thermoplastic aliphatic polyester, has excellent biodegradability in nature like in soil, lake, sea and compost.²⁴ It also has comparable mechanical properties with general-purpose thermoplastics such as polyethylene, polypropylene and polystyrene. PBS is completely combustible by fire without evolving toxic gases, recyclable, and processible by injection, extrusion, compression, and lamination moulding techniques. It is commercially available at lower cost than poly(3-hydroxybutyrate) and poly(lactic acid), which have been frequently studied as biodegradable polymer matrix in a biocomposite system. Therefore, PBS may be a good candidate material for utilizing as matrix polymer of biocomposite materials.

The objectives of this study are to fabricate novel silk/PBS biocomposites and to investigate the effect of short fibre content on the mechanical and thermal properties of the biocomposites. In this paper, fundamental results for understanding the performance and potential as a candidate biocomposite will be discussed in terms of tensile and flexural properties, thermal stability, thermal expansion, dynamic mechanical properties, and microscopic observations.

2. EXPERIMENTAL

2.1. Materials

Continuous silk fibres of 21 deniers were supplied from Daejeon Sangsa Co., Korea. The fibres were chopped to be short fibres of about 12.7 mm (1/2 inch) in length. As described earlier, each filament of the 'as-received' silk fibres (*Bombyx mori*) used in this study, which were spun out from silkworm cocoon, is composed of fibroin in the inner layer and sericin in the outer layer. Each thread of raw silk fibres is physically combined with seven silk filaments with a lengthwise striation having a diameter of 50~60 μm , as seen in Figure 1. The 'as-received' silk fibres in white or light gray were used as reinforcement without further modification except for chopping them.

Poly(butylene succinate) (PBS, EnPol G-5100), which is thermoplastic, aliphatic polyester, was supplied from IRe Chemical Ltd., Korea. The 'as-received' PBS pellets were finely pulverized using a kitchen mixer in order to make mixing with chopped silk fibres easy. Figure 2 shows the chemical structure of PBS used in this work. The melting temperature of the PBS is about 120°C. The density is 1220 kg/m^3 . It is also informed that the melt flow index is 10 ± 2 .

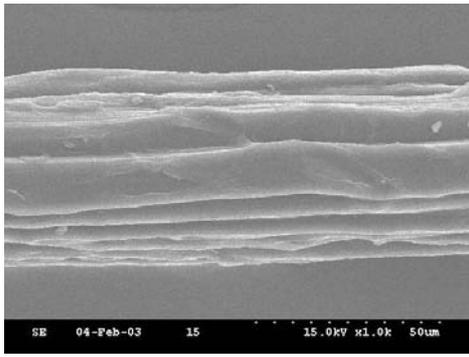
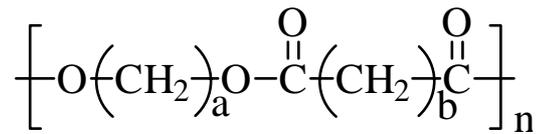


Fig. 1. SEM photo of a raw silk fiber.



(a = 4, b = 2 or 4)

Fig. 2. Chemical Structure of PBS used.

2.2. Fabrication of Biocomposites

The ‘as-received’ silk fibres and PBS pellets 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 composite fabrication, the pulverized PBS powder was mechanically mixed with the chopped silk fibres using a kitchen mixer. The mixture was placed in a steel mould and then moulded in a compression manner using a hot-press (Carver 2518). During processing, the mixture was melted enough to flow at 135°C for 15 min. A pressure of 1000 psi was applied right after 15 min at 135°C and then was retained until the mould was naturally cooled down to ambient temperature. Two steel moulds with different cavity dimensions (50mm×50mm and 100mm×150mm) were used. The thickness of the resulting biocomposites was varied depending on the specimen requirement for each analysis. The contents of chopped silk fibres in the silk/PBS biocomposites prepared were varied to be 10, 20, 30, 40, 50, and 60 % by weight.

2.3. Analysis

Single Fibre Tensile Test

The tensile properties of the ‘as-received’ continuous silk fibre were measured by a single fibre tensile test method according to ASTM D3379-75 using a universal testing machine (Instron 4467). A load cell of 250 g was used. The gauge length of each specimen was 25 mm. A crosshead speed used throughout the test was 2.0 mm/min. Fifteen specimens were tested in order to have the average values of tensile strength, tensile modulus and elongation at break.

