Mechanical Properties of an Injected Silk Fibre Reinforced PLA Composite

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Abstract

Chopped silkworm silk fibres and Poly-lactic acid (PLA) were mixed to form a fully biodegradable thermoplastic composite. Injection moulding process was used to mix these constituents together at a controlled temperature range. The mechanical properties of the composite were examined through tensile and flexural property and Izod impact tests. It was found that the Young's and flexural moduli of the composite increased while their strengths and impact resistance decreased during the tests as compared with a PLA sample. Early fibre fractures observed from micrographs explain the reasons of enhanced moduli and reduction of strengths.

Introduction

Excessive use of petroleum-based plastics that generate a huge amount of solid waste disposals would cause a serious depletion of landfill capacities. Therefore, biodegradable materials have continued attracting popular attention worldwide. Within the period of 2005 and 2009, the global market for the demand of biodegradable polymers was doubled in size [1]. Environmentally friendly composites are especially and keenly required by utilizing natural fibres as reinforcement combined with biodegradable polymers as matrices. Concerning the environmental issue, natural fibres are biodegradable which can reduce the amount of solid waste disposals so that the landfill capacities can be enlarged. Natural fibres are an abundantly-renewable resource so as the cost is comparatively low. According to their inherent properties, natural fibres are flexible on processing, cause less resulting wear of the processing machinery and have minimal health hazards during the manufacturing process. Moreover, natural fibres have a desirable fibre aspect ratio, low density and relatively high tensile and flexural modulus [2]. Silkworm silk fibre has been used commercially in the biomedical applications for centuries. It is an inhomogeneous material formed by silk protein and other associated molecules such as glycoproteins and lipids. The silkworm silk fibre is composed of two cores of triangular fibroin because of their gland is a paired organ which surrounded by a cementing layer of sericin in a structure known as bave. The core fibres are encased in a sericin coat, a family of glue-like proteins that hold two fibroin fibres together to form the composite fibres of the cocoon case and ensure the structural integrity of the cocoon. The fibroin fibre itself is a bundle of several fibrils with a diameter of 1µm. A fibril contains 15nm wide microfibrils. Microfibrils are packed together to form the fibril bundle and several fibril bundles produce a single strand [3-6]. In this study, silkworm silk fibre reinforced PLA composite was made, and its mechanical properties were investigated.

Experiments

In this study, tussah silk was utilized for the fabrication of silkworm silk fibre reinforced composite. Degumming of binds of long and continuous silk fibres that were supplied by Ocean Verve Limited had been conducted when they were received, to remove their surface layer (commonly called “sericin coating”). This layer is mainly made by protein. With the existence of this layer for composite materials, it would weaken the bonding between the fibres and surrounding matrix, and thus, affect their overall mechanical and thermal properties. The diameter of the supplied fibres was around 100 µm. In general, the composite should be made at high fibre volume fraction in order to maximize their mechanical performance. However, this factor is constrained by the injection moulding process.

Based on our previous trials, an optimal fibre content, in terms of the mouldability for making composites by using injection moulding method was 5 wt%. The injector is comprised of two screws which are used to mix short silk fibres with molten PLA together in a uniformly-distributed matter before being injected into the cavity of a mould. Care must be taken using long fibres as they may be coiled inside a barrel and stressed plastically. 5 mm long fibre in average has been found to be the most appropriated for the injection moulding with PLA at specified processing temperature.

PLA used in this study was a neat grade commercialized by Cargill-Dow under the brand name of NatureWorks®PLA Polymer. PLA is a highly versatile, biodegradable, aliphatic polyester derived from 100% renewable resources, such as corn and sugar beets. Tensile property and three-point bending (commonly called "flexural strength") tests were carried out for the composite by using the MTS Alliance RT-50 (50kN) testing machine (MTS Systems Corporation, USA). The geometry of specimens was 90 mm x 10 mm for the tensile property and three-point flexural tests. Grip separation was set to be 48mm in length and the crosshead speed was adjusted to 1.5 mm/min for the tensile property test. During the flexural strength test, samples were tested according to the ASTM D790 standard. The default radii of the loading nose and support span were 5.0 and 30 mm apart, respectively. The crosshead speed of the flexural strength test was 0.946 mm/min. An Izod impact test was also carried out for cantilever composite beams followed the standard 256. The bulk densities of the pure PLA and composite were determined according to ASTM D 792-91.

