Effect of silkworm silk fibre content and length on mechanical and thermal properties of green composites based on poly(butylene succinate)

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In the present study, silkworm silk fibre (SF) reinforced poly(butylene succinate) (PBS) green composites have been fabricated with different fibre contents and fibre length by twin screw extruder and injection molding machine. The filler was treated with 5% w/v aqueous sodium hydroxide (NaOH) solution for 1 h to remove the sericin on the surface of fibre. The tensile, impact and thermal properties of biocomposites have been investigated. The results demonstrate that tensile strength, tensile modulus and impact strength of the composites increased with fibre content whereas the % elongation at break decreased. Better interfacial bonding between the fibres and the polymer matrix was observed by scanning electron microscope (SEM). The thermal stability and crystallinity (Xc) of PBS/SF biocomposites increased with increasing filler content. Based on the current results, animal-based fibres can be effectively used as a reinforcement in composites system by improving the properties and performances of biopolymer matrix.

1. Introduction

In recent years, natural fibre reinforced polymer composites have been the focus of academic and industrial research (e.g. food packaging, medicines automotive and construction) interest due to several advantages, such as low cost, low density, high strength to weight ratios, low abrasive wear of processing machinery and recyclability compared to the synthetic fibre composites [1]. However, the natural fibre composites are not fully environmentally-friendly because polymer matrixes are non-biodegradable [2]. Therefore, biocomposites based on natural fibres and biodegradable polymeric matrix made from natural resources are called ''green composites'' and have been developed because of their environmentally beneficial properties [3].

Poly(butylene succinate) (PBS) is a biodegradable, thermoplastic and aliphatic polyester. PBS has excellent processibility with relatively low melting temperature (T_m) and comparable mechanical properties with general-purpose thermoplastics like polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(ethylene terephthalate) (PET) and poly(lactic acid) (PLA) [4]. PBS is also completely biodegradable in natural conditions, has thermal and chemical resistance, and recyclability [5]. It is commercially available at lower cost than PLA and poly(3-hydroxybutyrate) (P3HB), which have been frequently studied as biodegradable polymer matrix in a biocomposite system. Therefore, PBS may be a good candidate material for utilizing as a polymer matrix of green composite materials [6].

Silks are generally defined as protein polymers that are spun into fibres by some Lepidoptera larvae (such as silkworms, spiders, scorpions, mites, bees and flies). Silks differ widely in composition, structure and properties depending on the specific source. The most extensively characterized silks are from the domesticated silkworm (*Bombyx mori*) and from spiders (*Nephila clavipes* and *Araneus diadematus*) [7, 8]. Silkworms silk fibre (SF) has impressive mechanical properties, biocompatibility, environmental stability, morphologic flexibility and the ability for amino acid side change modification to immobilize growth factors. Silk offers an attractive balance of modulus, breaking strength, and elongation, which contributes to its good toughness and ductility. SF is tougher than Kevlar, which is used as a bench mark in high performance fibre technology. Degradation of silk could be regulated by changing crystallinity, pore size, porosity and molecular weight distribution (MWD) of the SF [9-11]. Lam et al. [12] described silk as biodegradable material due to its susceptibility to proteolytic enzymes. The study compared dry-spun hot-drawn poly(l-lactic acid) (PLLA) fibres to several absorbable and non-degradable sutures in the muscle layer surrounding the abdomen of rats.

However, raw SF consists of silk fibroin that is bound together by a hydrophilic glued-liked protein layer called "sericin". Degumming is a surface modification process for sericin removal which allows a wide control of the SF's properties, making the fibre possible to be properly used for the development and production of novel bio-composites with specific mechanical, thermal and biodegradable properties. When the SF is degummed by a sodium hydroxide solution (NaOH), non-covalent bonds of silk fibroins are then modified and thus to cause the swell of the fibre. The swelling effect of the fibre is mainly governed by the difference of osmotic pressure arising between the fibre and the solution to form the protein salts [13].

The objectives of this research are to fabricate PBS/SF biocomposites and to investigate the effects of the fibre content and length on the mechanical and thermal properties of the green composites. In this paper, the performance of the materials and suitability of the composites are discussed in terms of the tensile and impact properties, crystallization and melting behaviors, and thermal stability.

2. Experimental details

2.1 Materials

The biopolymer PBS (GS Pla®, AZ91TN grade, Mitsubishi Chemical Corporation, Japan) was used as a thermoplastic matrix. The industrial SF was supplied by Spun Silk World Co., Ltd., Thailand. Sodium hydroxide (NaOH) was purchased from SPOLCHEMIE. All other chemicals used were analytical grade reagents.

