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Mechanical and thermal properties of silk fiber reinforced poly(lactic acid) biocomposites

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The purpose of these studies is to add value to the animal fibers and consequently to improve the properties of poly(lactic acid) (PLA)/silk fiber (SF) green composites for the potential use in environmental engineering applications such as food packaging and medicines. PLA/SF biocomposites were prepared by internal melt mixer and compression molding machine. Surface treatment of fiber was investigated in order to improve interfacial adhesion of SF reinforced PLA composites. Fiber was treated with sodium hydroxide (NaOH) 5% w/v for 1 h. The effect of fiber content and length on the mechanical and thermal properties of PLA matrix were studied. Experimentally, it was found that the weight content and fiber length of fillers are key parameters that substantially influence the tensile modulus and impact strength of the composite samples. The surface of the fibers was well bonded with the matrix, as observed by a scanning electron microscope (SEM) image of fractured sample. The thermal stability and crystallinity (Xc) of PLA/SF composites increased with increasing fiber content.

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1. Introduction

Biocomposites made of polymer matrices and natural fiber reinforcements have been actively investigating and applying to food packaging, medicines and automobile industries [1]. Among the biopolymers, poly(lactic acid) (PLA) has been paid more attention academically and commercially [2]. PLA is one of the most promising biodegradable polymers with a good transparency, high mechanical properties, and good biocompatibilities [3]. It has excellent processibility with relatively low melting temperature (T_m), and has thermal and chemical resistance. It is a thermoplastic, aliphatic polyester and bio-renewable polymer that can be prepared by both direct condensation of lactic acid and ring-opening polymerisation of lactide [4].

Within the past few years, there has been a dramatic increase in the use of natural fibers such as leaves from flax, jute, hemp, pineapple and sisal for making a new type of environmentally-friendly composites [5]. Advantages of natural fibers over traditional reinforcing fibers such as glass and carbon fibers are low cost, low density, low pollutant emissions, high toughness, acceptable specific strength, enhanced energy recovery, recyclability, complete biodegradability, unlimited and sustainable availability, and low abrasive wear of processing machinery [6,7]. These advantages make natural fibers a potential replacement for traditional fibers in composite materials, and various researchers investigated the strengthening effects on the natural fillers reinforced polymer composites [8].

Recently, many studies have been conducted on exploitation of natural materials for modern product development and bioengineering applications. Animal-based fiber is a kind of sustainable natural materials for making novel composites [9]. Silks are fibrous proteins with remarkable mechanical properties produced in fiber form by silkworms and spiders. Silk fibroin polymers consist of repetitive protein sequences and provide structural roles in cocoon formation, nest building, traps, web formation, safety lines and egg protection [10]. Silk fiber is a renewable protein biopolymer which is not only valuable in the textile industry, but also for biomedical engineering applications because of its superior mechanical properties and biocompatibility. Moreover, this fiber can be easily functionalized, and its structure and morphology can be modulated to match a wide range of working requirements [11]. Natural composite fibers produced by silkworms and spiders have been used by humans for centuries. Human creativity has produced a variety of composite materials (including fibers, films, gels, foams and particulates) based on silk proteins with a number of exciting applications [12].

The properties of fiber reinforced composites mainly depend upon the nature of fiber, matrix and fiber/matrix adhesion. Therefore, the objectives of this study are to fabricate PLA/SF biocomposites and to investigate the effect of fiber content and length on the mechanical and thermal properties of the green composites.

2. Experimental

2.1 Materials

PLA pellet (3025D injection grade, BP Polymers Marketing Co., Ltd., Thailand) 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®. Dichloromethane was obtained from RCI Labscan Co., Ltd., Thailand. All other chemicals used were analytical grade reagents.

2.2 Biocomposites preparation

The SF was soaked in 5% w/v sodium hydroxide solution for 1 h at ambient temperature (alkaline treatment or degumming), rinsed with distilled water and dried at 80 °C for 24 h in an oven. All samples were prepared by internal melt mixer and compression molding machine. The weight content of fibers varied from 0 to 6% w/w. SF and PLA pellets were fed into a Brabender Mixer Docking Station (W50EHT), and a uniform temperature of 170 °C was maintained inside the machine. The screw speed and the mixing duration were set to be 40 rpm and 13 min, respectively. The biocomposites were then compression molded (Scientific, Labtech) to make the mechanical testing specimens at 180 °C and 100 bar for 10 min.