Results and Discussion

According to the results obtained from the experiments, the Young's modulus of silk fibre/PLA samples increased by 27% from 3.21 to 4.08 GPa as compared with a pristine PLA sample. The ultimate tensile strength and strain at break decreased by 0.2% and 30 % (from 5.5 down to 3.8%), respectively. Fig. 1 shows two stress-strain curves obtained from the tensile property test, one is for the pure PLA sample while another is for the composite sample. Besides, the flexural modulus of the composite sample increased by 2.0% from 3.98 to 4.06 GPa while the strength decreased by 11% from 109.4 to 97.41 MPa as compared with the result for the PLA sample. The mean Izod impact resistance of the composite also decreased by 29.1% due to the incorporation of silkworm silk fibres in the PLA matrix.

Increment in modulus was governed by the strength of the fibre at the low strain condition due to a good bonding between the fibre and matrix. During the tensile loading process, matrix supposedly takes load a bit earlier than that of the fibre at the very beginning stage. Continuously increasing the load may cause fibre and matrix to share the load and fibres take more load subsequently through the stress transfer by surface friction of the fibres. The Young's modulus is determined in between 0.05 and 0.25 % of strain. The modulus is determined at low strain levels where the fibre-matrix interfaces are under very low shear force and thus the modulus of composite is shown as higher than that of a pure PLA.

The reduction of the percentage of strain at break of silk fibre /PLA composite was due to the low percentage of strain at break of the fibres (brittle nature) as compared with the matrix [10]. Craven et al. [7] have pointed out that the elongation of the fibre to failure is normally below 20%, which is lower than that of the pure PLA. In such case, at the certain level of load applied at that time the strain increased into the non-elastic region, the fibre breakage happened earlier than the failure of surrounding matrix, and thus caused the decrement in the effective cross sectional area. It resulted in reducing the strain at break of the composite. Apart from the relatively low ductility of the silk fibre as compared to that of PLA, it can be used to explain the reason why many natural fibre reinforced composites provide very good modulus enhancement while their strength is relatively lower as compared with their host matrix material.

The SEM used in this report was the model JEOL JSM-6490 SEM to test the fracture surface of pure PLA and silk fibre/PLA composite. Apart from the relatively low ductility of the silk fibre as compared with PLA, Fig. 2 shows the fracture of the fibre after elongation. The surface of the fibre was totally damaged based on the tear patterns aligned perpendicular to the fibre's direction. As silk fibre is comprised of a lot of small filaments, few separations of these filaments during extrusion process were also found, and it can be seen in Fig.3. In the figure, it shows that all these filaments were randomly oriented inside the samples. In Fig 4, good distribution of the fibre in the composites is also shown and compared with pure PLA image on Fig.5. The density of the composite decreased by 0.78% as compared with the PLA. Thus, it allows the preparation of polymer composites with good specific properties.

The alignment of fibres along the loading direction allows good stress transfer properties when the composite is under a tensile load. However, less study has been focused on studying the alignment of fibres in injected natural fibre composites. A dumbbell shaped silk/PLA composite sample was made by injection moulding, it is expected that all fibres should be aligned along the direction of injection, unless the cavity of the mould is very large to allow the fibres freely rotate in an unconfined space.

In the present study, the sample was made, its longest axis was perpendicular to the barrel’s direction. Therefore, it was hard to predict the alignment of the fibres. Therefore, the sample was polished perpendicularly to its loading direction, and then examined under a microscope. As the sample is thin, all fibres are well aligned as shown in Figure 6, and it further proves that the load was effectively taken by the fibres.