2.2 Surface modification

Alkaline processing is one of the most common chemical treatments in the industry which is aimed at increasing the surface roughness of natural fibre that results in better mechanical interlocking [13]. The SF was degummed in 5% w/v NaOH solution for 1 h at ambient temperature, filtered and rinsed with distilled water, and dried in an oven.

2.3 Processing

Before compounding all natural raw materials were pre-dried at 80 °C during 24 h to stabilise the PBS and SF in terms of moisture content. The polymer in form of pellets and dried fibres (2, 5 and 7 mm) with various weight percents (2.5, 5.0 and 7.5% w/w) were extruded altogether using the co-rotating parallel twin-screw compounding extruder machine (model SHJ-25, Nanjing Kerke Extrusion Equipment Co., Ltd., China) equipped

with 9 heating zones (130/140/140/145/150/155/160/160/150 °C). The extruder screws were configured to ensure a better dispersion-distribution of the fibres within the polymeric matrix [14]. The co-rotating screws were operating at 80 rpm while a side feeder screw for feeding fibres was set at 30 rpm. The outlet side of the extruder was equipped with a wire die of 3 mm in diameter. The resulting strands was cooled in a water bath and cut into 2 mm length pellets using a plastic grinder (model BG 2523, Bosco, Thailand). In a further step, the obtained pellets were injection molded. The standard specimens for mechanical and thermal properties measurements were prepared using an injection molding machine (model BA250 CDC, Battenfeld, Germany). The melt temperatures from hopper to nozzle were set as 150-160 °C, and the mold pressure was 40 bar.

2.4 Characterization

2.4.1. Scanning electron microscopy (SEM)

The fibre surface morphology and fractured surface of the green composites after impact testing were examined using a Camscan-MX 2000 (England) equipped with an energy dispersive spectroscope (EDS). The specimens were coated with gold before SEM examination. Testing was performed at room temperature with tungsten filament, and an accelerating voltage of 15 kV was used to capture SEM images for all the samples.

2.4.2. Fourier transform infrared spectrometer (FT-IR)

Characterization of functional groups of pure PBS and green composites was obtained by FT-IR with 4,000-400 cm^{-1} wavenumber. Infrared spectrogram was recorded with a Nicolet FTIR (model Impact 410, USA) using potassium bromide (KBr) pellets.

2.4.3. Mechanical testing

Tensile properties of the biocomposites were measured with a Universal Testing Machine LR 50 K (England) using a 1 kN load cell, a crosshead speed of 10 mm/min. Samples for tensile tests conformed to ASTM D638 dumb-bell geometry.

The impact test was run using Pendulum Impact Tester Zwick I (USA) with a pendulum length of 225 mm and a pendulum size of 4 J. The dimension of specimens followed ASTM D256 (unnotched Izod test).

The mechanical properties reported hereinafter are the average of ten successful tests.

2.4.4. Thermal testing

All differential scanning calorimetry (DSC) measurements were performed in a Perkin Elmer (model Pyris 1, USA), using the following cycle for all composites and pure PBS: (i) the sample was heated from 50 to 250 °C at the heating rate of 10 °C/min and maintained at 250 °C for 3 min to erase the thermal history, (ii) the sample was cooled down to 50 °C at the cooling rate of 10 °C/min and maintained at 50 °C for 3 min, (iii) for the annealed specimens, the sample was directly heated from 50 to 250 °C at the heating rate of 10 °C/min. The peak of cold crystallization temperature (T_{cc}) and the second heating cycle of samples were obtained.

Thermal stability of both the pure PBS and PBS/SF biocomposites were revealed by making use of the Perkin Elmer (model TGA 7 HT, USA) system at ambient condition. The weight of each sample was about 6-7 mg. The temperature was set to start at 50 °C and end at 800 °C with the temperature scanning rate of 10 °C/min, and gas flow rate was set to be around 400 cc/min. Changes in weight percentage during temperature scanning and the decomposition temperatures of the materials can be determined.

3. Results and discussion

3.1 Fibre and green composites characterization

Chemical modifications of natural fibre surfaces have been reported to improve their wettability and to modify their microstructure, surface topography and surface chemical groups. Other advantages include the enhancement on the interaction between matrix and filler in the polymer-fibre biocomposites [15, 16].