2.3 Characterization

The effect of fiber content (1, 2, 3, 4, 5 and 6% w/w) and fiber length (1, 3, 5 and 7 mm) on the PLA matrix was studied and the properties of the resulting biocomposites were compared with neat PLA polymer (control). The types of characterizations carried out are discussed below.

2.3.1. Fourier transform infrared spectrometer (FT-IR)

Characterization of functional groups of degummed SF, neat PLA and biocomposites was obtained by FT-IR with 4,000-400 cm^{-1} wavenumber. Infrared spectrogram was recorded with a Nicolet Impact 410 FTIR using potassium bromide (KBr) pellets.

2.3.2. Scanning electron microscopy (SEM)

The morphology of degummed fiber was conducted using a SEM. Fractured surfaces of the biocomposites were studied with a Hitachi S-4800. The sample surfaces were sputter coated with platinum to avoid charging and make them conductive prior to SEM observation.

2.3.3. Mechanical testing

Tensile tests were performed in a Universal Testing Machine (Instron 5969) at a crosshead speed of 10 mm/min and load cell 50 kN. Samples for tensile tests conformed to ASTM D638 dumb-bell geometry. The impact test was run using Pendulum Impact Tester Zwick I (USA). The dimension of specimens followed ASTM D256 (unnotched Izod test).

2.3.4. Thermal testing

Differential scanning calorimetry (DSC) equipment Perkin Elmer Model: Pyris 1 (USA) was used to study the crystallization and melting behaviors of the samples. DSC scanning program was set as follows: firstly, the sample was heated from 50 to 200 °C at the heating rate of 10 °C/min and maintained at 200 °C for 5 min to erase the thermal history; secondly, the sample was cooled down to 50 °C at the cooling rate of 10 °C/min. For the annealed specimens, the sample was directly heated from 50 to 200 °C at the heating rate of 10 °C/min. Thermogravimetric analysis (TGA) equipment Perkin Elmer Model: TGA 7 HT (USA) was employed to examine the thermal stability of the samples. The weight of each sample was about 7 mg. Experiments were carried out from 50 to 600 °C with a heating rate of 10 °C/min in a nitrogen (N_2) atmosphere.

3. Results and discussion

3.1 Characterization of fiber and biocomposites

The FT-IR spectra of SF and PLA/SF biocomposites are shown in Fig. 1. Neat PLA showed typical peaks at 2950, 1750, 1456, 1381 and 1188 cm^{-1}. When SF was introduced into PLA matrix, new peaks appeared at 3273, 1634, and 1264 cm^{-1}, which were assigned to the b-sheet conformation of fibroin [13]. The results indicate that SF appeared at the surface of the biocomposites. Additionally, these changes of surface structure would be expected to facilitate the interaction between filler and matrix.

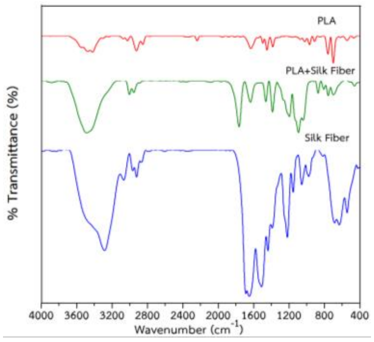

Fig. 1. The FT-IR spectra of samples.

Chemical treatments of fiber 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-fiber biocomposites [14]. Fig. 2(a) present SEM micrograph of treated fiber. After the treatment with sodium hydroxide solution, organic components on fiber surfaces were removed, which resulted in an increase in the adhesion between fillers and matrix [15]. The SEM fractographs on the fractured surface of the neat PLA and PLA/SF biocomposites are shown in Figs. 2(b) and 2(c), respectively. It illustrates that the topology of the neat PLA is relatively smooth and no voids are observed. Moisture absorption during the manufacturing process did not occur in the sample [16]. The results clearly showed a rougher surface for a biocomposite sample, compared to PLA sample. In addition, it was observed that the fiber breakage occurred at the fractured surface, which indicated a good interfacial adhesion between the degummed fiber and PLA matrix [17]. The good interfacial interaction of this sample was found to enhance the mechanical properties of composite, which would be discussed in the mechanical test results.