Biomedical application

The drawbacks of the traditional metallic materials for bone fixation motivate the study for a new material for bio-engineering. These drawbacks include: (1) osteoporosis causes of stress-shielded effect, (2) increase in the risk of refracture by drop in mechanical properties of recovered bone, (3) second surgery in order to avoid corrosion and infection, (4) radiotherapy impediment. Hence, polymer composites as replacement of the traditional metallic materials are becoming popular for bone implant applications. The advantages of these implants are not only limited to the mechanical properties which can be tailor-made to fit to the properties of the human bone. These polymeric implants are also able to combine physiologically active components which accelerate or facilitate tissue healing [8]. Natural fibre has a long standing history of use in clinical applications. Novel mechanical properties of silks are superior to any other natural fibre and rival many high performance fibres. Silk fibre as suture for human wound dressing have been used for centuries. Recently, regenerated silk solutions have been used to form a variety of biomaterials, such as gels, sponges and films, for medical applications. Moreover, silk has been exploited as a scaffold biomaterial for cell culture and tissue engineering in vitro and in vivo [6]. There are various advantages of silk fibre for medical applications. It is relatively simple to process silks in aqueous solutions for subsequent formation of films and other material formats. Silk fibre are insoluble in most of solvents including water, acid and alkaline solution. Moreover, silk fibre is insolubilization via exposure to alcohols and other environmental factors. The mechanical properties can be adjusted by spinning speed. Therefore, specific features, such as molecular weight, crystallinity, solubility can be tailor-made genetically. Tissue healing can also be accelerated or facilitated by combining with other physiologically active components. Last but not least, silk fibre does not subsist risk which increases the bio-burden in the human body [9].

Conclusion

By mixing with 5 wt% of silk fibres, the Young's modulus of PLA was increased by 27%. However, their tensile and flexural strengths were decreased because of the failure of fibre at the strain level below the failure strain of PLA.

One of the major applications for silk fibre reinforced biodegradable composites is for bio-engineering and tissue engineering applications. Since the exploration of biomaterial applications for silks fibre related materials, aside from sutures, is only a relatively recent advance, the future for this material to impact clinical needs appears promising.

In the bone fixation application, the modulus is relatively important as compared with the strength of materials as they would be degraded or resorbed by human body with time. However, their resultant modulus should be close to the modulus of human bone in order to avoid aforementioned problems.

Acknowledgements

This project is supported by The Hong Kong Polytechnic University and The Research Grant Council (G-U688/PolyU 5219/09E) and the Research Grant from the University of Southern Queensland.

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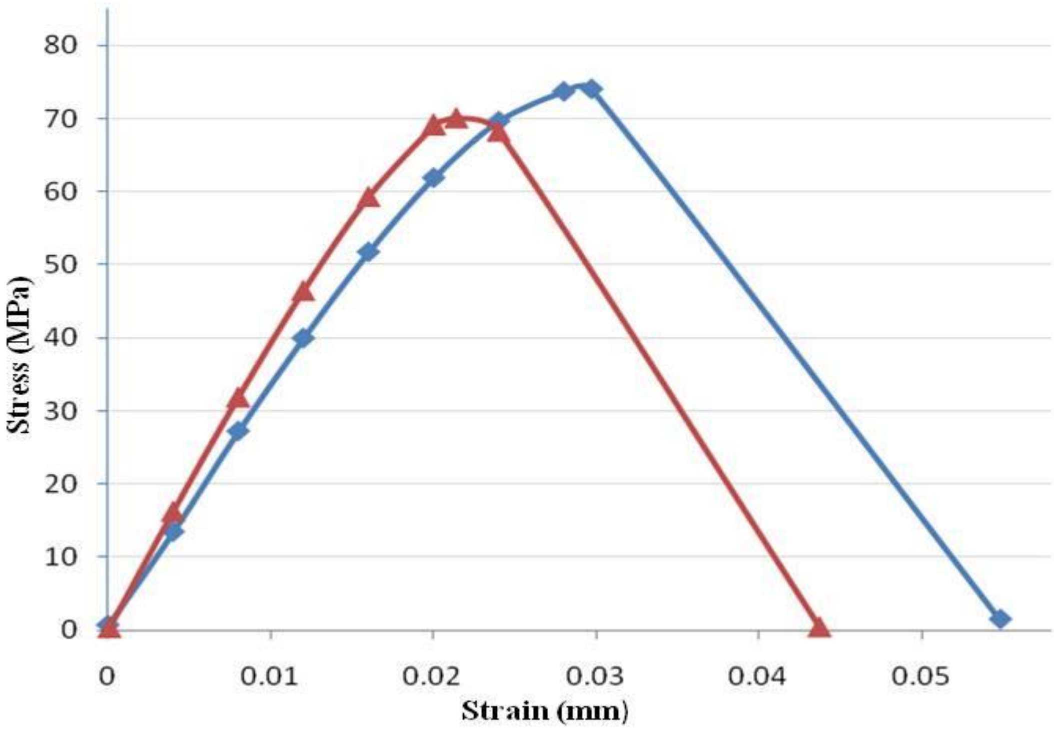

Figure 1. Tensile stress-strain curves of (i) pure PLA – square marker and (ii) silk/PLA composite – triangular marker.