The morphology of the fibre surface and fractured surface of the pure polymer and green composites was investigated through SEM. Fig. 1(a) present SEM image of degummed fibre. During the degumming process, sericin is hydrolysed, and solubilised in degumming agents and media. Silk degumming causes 20-25% weight loss, which is depended on the source and sort of silk [13, 17]. After the alkaline treatment with sodium hydroxide solution, organic components on fibre surfaces were removed, which resulted in an increase in the adhesion between fillers and matrix [18].

Tensile fractured surface morphologies of the pure PBS and alkali treated SF/PBS composites were shown in Figs. 1(b) and 1(c), respectively. It illustrates that the topology of the pure PBS is relatively smooth and no voids are observed. Moisture absorption during the manufacturing process did not occur in the sample [19]. This concludes that the processing of the sample was in a good condition. The results clearly showed a rougher surface for a biocomposite sample, compared to PBS sample. It was observed that the fibre breakage occurred at the fractured surface, which indicated a good interfacial adhesion between the degummed fibre and PBS matrix [20]. In addition, alkali-treated fibre having a good adhesion with PBS matrix can effectively disperse and transfer stress, leading to the improvement in mechanical properties of PBS/SF biodegradable composites. Consequently, the results suggest that alkali treatment of fibre is necessary to enhance the interfacial fibre-polymer matrix adhesion prior to composite processing [3].

The FT-IR spectra of pure PBS and PBS/SF green composites are shown in Fig. 2. The spectra show characteristic ester absorption peak at 1663 cm^{-1} for the stretching vibration of the –COO– and at 1390 cm^{-1} for the stretching vibration of the C-O-C [21]. When degummed fibre was introduced into PBS matrix, new peaks appeared at 3484, 1668, and 1253 cm^{-1}, which were assigned to the b-sheet conformation of fibroin [22]. The results indicate that SF appeared at the surface of the green composites. Additionally, these changes of surface structure would be expected to facilitate the interaction between filler and polymer matrix.
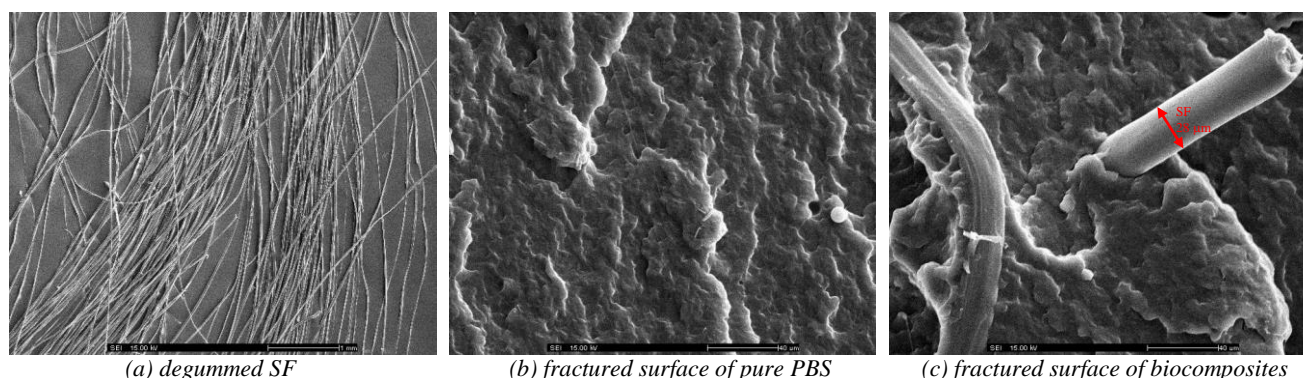