3.2 Mechanical properties of biocomposites

The mechanical properties of neat PLA and biocomposite samples were compared by making use of traditional tensile and impact property test. Table 1 shows the effect of weight content and fiber length of fillers on the mechanical properties of biocomposites. It is observed that the tensile strength of the composites decreased with 1-6% w/w fiber incorporation. Tensile strength of composites also decreased with increasing filler (agro, animal or natural fiber) content in biodegradable polymers [18]. The results were attributed to the slightly weak interfacial adhesion between the hydrophilic filler and the hydrophobic polymer matrix. In other words, the strength of fibers is insufficient to reinforce the composites [19]. Moreover, as all silk fibers were randomly oriented inside the biocomposites, the failure of the biocomposites might be initiated by the failure of the matrix and then followed by fiber breakage. Unlike uni-directional fibre-reinforced composites, all stress along the fiber direction would be directly transferred from the matrix to the fibers during loading condition [16]. The Young’s modulus of every biocomposite sample in our experiments is higher than that of neat PLA sample. A maximum value of 1,205 MPa (increment of 37.6%) is reached for the composite sample with 3 mm degummed fiber content of 4% w/w. The values of elongation at break obtained at 1-6% w/w of fiber content and 1-7 mm of fiber length are lower than that of neat PLA sample. The high tensile modulus but low elongation at break, compared with PLA, indicates that this material exhibits brittle behavior [20,21].

Impact strength measures the ability of the material to resist fracture under high rate stress applied at a high speed. Fibers play a key role towards the impact resistance or toughness of a material [19]. In this research, impact strength of biocomposites increased drastically with filler incorporation (Table 1). A similar trend was observed in the impact strength of natural filler/biodegradable polymer composites. It is reported that the incorporation of agro fibers, a toughness material, increases the impact strength of composites [7,18,22]. Experimentally, it was found that the fiber content and length of SF are key parameters that substantially influence the Young’s modulus and impact strength of the biocomposite samples.

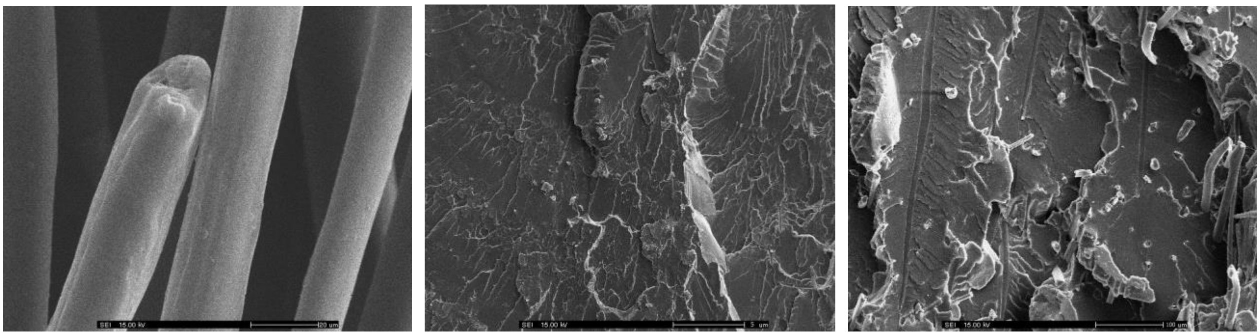
(a) surface of degummed fiber (b) fractured surface of neat polymer (c) fractured surface of biocomposites

Fig. 2. The SEM images of samples.

Table 1. Mechanical properties of neat polymer and biocomposites from tensile and impact testing.

Type of sample	Tensile strength (MPa)	Young’s modulus (MPa)	Elongation at break (%)	Impact strength (kJ/m^2)
Neat PLA	55.7 ± 1.2	876 ± 99	7.35 ± 0.70	15.8 ± 0.7
PLA / 1% SF (3 mm)	47.3 ± 1.6	1,117 ± 44	6.63 ± 0.85	13.2 ± 1.6
PLA / 2% SF (3 mm)	50.1 ± 3.4	1,131 ± 67	6.44 ± 0.63	14.5 ± 0.6
PLA / 3% SF (3 mm)	48.7 ± 1.6	1,118 ± 55	6.42 ± 0.38	17.1 ± 1.1
PLA / 4% SF (3 mm)	47.7 ± 1.3	1,205 ± 63	6.31 ± 0.77	17.8 ± 1.3
PLA / 5% SF (3 mm)	52.7 ± 1.3	1,053 ± 64	6.22 ± 0.40	21.4 ± 3.2
PLA / 6% SF (3 mm)	51.7 ± 0.9	998 ± 26	6.40 ± 0.24	15.8 ± 1.0
PLA / 5% SF (1 mm)	52.0 ± 2.0	991 ± 75	6.72 ± 0.34	19.7 ± 1.6
PLA / 5% SF (5 mm)	53.5 ± 1.0	1,033 ± 45	6.83 ± 0.50	16.4 ± 0.9
PLA / 5% SF (7 mm)	55.1 ± 1.6	1,027 ± 56	6.96 ± 0.58	16.0 ± 2.3