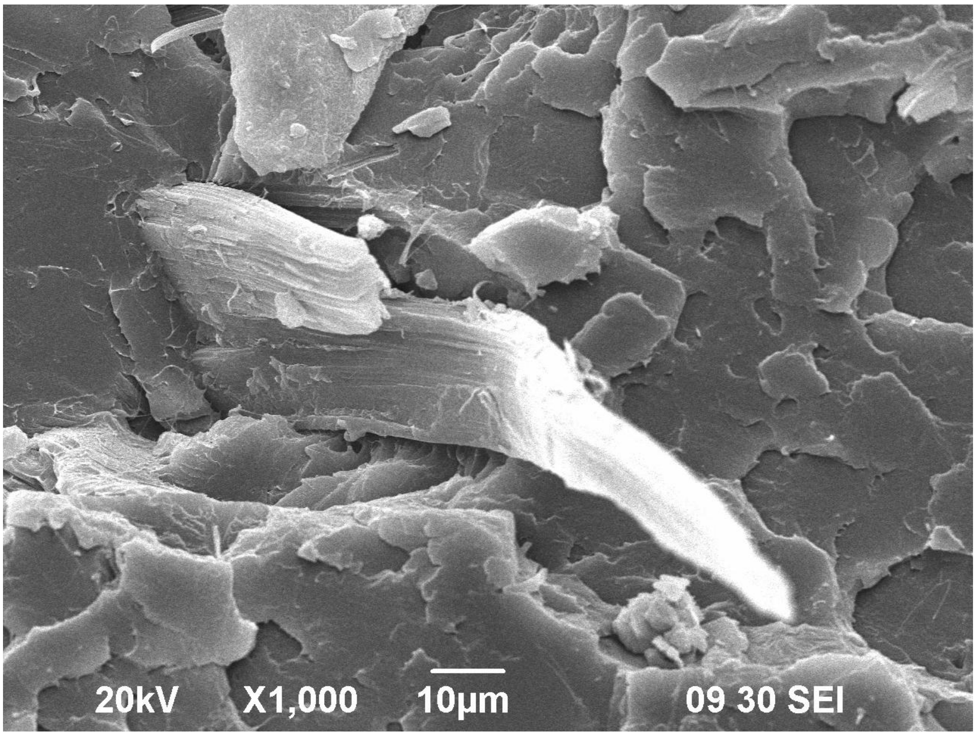

Figure 2. The fracture of the fibre after elongation is shown.