Composite Tensile Test

The tensile properties of silk/PBS biocomposites were measured according to DIN 53455 using a universal testing machine (Instron 4467). The specimen dimensions were 150mm×15mm×5mm and the gauge length was 100 mm. A load cell of 30 kN was used. A crosshead speed of 10 mm/min was used. Ten specimens were tested in order to average the values of tensile strength, modulus and elongation at break.

Composite Flexural Test

The flexural properties of silk/PBS biocomposites were measured using a three-point bending method according to ASTM D790M-86 using a universal testing machine. The specimen dimensions were 50mm×25mm×2mm. 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. Ten specimens were tested in order to have the average values of flexural strength and modulus.

Thermogravimetric Analysis

The thermal stability of each silk/PBS biocomposite was examined up to 500°C with a purging N₂ gas of 80cc/min using a thermogravimetric analyser (TGA 951, DuPont). A heating rate of 10°C/min was used. About 20 mg of each specimen was loaded for each measurement. Derivative thermogravimetric (DTG) curves were also recorded.

Thermomechanical Analysis

The thermomechanical stability and the coefficient of thermal expansion (CTE) were examined up to 100°C with a purging N₂ gas using a thermomechanical analyser (TMA 2940, TA Instrument). A heating rate of 2°C/min was used. The specimen dimensions, which were machined using a low-speed diamond saw (Buehler Co.) were 5.5mm×5.5mm×5.5mm in a regular tetrahedron.

Dynamic Mechanical Analysis

The storage modulus, loss modulus and tan δ were measured from -50°C to 110°C with a purging liquid N₂ gas using a dynamic mechanical analyser (DMA 983, TA Instrument). The specimen dimensions were 30mm×10mm×2.7mm. A heating rate of 2°C/min was used to be slow enough to thermally equilibrate 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.

3. RESULTS & DISCUSSION

3.1. Mechanical Properties

The single fibre tensile test was performed with the raw silk because the raw silk tread was used as-received without separation of the multiple filaments or surface modification during the composite fabrication. The tensile strength and modulus are about 750 MPa and 14 GPa, respectively, and the percent elongation at break is about 25.

Figs. 3 and 4 depict the tensile strength and modulus for PBS and five different silk/PBS biocomposites with different fibre contents, respectively. The tensile strength and modulus gradually increase with increasing the silk fibre content. It is likely that an increase of the tensile strength at higher loadings of the chopped fibres is relatively smaller than that at lower loadings. It can be seen that an approximately linear relationship between the tensile modulus and the fibre content is obtained over the whole range of fibre loading. The presence of chopped silk fibres in the PBS matrix contributes more effectively to enhancing the tensile modulus of the PBS than to enhancing the tensile strength. Even at the fibre loading of 10wt%, the modulus of PBS is increased by about 85 %, whereas the strength of PBS is slightly increased.

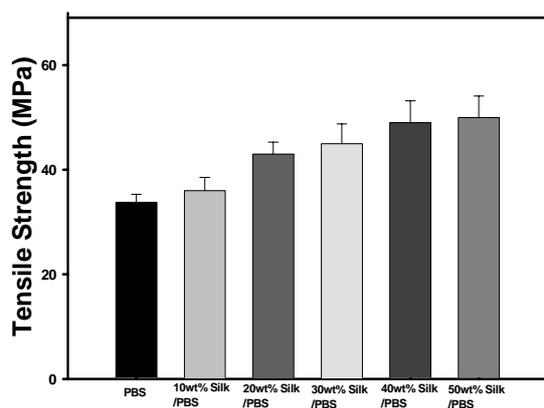


Fig. 3. Tensile strength of PBS and silk/PBS biocomposites with various silk contents.

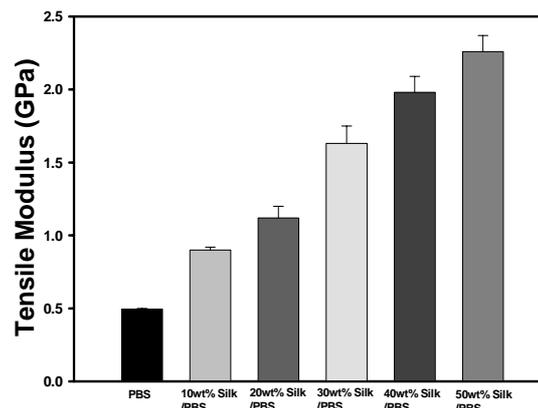


Fig. 4. Tensile modulus of PBS and silk/PBS biocomposites with various silk contents.