3.3 Thermal properties of biocomposites

The effect of degummed fiber on the crystallization and melting behavior of biocomposites was studied in DSC experiments. It can be seen that the glass transition temperature (T_g) of neat PLA is about 60 °C. The addition of SF in PLA matrix slightly increases the T_g value such as PLA/5% SF 5 mm (61.5 °C), which indicates good interaction between the polymer matrix and fiber [23]. This result reveals that the fiber may restrict the mobility of the polymer chain and lead to a higher transition temperature [24]. From Table 2, it also can be seen that the melting temperature (T_m) of neat PLA is about 150 °C, and PLA shows double melting peaks. It can be due to the fact that the less perfect crystals have enough time to melt and reorganize into crystals with higher structural perfection, and melt again at higher temperature [2]. SF had no effect on the melting behavior of the polymer. In our current study, it is apparent that the degree of crystallinity (X_c) of PLA in composites increased with increased fiber content which could be due to the increased availability of nucleation sites leading to the formation of increased transcrystallinity [25]. This could be because impurities were removed from the fibers after treatment, which is in agreement with findings in the literature [7,26]. Furthermore, X_c increased due to the nucleating effect of the filler, and it decreased due to the restrictions placed on the polymer chain by the filler when the polymer attempts to rearrange to achieve crystallization [27]. This phenomenon may be due to the occurrence of filler agglomeration at a fiber length of 7 mm.

TGA is an effective approach for evaluating the thermal stability of polymeric materials. The thermal degradation of neat PLA and biocomposites was investigated in terms of onset degradation temperature (T_{onset}), peak degradation temperature (T_{peak}) and weight percentage of the residue (wt_R) at 600 °C by thermal testing in pure nitrogen environment. The neat PLA possesses a single stage in the thermal degradation at around 315-332 °C. It is found that pure PLA showed the highest thermal stability, based upon high initial temperature of degradation. PLA/SF biocomposites have lower T_{onset} and T_{peak} compared with biopolymer. The observation also showed that polymer matrix and fiber formed little char at high temperature, which is consistent to previous research [21,28]. This can be interpreted as the composites exhibited higher thermal stability compared with neat PLA because of the high thermal stability of fiber [17]. Additionally, the treatment of fiber with NaOH promoted an increase in thermal stability [14].

The fiber reinforced polymers (FRPs) have been reported [2,5,11,13,16]. It is found that the thermal and mechanical properties of biopolymers like PLA and poly(butylenes succinate) (PBS) could be significantly modified by the presence of SF. These results suggest that SF could be considered as a promising reinforcement for biocomposites [2]. Although animal-based fibers are attracted much attention to various industries and researchers in the past few years, more research on the further applications of these fibers in solving environmental problems is still needed [5].

Table 2. Thermal properties of neat polymer and biocomposites from DSC and TGA experiments.

Type of sample	T_g (°C)	T_{cc} (°C)	T_{m1} (°C)	T_{m2} (°C)	X_c (%)	T_{onset} (°C)	T_{peak} (°C)	wt_R (%)
Neat PLA	60.3	116.0	149.1	154.8	12.8	315.6	332.3	0.57
PLA / 1% SF (3 mm)	59.8	115.8	148.9	155.3	16.8	305.4	324.5	0.88
PLA / 2% SF (3 mm)	60.4	115.9	149.2	155.4	18.0	304.4	323.6	1.13
PLA / 3% SF (3 mm)	60.8	115.1	148.9	155.6	18.5	303.7	322.6	1.17
PLA / 4% SF (3 mm)	60.6	114.8	148.8	155.6	20.4	303.2	321.7	2.08
PLA / 5% SF (3 mm)	60.5	114.8	148.3	155.2	20.9	302.0	321.0	2.35
PLA / 6% SF (3 mm)	60.3	116.8	149.5	155.8	22.4	301.6	320.3	3.20
PLA / 5% SF (1 mm)	60.4	114.7	148.7	155.5	14.0	302.0	321.4	2.22
PLA / 5% SF (5 mm)	61.5	117.8	150.0	155.7	21.1	301.9	320.7	2.34
PLA / 5% SF (7 mm)	60.6	117.2	149.8	156.0	17.6	302.1	320.8	2.40

4. Conclusions

The potential use of animal fiber composites is discussed in this paper. Effects of fiber content and length on the interfacial, mechanical and thermal properties of PLA matrix were studied. The enhanced adhesion between the degummed fiber and polymer matrix resulted in a PLA/SF biocomposite with the excellent portfolio of mechanical and thermal properties, much better than those of the neat PLA counterpart. The mechanical properties in terms of the Young’s modulus and impact strength of these composites increased substantially compared to the biopolymer. The thermal stability and crystallinity of PLA/SF composites increased with increasing fiber content. These studies were aimed at adding value to the animal fibers. The PLA/SF green composites can be considered for food packaging and medicines.