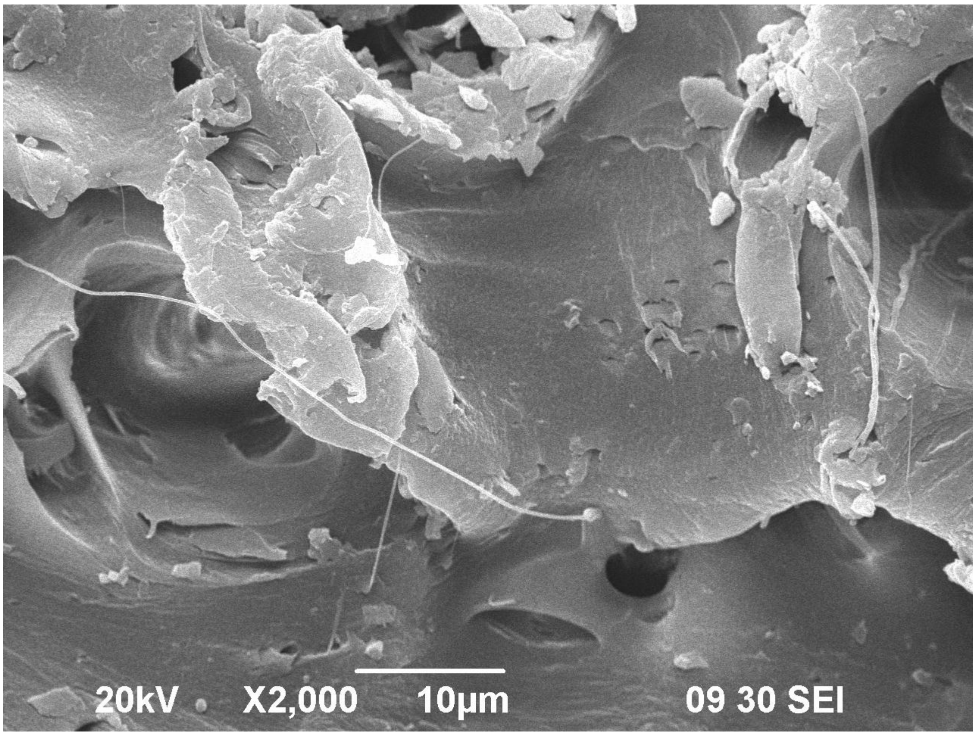

Figure 3. Filaments of the silk fibre are shown.

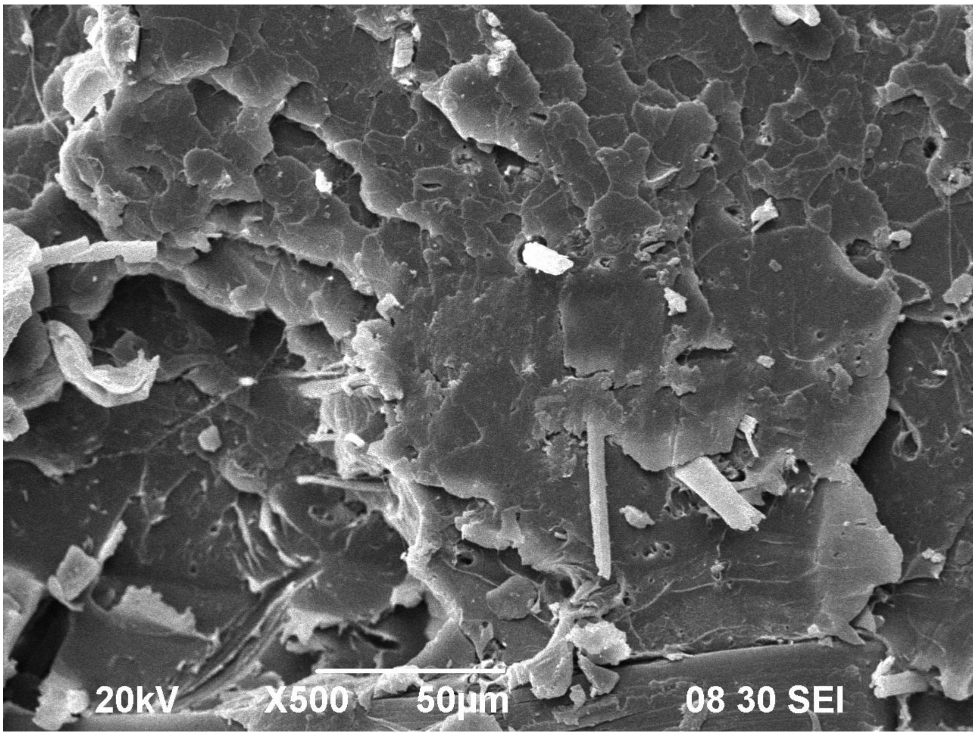

Figure 4. All fibre are uniformly distributed in the silk fibre/PLA sample.