Figs. 5 and 6 show the flexural strength and modulus of PBS and five different silk/PBS biocomposites loaded with chopped silk fibres from 10wt% to 50wt%, respectively. The flexural strength gradually increases with increasing the fibre content. Above 40wt%, an increase of fibre content is likely to bring a lower improvement of the flexural strength than that obtained at lower contents. It was found that a further addition of 60wt% fibre in the PBS

adversely decreases to a large extent the flexural properties resulting in an incomplete composite to be used. This is due to the insufficient filling of the melted PBS matrix resin into the surrounding fibres during the composite processing at such a high loading of about 60wt%. The flexural modulus almost linearly increases with the addition of chopped silk fibres up to 50wt%. Compared with PBS, the tensile strength and flexural strength are improved by 34% and 105% in the 30wt% silk/PBS biocomposites and by 48% and 172% in the 50wt% silk/PBS composites, respectively, reflecting a greater enhancement in the flexural property.

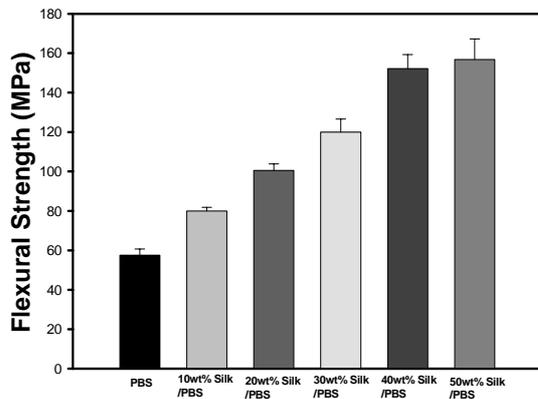


Fig. 5. Flexural strength of PBS and silk/PBS Biocomposites with various silk contents.

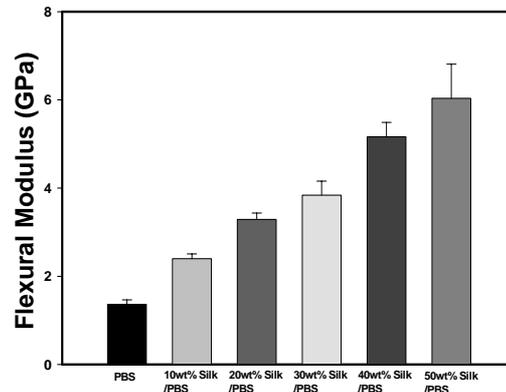


Fig. 6. Flexural modulus of PBS and silk/PBS biocomposites with various silk contents.

Combining the results in Figs. 3-6, it is noted that the tensile and flexural strengths of PBS matrix gradually increase with the incorporation of chopped silk fibres up to 50wt%. The smaller improvement of the strengths at 50wt% may be attributed to the competition phenomenon between the fibre reinforcing effect and microcrack initiation as a result of relatively high loading of chopped silk fibres.

The tensile and flexural moduli also increase remarkably with increasing the fibre content, showing a greater percent improvement than that seen in the strengths. This is known that the tensile modulus of a short fibre-reinforced polymer composite mainly depends on the modulus of the fibre and the resin matrix, the fibre content and orientation, and fibre length. Among these factors, the result may be taken account into the fibre content and orientation effect only because the same fibre and matrix have been used and the fibre length was approximately constant. The short fibre can be, in general, oriented with a higher degree of alignment with increasing the content, resulting in an increase of the tensile modulus in a short fibre-reinforced composite system.

The result demonstrates that up to 50wt% the greater the fibre content, the higher the mechanical properties. It is stressed that the optimum loading of chopped silk fibres with 12.7 mm long for successfully fabricating a silk/PBS biocomposite using the present processing technique and for obtaining the highest mechanical properties is approximately 50% by weight. Therefore, it is concluded that chopped silk fibres play an effective role as reinforcement for improving the mechanical properties of PBS in the present system even though the raw silk fibres have been utilized without any surface modification in order to enhance the interfacial adhesion between the fibre and the matrix.