(a) degummed SF   (b) fractured surface of pure PBS   (c) fractured surface of biocomposites
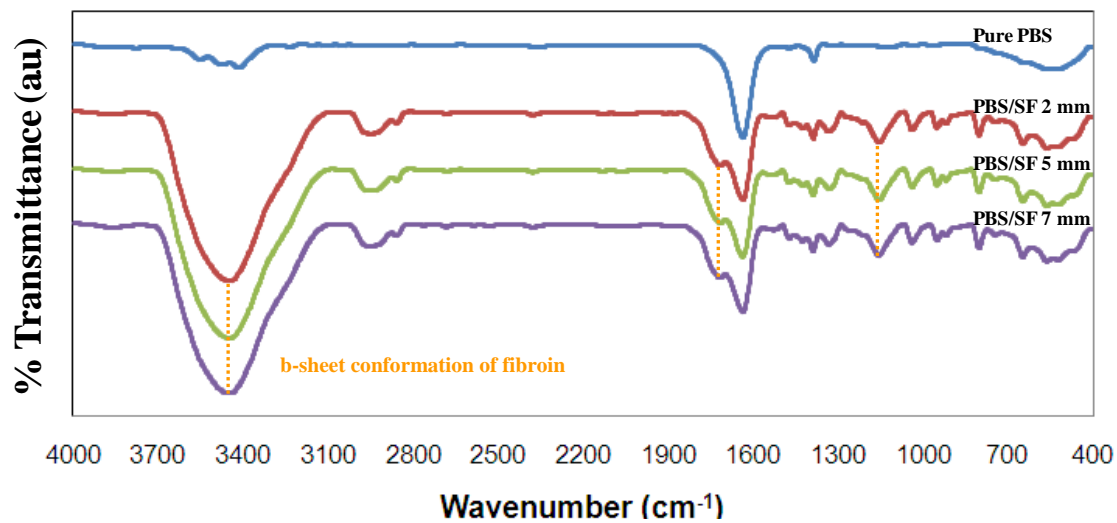
Fig. 1. The SEM images of samples.

Fig. 2. The FT-IR spectra of samples.

3.2 Mechanical properties of green composites

The mechanical properties of pure PBS and green composites were compared by making use of tensile and impact testing methods. Table 1 depicts the tensile strength, tensile modulus and elongation at break for pure PBS and nine different PBS/SF biocomposites with different fibre contents and lengths. The tensile strength and modulus gradually increase with increasing the fibre content and length. It is likely that the increase of the tensile strength at higher loadings of degummed fibres is relatively smaller than that at lower loadings [6]. The increase in tensile strength and modulus of the green composites is due to the reinforcement of degummed fibres in PBS matrix in the direction of external load, because the tensile strength and modulus of fibre are higher than those of neat PBS matrix. Similar results were also reported earlier for fibre reinforced polyester composites [23]. An approximately linear relationship between the tensile modulus and fibre content is obtained over the whole range of fibre loading. The presence of SF in the PBS matrix more effectively enhances the tensile modulus of the PBS compared to the tensile strength [24]. It is known according to composite theory that the tensile modulus of a fibre-reinforced composite depends on the modulus of the fibre and the matrix, the fibre content and orientation [3]. The values of elongation at break obtained at 2.5-7.5% w/w of fibre content and 2-7 mm of fibre length are lower than that of pure PBS sample. This is understandable as the SF has lower % elongation at break [25]. It indicates that the ductile nature of PBS resin reduces with the addition of SF and therefore the percent elongation at break decreases with fibre loading, resulting in the increase of Young's modulus [6]. The high tensile modulus but low elongation at break, compared with PBS, indicates that this material exhibits brittle behavior [26, 27].

Impact strength measures the ability of the material to resist fracture under high rate stress applied at a high speed. Fibres play a key role towards the impact resistance or toughness of a material [28]. The impact strengths of biocomposites are decreased with the increased content of fibres. This is consistent with the tendency of decreased strain, indicating that the rigidness of PBS is improved by the addition of fibres, but leading to the brittleness [29]. A similar trend was observed in the impact strength of natural filler/biodegradable polymer composites. It is reported that the incorporation of animal fibres, a toughness material, decreases the impact strength of green composites [30, 31].

Experimentally, it was found that the fibre content and length of SF are key parameters that substantially influence the tensile strength, tensile modulus, elongation at break and impact strength of the biocomposite samples.

Table 1. Mechanical properties of pure PBS and PBS/SF green composites from tensile and impact testing.

3	Fibre content (w/w)	Fibre length (mm)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Impact strength (kJ/m^2)
PBS100	0.0	-	29.8 ± 0.6	240 ± 13	101.2 ± 4.3	6.5 ± 0.6
PBS97.5/SF2.5L2	2.5	2	32.2 ± 0.5	233 ± 10	36.4 ± 2.1	5.3 ± 0.8
PBS95.0/SF5.0L2	5.0	2	33.4 ± 0.3	305 ± 21	30.8 ± 0.4	5.6 ± 0.6
PBS92.5/SF7.5L2	7.5	2	35.9 ± 0.5	356 ± 19	28.4 ± 0.4	6.6 ± 0.8
PBS97.5/SF2.5L5	2.5	5	32.3 ± 0.6	248 ± 10	33.1 ± 2.5	5.2 ± 0.4
PBS95.0/SF5.0L5	5.0	5	33.7 ± 0.3	315 ± 14	29.8 ± 0.6	5.4 ± 0.6
PBS92.5/SF7.5L5	7.5	5	36.4 ± 0.4	364 ± 10	27.7 ± 1.2	6.4 ± 0.8
PBS97.5/SF2.5L7	2.5	7	32.9 ± 0.6	293 ± 8	31.2 ± 0.6	4.8 ± 0.3
PBS95.0/SF5.0L7	5.0	7	34.8 ± 0.3	338 ± 12	25.6 ± 0.8	5.3 ± 0.8
PBS97.5/SF7.5L7	7.5	7	36.7 ± 0.5	396 ± 13	24.8 ± 0.5	6.0 ± 0.2