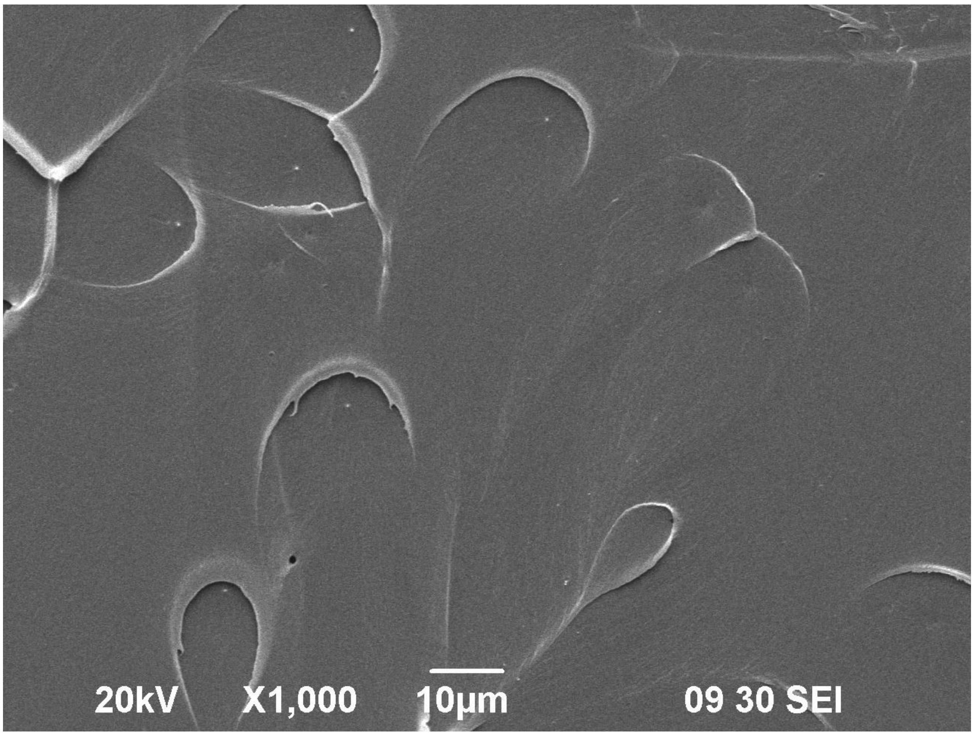

Figure 5. Image of the pure PLA sample.

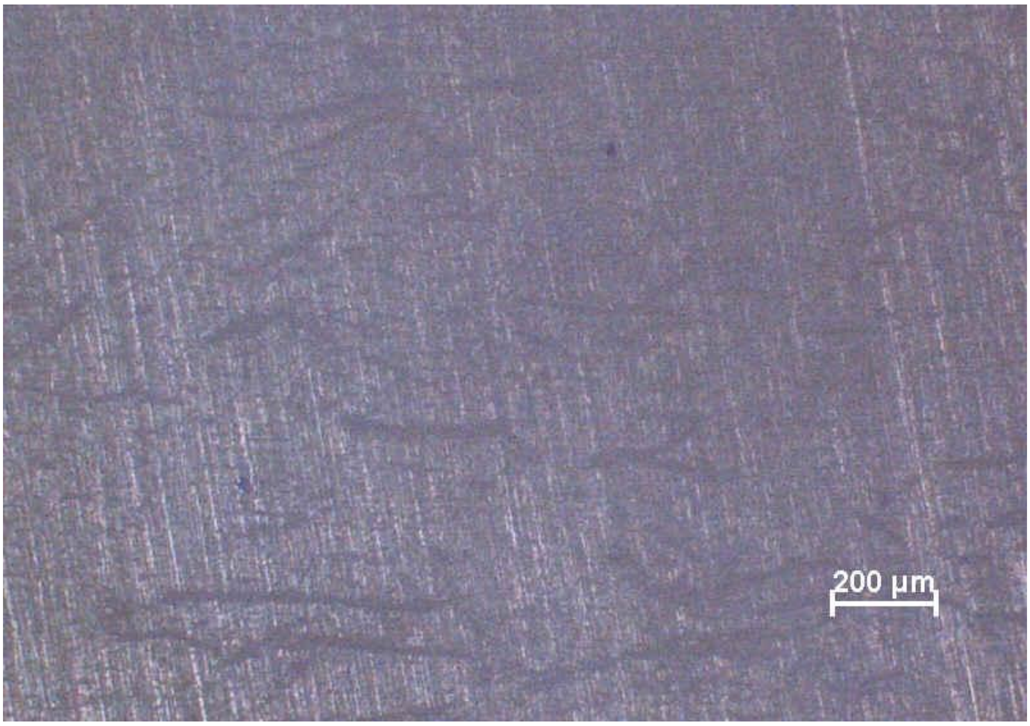

Figure 6. Micro graphs of cut-off view (along the longitudinal direction of the sample) of the silk fibre/PLA composite with 5 vol% silk fibre