3.2. Thermal Properties

Fig. 7 shows the thermal stability of PBS matrix, raw silk fibre, and five silk/PBS biocomposites. As can be seen, the PBS matrix begins to degrade at about 300°C having a peak temperature of weight loss (fastest weight change) at about 384°C. The raw silk fibre

begins to significantly lose the weight at about 250°C having a peak temperature of weight loss at about 309°C. The initial weight loss may be due to the evaporation of water contained in the silk fibre. There is no significant weight loss in the approximate range of 100°C-200°C. It has been reported [25] that chemical changes in the *Bombyx mori* silk fibre starts gradually at around 190°C and there is a large endothermic reaction corresponding to a substantial weight loss starting at around 280°C, which is ascribed to the thermal decomposition of silk fibres. Further weight loss takes place from 320°C to 500°C at lower rate.

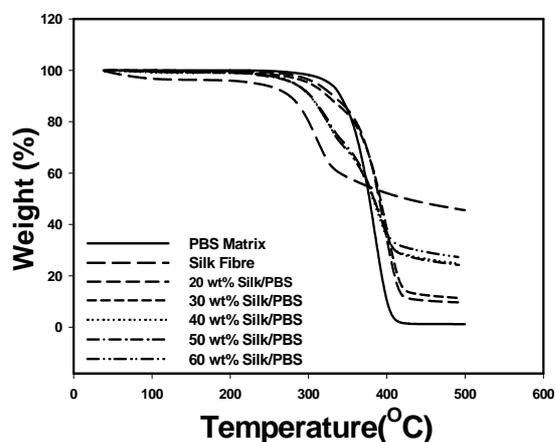


Fig. 7. TGA thermograms showing the thermal stability of PBS, silk, and various silk/PBS biocomposites.

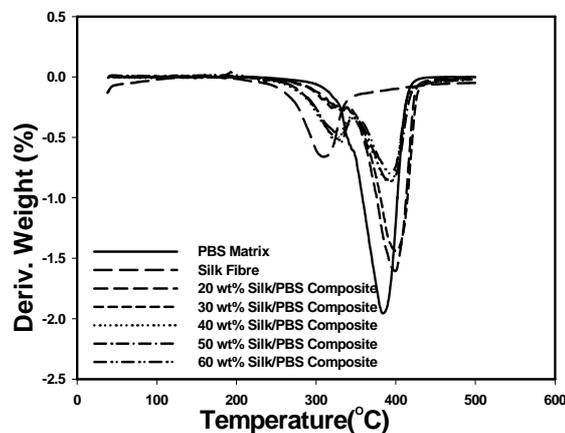


Fig. 8. DTG curves obtained from each thermogram in Fig. 7.

The thermal stability of silk/PBS biocomposites is likely to be intermediate between the PBS matrix and the silk fibre depending on the chopped fibre content. There are two distinguishable peak temperatures of weight loss in the composite specimens. In the DTG curves of Fig. 8, the primary peak temperature slightly increases with increasing the chopped fibre content incorporated into the PBS matrix whereas the secondary peak temperature more or less decreases with increasing the fibre content. This can be explained by that the PBS matrix, which has greater thermal stability than the silk fibre below about 350°C, can play a dominant role in the thermal stability of the biocomposites and also by that the silk fibre, which has greater thermal stability than the PBS above about 350°C, can play a dominant role in the thermal stability. Below 350°C, the thermal stability of the composites decreases with increasing the silk fibre content. On the other hand, above 350°C it increases with increasing the fibre content. Therefore, it can be said that in the biocomposite the less thermal stability of the natural fibre in the low temperature region may be compensated by the PBS matrix whereas the less thermal stability of the PBS in the high temperature region may also be compensated by the presence of silk fibres.

The coefficient of thermal expansion (CTE) is useful for understanding dimensional changes as well as thermal stresses caused by thermal variation. In general, the CTE of a fibre-reinforced polymer matrix composite may be lower than that of a pure polymer material because polymers thermally expand with a greater extent than most reinforcing fibres like glass and carbon. Lowering the CTE value is desirable in minimizing thermo-dimensional changes in composites exposed to temperature changes during composite fabrication or use. In the present composite system with randomly oriented chopped fibres, which is quasi-isotropic, the CTE values may be assumed to be equal in all directions in the plane of the composite.

