Strengthening Mechanism and Bio-degradability of a Silk-based Polymer Composite

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Certification of Dissertation

I certify that the ideas, experimental works, results, analysis and conclusion reported in this dissertation are entirely my own effort, except where otherwise acknowledged. I also certify that the work is original and has not been previously submitted for any award, except where otherwise acknowledged.

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Abstract

Silkworm silk fibre is one kind of well recognized animal fibres for bio-medical engineering and surgical operation applications because of its mechanical, biocompatible and bio-resorbable properties. Recently, the use of natural fibre as reinforcement for bio-polymers to enhance the stiffnesses of scaffolds and bone fixators has been a hot research topic. However, their mechanical and biodegradable properties have not yet been fully understood by many researchers, scientists and bio-medical engineers although these properties would govern the usefulness of resultant products.

Considering the increasing demand and potential use of biodegradable and bioresorbable polymers in coming centuries, elevated environmental awareness of the general public in reducing carbon footprints and non-naturally decomposed solid waste, as well as foreseeable drawbacks of using metallic materials for biomedical engineering, a comprehensive study on the mechanical and materials properties of a silkworm silk fibre reinforced Polylactic acid (PLA) composite is conducted through experimental and theoretical approaches in this project.

Current study aims at investigating various properties of degummed and non-degummed silkworm silk fibres and, the effect on the mechanical and thermal properties and biodegradability of their reinforced PLA composites.

An extensive review is provided to introduce the properties of the natural fibres and degradable polymers. Some critical issues including poor wettability, biodegradability and bonding properties at the fibre/matrix interface and, damage of the fibre during the manufacturing processes which are the main causes of the reduction of the composites‟ strength are addressed. Furthermore, different manufacturing processes and their suitability for natural fibre composites, based on the materials, mechanical and thermal properties of the fibres and matrics are discussed in detail. The potential applications on the degradable fibre reinforced polymer composites are also addressed.

Following the comprehensive review, results obtained from preliminary experimental studies are given. The hybridization of a glass fibre reinforced composite is achieved by using short silkworm silk fibre as a medium to enhance its cross-ply strength. The comparison on the tensile and impact properties of the glass fibre composite reinforced by the short silkworm silk fibre with a neat glass fibre composite sample is conducted. Experimental results indicated that the higher Young‟s modulus and ductility index (DI) of a silkworm silk fibre reinforced glass fibre composite was obtained as compared with the neat sample. Moreover, the visual examination on drop-weight test samples proved that the impact resistance of the silkworm silk fibre reinforced glass fibre composite was better than that of the neat sample as well. Nevertheless, as the non-fully biodegradable issue rose from the ultilization of glass fabrics and resin, the combination of the silkworm silk fibre and a biodegradable polymer- PLA is chosen for the following study.

Mechanical properties of different silkworm silk fibres including Bombyx mori, twisted Bombyx mori, and Tussah silk fibres were investigated. Their ultimate tensile strength, elongation at break, and Young‟s modulus were examined by performing a uniaxial tensile test on a single fibre. The apparent diameters of the silkworm silk fibres were measured for stress-strain analysis. Based on the

experimental results, it was found that Tussah silk fibre has a relatively high extensibility as compared to Bombyx mori silk fibre.

When producing a biodegradable silkworm silk fibre reinforced PLA composite, hydrophilic sericin has been found to cause poor interfacial bonding with most polymers and thus, it results in affecting the resultant properties of the composite. Besides, a sericin layer on fibrils surface may also cause an adverse effect toward biocompatibility and hypersensitivity to silkworm silk fibre for implant applications. Therefore, degumming should be done for sericin removal. Different degumming processes and their influences on silkworm silk fibre are discussed. The effectivenesses of degumming parameters including degumming time and temperature on Tussah silk by using boilibg water are discussed. Based on the results obtained, it was found that the mechanical properties of Tussah silk are affected by the degumming time due to the change of fibre structure and fibrils alignment. It was also found that the degumming time has a little effect on the thermal properties and the secondary structure of the fibre.

Besides, silkworm silk fibre was degummed by different concentrations of $NaHCO_3$ (Sodium Bicarbonate) solution to study its tensile properties. Measurement of weight loss, tensile property test and differential scanning calorimetric (DSC) analysis were conducted to elucidate the effect of $NaHCO_3$ to the fibre. Experimental results revealed that the disruption of hydrogen bonds (water effect) dominated the effect of the fibre at low $NaHCO_3$ concentration. Increasing the concentration of $NaHCO_3$ resulted in increasing the pH level and thus, distorted the binding force between fibrils of the fibre. DSC analysis revealed that the fibre degummed in the solution over 5 wt% $NaHCO_3$ requires higher energy for melt and thermal decomposition from their crystalline states. However, using $NaHCO_3$ would minimize the risk of damage of silkworm silk fibrils as compared with commonly used strong alkali solutions for degumming. A microbond test of the composite was conducted to investigate the bonding effect of the silkworm silk fibre with/ without the sericin layer. The results showed that the fibres degummed by both processes increased the interfacial shear strength.

A novel biodegradable composite for biomedical engineering applications was developed by mixing chopped silkworm silk fibre and PLA through the injection moulding process. A study on the mechanical properties and biodegradability of a silkworm silk fibre reinforced PLA composite was conducted. It was found that the Young‟s and flexural moduli of the composite increased with the use of silkworm silk fibre as reinforcement while their tensile and flexural strengths decreased. This phenomenon is attributed to the disruption of inter- and intra-molecular bonding on the silkworm silk fibre with PLA during the mixing process, and consequent reduction of the strength of the composite.

Bio-degradability tests showed that the silkworm silk fibre altered the biodegradable properties of the composite as compared with a pristine PLA sample. The initial storage modulus of the composite increased while its glass transition temperature decreased as compared with the PLA sample. Besides, the coefficient of linear thermal expansions (CLTE) of the composite was reduced by 28%. This phenomenon was attributed to the fibre-matrix interaction that restricted the mobility of polymer chains to adhere to the fibre surface, and consequently reduced the Tg and CLTE. As compared with the composite, it was found that the degraded composite exhibited lower initial storage modulus, loss modulus and tan delta (Tan(δ)) but the Tg had higher than that of a non-dergraded sample.

A linear, elastic and isotropic theoretical model to evaluate the differential stress between a core fibre and a sericin layer with different thicknesses of the layer is firstly introduced in this report. The influence of moisture absorption during the early degradation stage, on shear stress between the fibre and the sericin is also discussed.

Finally, concluding remarks and the suggestions for the further study in the development of the silkworm silk fibre reinforced PLA composite for fracture bone fixator are addressed.

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II. Publications arising from other research projects

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18. **Ho, M.P.**, Wang, H., Ho, C.K. and Lau, K.T. (2011). A Study on the Dynamic Mechanical Properties of Silk Fibre Composites. The 20th International Symposium on Processing and Fabrication of Advanced Materials (PFAM XX).

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