Table 2. Thermal properties of pure PBS and PBS/SF green composites from DSC and TGA experiments.

Type of sample	T_{cc} (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)	T_{onset} (°C)	T_{peak} (°C)	wt_R (%)
PBS100	78	111	67.6	33.8	370	397	0.75
PBS97.5/SF2.5L2	73	91	73.9	37.9	368	394	1.03
PBS95.0/SF5.0L2	75	95	75.9	40.0	363	386	3.12
PBS92.5/SF7.5L2	77	95	105.8	57.2	360	382	4.49
PBS97.5/SF2.5L5	74	95	110.8	56.8	369	395	1.55
PBS95.0/SF5.0L5	74	94	79.4	41.8	367	393	4.15
PBS92.5/SF7.5L5	75	95	85.9	46.4	365	383	4.62
PBS97.5/SF2.5L7	73	97	91.1	46.7	365	395	2.01
PBS95.0/SF5.0L7	75	94	78.3	41.2	364	393	3.85
PBS97.5/SF7.5L7	76	94	94.3	51.0	363	392	4.52

3.3 Thermal properties of green composites

The thermal properties of pure PBS and PBS/SF green composites such as cold crystallization temperature (T_{cc}), melting temperature (T_m), melting enthalpy (ΔH_m) and degree of crystallinity (X_c) obtained from the DSC studies are summarized in Table 2. For the case of biocomposite, the width of crystallization peaks becomes a little narrower, indicative of an increase in crystallization rate. The effect is not significant as observed from the small changes of the crystallization properties when compared to pure PBS [26]. For all samples, T_m decreased with increasing fibre content and length. This may be due to in the composites, SF will expand PBS, hence causing slack polymer structure and reduced T_m [32]. The values of ΔH_m and X_c increased in the presence of degummed fibres. These results suggest that SF plays the role of a nucleating agent for PBS leading to the formation of increased transcrystallinity [33]. This could be because impurities were removed from the fibres after treatment, which is in agreement with findings in the literature [34].

TGA is a useful method for the quantitative determination of the degradation behaviour and the composition of the fibre and the polymer matrix in a composite. The magnitude and location of peaks found in the derivative thermogravimetric (DTG) curve also provide information on the component and the mutual effect of the composite components on the temperature scale [6, 35]. The thermal degradation of pure PBS and green composites was investigated in terms of onset degradation temperature (T_{onset}), peak degradation temperature (T_{peak}) and weight percentage of the residue (wt_R) at 800 °C by thermal testing in pure nitrogen environment (Table 2). The pure PBS possesses a single stage in the thermal degradation at around 370-397 °C. It is found that pure PBS showed the highest thermal stability, based upon high initial temperature of degradation. PBS/SF biocomposites have lower T_{onset} and T_{peak} compared with biopolymer. The observation also showed that polymer matrix and fibre formed little char at high temperature, which is consistent to previous research [36]. This can be interpreted as the composites exhibited higher thermal stability compared with pure PBS because of the high thermal stability of fibre [20]. Additionally, the treatment of fibre with NaOH promoted an increase in thermal stability [15].

4. Conclusions

The potential use of natural fibre composites is discussed in this paper. SF-reinforced biodegradable PBS composites have been successfully fabricated with various fiber loadings and lengths, and their mechanical and thermal properties have been investigated. The degummed fibres play an important role as reinforcement and improve the mechanical and thermal properties of the PBS in this system. The tensile strength, tensile modulus and impact strength of the PBS matrix resin are improved significantly by increasing the fibre loading in the composites. The thermal stability and crystallinity of PBS/SF green composites increased with increasing fibre content and length. The results suggest that the PBS/SF biocomposites may be a potential candidate of PET or PET composites to manufacturing some daily commodities to solve the "white pollution" in environmental management.

Acknowledgements

Conflict of interest

The authors declare that there is no conflict of interest.

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