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References

[1] S. O. Han, H. J. Ahn, D. Cho, Composites Part B: Engineering **41**, 491 (2010).

[2] Y. Q. Zhao, H. Y. Cheung, K. T. Lau, C. L. Xu, D. D. Zhao, H. L. Li, Polymer Degradation and Stability **95**, 1978 (2010).

[3] P. Laonuad, N. Chaiyut, B. Ksapabutr, Optoelectron. Adv. Mater. – Rapid Comm. **4**, 1200 (2010).

[4] K. Boua-in, N. Chaiyut, B. Ksapabutr, Optoelectron Adv. Mater. – Rapid Comm. **4**, 1404 (2010).

[5] H. Cheung, M. Ho, K. Lau, F. Cardona, D. Hui, Composites Part B: Engineering **40**, 655 (2009).

[6] S. M. Lee, D. Cho, W. H. Park, S. G. Lee, S. O. Han, L. T. Drzal, Composites Science and Technology **65**, 647 (2005).

[7] A. Buasri, N. Chaiyut, V. Loryuenyong, K. Yernpeng, P. Suksamran, S. Boonnin, Journal of Biobased Materials and Bioenergy **6**, 617 (2012).

[8] Y. F. Shih, C. C. Huang, P. W. Chen, Materials Science and Engineering A **527**, 1516 (2010).

[9] M. Ho, H. Wang, K. La, Applied Surface Science **258**, 3948 (2012).

[10] C. Vepari, D. L. Kaplan, Progress in Polymer Science **32**, 991 (2007).

[11] M. Ho, H. Wang, K. Lau, J. Lee, D. Hui, Composites Part B: Engineering **43**, 2801 (2012).

[12] J. G. Hardy, T. R. Scheibel, Progress in Polymer Science **35**, 1093 (2010).

[13] Q. Lv, K. Hu, Q. Feng, F. Cui, C. Cao, Composites Science and Technology **67**, 3023 (2007).

[14] A. I. S. Brígida, V. M. A. Calado, L. R. B. Gonçalves, M. A. Z. Coelho, Carbohydrate Polymers **79**, 832 (2010).

[15] Y. Li, K. L. Pickering, R. L. Farrell, Industrial Crops and Products **29**, 420 (2009).

[16] H. Cheung, K. Lau, X. Tao, D. Hui, Composites Part B: Engineering **39**, 1026 (2008).

[17] Y. Zhao, J. Qiu, H. Feng, M. Zhang, L. Lei, X. Wu, Chemical Engineering Journal **173**, 659 (2011).

[18] C. Nyambo, A. K. Mohanty, M. Misra, Biomacromolecules **11**, 1654 (2010).

[19] S. Sahoo, M. Misra, A. K. Mohanty, Composites Part A: Applied Science and Manufacturing **42**, 1710 (2011).

[20] S. Cheng, K. T. Lau, T. Liu, Y. Zhao, P. M. Lam, Y. Yin, Composites Part B: Engineering **40**, 650 (2009).

[21] A. Buasri, N. Chaiyut, T. Petsungwan, Y. Boonyuen, S. Moonmanee, Advanced Materials Research **463-464**, 449 (2012).

[22] H. S. Kim, H. S. Yang, H. J. Kim, Journal of Applied Polymer Science **97**, 1513 (2005).

[23] K. Weihua, Y. He, N. Asakawa, Y. Inoue, Journal of Applied Polymer Science **94**, 2466 (2004).

[24] Y. F. Shih, C. C. Huang, Journal of Polymer Research **18**, 2335 (2011).

[25] A. P. Mathew, K. Oksman, M. Sain, Journal of Applied Polymer Science **101**, 300 (2006).

[26] K. L. Pickering, M. A. Sawpan, J. Jayaraman, A. Fernyhough, Composites Part A: Applied Science and Manufacturing **42**, 1148 (2011).

[27] K. S. Chun, S. Husseinsyah, H. Osman, Journal of Polymer Research **19**, 9859 (2012).

[28] B. Li, J. He, Polymer Degradation and Stability **83**, 241 (2004).

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