Fig. 9 represents the thermal expansion behaviour of pure PBS matrix resin and four different silk/PBS biocomposites with different fibre contents. As can be seen, the thermal expansion, which is reflected by the dimensional change, is dramatically diminished by the increasing addition of chopped silk fibres in the PBS matrix. The pure PBS resin shows a

slight curvature of thermal expansion whereas all the silk/PBS biocomposites exhibit an almost linear expansion over the temperature range examined. Table 1 indicates the CTE values measured in the temperature range of 30°C~100°C. The CTE value of PBS resin, $294 \times 10^{-6}/^{\circ}\text{C}$, is markedly decreased to be $52 \times 10^{-6}/^{\circ}\text{C}$ by adding only a 20wt% of chopped silk fibres in the matrix. The greater the reinforcing fibre content added, the lower the CTE value. The addition of 50wt% chopped silk fibres in the composite reduces the CTE value of PBS to be about 1/30 of it. This is because the thermal expansion becomes much less with increasing the fibre loading, reflecting the thermal restraint of the PBS matrix by the reinforcing silk fibres in the silk/PBS biocomposite. Therefore, it is concluded that the thermomechanical stability or dimensional stability of PBS resin is remarkably improved by the incorporation of reinforcing silk fibres in the composite matrix.

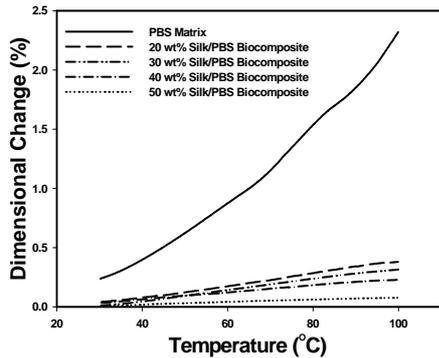


Fig. 10. TMA results of PBS and various silk/PBS biocomposites

Specimen	From 30°C to 100°C ($\mu\text{m}/\text{m}\cdot^{\circ}\text{C}$)
PBS Matrix Resin	294
20 wt% Silk/PBS Biocomposite	52
30 wt% Silk/PBS Biocomposite	46
40 wt% Silk/PBS Biocomposite	29
50 wt% Silk/PBS Biocomposite	10

Table 1. CTE values for PBS and various silk/PBS biocomposites.

Fig. 10 shows the variation of the storage modulus as a function of temperature observed for PBS matrix resin and six silk/PBS biocomposites with different fibre contents. The behaviour of the storage modulus for the PBS resin without reinforcement is typical of thermoplastic aliphatic polyester. It can be seen from the figure that beyond the glass transition region near -10°C the storage modulus in logarithmic scale is much greater than that of PBS control, with the exception of a 60wt% silk/PBS composite specimen. With the gradual addition of reinforcing chopped silk fibres, the storage modulus is increased. With an initial introduction of 10wt% to 20wt% silk fibres, the modulus is largely enhanced and then it is slightly increased with an additional introduction of the fibres up to 50wt%. This is ascribed to the reinforcing effect imparted by the natural fibres that allows stress transfer from the PBS matrix to the silk fibres. However, in the case of 60 wt% silk/PBS composite, the modulus is adversely dropped to a large extent, showing a much lower E' value than PBS control over the whole temperature range. This is due to the insufficient filling of the PBS resin into the chopped silk fibres at such a high fibre loading during the composite processing, as described earlier.

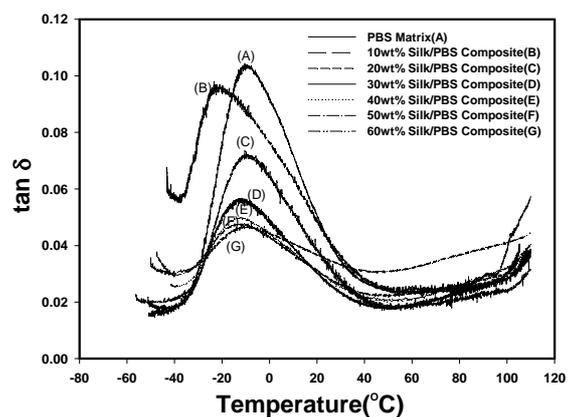
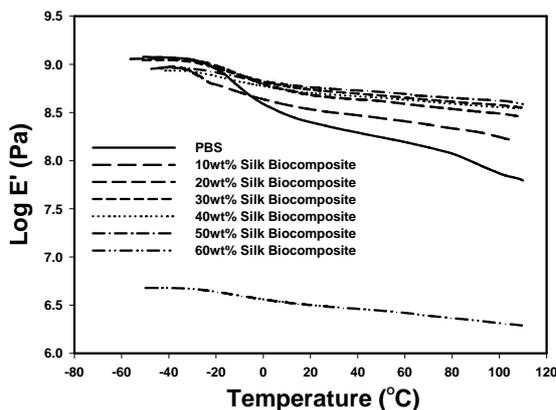


Fig. 10. Variation of the storage modulus of PBS and various silk/PBS biocomposites. Fig. 11. Variation of $\tan \delta$ curve for PBS and various silk/PBS biocomposites.

Below the glass transition, it was difficult to observe any significant change in the storage modulus with varying the fibre loading, indicating that no obvious fibre reinforcing effect was examined. This is probably because the brittle PBS matrix below the glass transition temperature (T_g), at which the molecular motion of polymer chains themselves is largely restricted, may contribute to the modulus of each composite more importantly. Table 2 summarizes the values of the storage modulus observed at T_g (glass transition region), at 50°C (near rubbery plateau region), and at 100°C (near melting region). It is known that the melting point of PBS used in this work is in the range of 110°C~120°C. It is likely that the storage moduli at 50°C and at 100°C have an increasing tendency more or less with increasing the fiber content, with the exception of 60wt%, as pointed out earlier. However, the modulus obtained at T_g has no tendency with varying the content. Therefore, it can be said that the addition of chopped silk fibres into the PBS matrix significantly increases the storage modulus in the temperature region far above the T_g . The maximum storage modulus of the silk/PBS biocomposite can be obtained with the 50wt% fibre content, as suggested in the static mechanical data above-mentioned.

Table 2. A summary of the storage modulus obtained from different temperature regions for PBS and various silk/PBS biocomposites with different fibre contents.

Specimen	E' (MPa) at T_g	E' (MPa) at 50°C	E' (MPa) at 100°C	T_g (°C)
PBS Matrix Resin	575	173	74	-10
20 wt% Silk/PBS Biocomposite	759	415	308	-9
30 wt% Silk/PBS Biocomposite	794	457	378	-12
40 wt% Silk/PBS Biocomposite	676	449	360	-12
50 wt% Silk/PBS Biocomposite	776	515	420	-12
60 wt% Silk/PBS Biocomposite	4	3	2	-11

Fig. 11 shows the variation of $\tan \delta$ as a function of temperature of silk/PBS biocomposites with various fibre contents. It is found that the introduction of chopped silk fibres decreases the peak height of $\tan \delta$ curve with increasing the fibre content, reflecting a lower damping property. This may be due to the restriction of the mobility of poly(butylene succinate) chains by the reinforcing silk fibres. The T_g determined from the peak temperature of each $\tan \delta$ curve is not significantly influenced by fibre loading.

3. CONCLUSIONS

In this study, novel short silk fibre-reinforced poly(butylene succinate) biocomposites have been successfully fabricated with various fibre contents and their mechanical and thermal properties have been studied with the following conclusions.

1. The tensile and flexural properties of PBS matrix resin are markedly improved with increasing the short fibre content in the composites, showing a maximum value at 50w% of fibre loading. The result demonstrates that chopped silk fibres play an effective role as reinforcement for improving the mechanical properties of PBS in the present system although raw silk fibres are used without any surface modification in order to enhance the interfacial adhesion between the fibre and the matrix.

2. The thermal stability of silk/PBS biocomposites is likely to be intermediate between the PBS matrix and the silk fibre depending on the chopped fibre content. Below 350°C, the

thermal stability of the composites decreases with increasing the silk fibre content whereas above 350°C it increases with increasing the fibre content.

3. The thermomechanical stability or dimensional stability of PBS resin is remarkably improved by the incorporation of reinforcing silk fibres in the composite matrix. All the silk/PBS biocomposites used exhibit much lower linear CTE values than PBS control in the whole temperature region.

4. Above the glass transition region, the storage modulus of silk/PBS biocomposites is significantly greater than that of PBS resin, especially in the higher temperature region. With the addition of reinforcing silk fibres up to 50wt%, the storage modulus increases. The $\tan \delta$ of the composites decreases with increasing the silk fibre content.

As concluding remarks, the present results suggest that animal-based natural silk fibres (*Bombyx mori*) as reinforcement in a natural fibre composite system may be a potential candidate for effectively improving the properties and performances of biodegradable polymer matrix resins and the composite properties may be further enhanced by fibre surface modification leading to better interfacial adhesion between the fibre and the matrix.

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