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Characteristics of a Silk Fibre Reinforced Biodegradable Plastic

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Abstract

Silk fibre is one kind of well recognized animal fibres for bio-medical engineering and surgical operation applications because of its biocompatible and bio-resorbable properties. Recently, the use of silk fibre as reinforcement for some 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. In this paper, a study on the mechanical properties and bio-degradability of silk fibre reinforced Poly (lactic-acid) (PLA) composites is conducted. It has been found that the Young's modulus and flexural modulus of the composites increased with the use of silk fibre reinforcement while their tensile and flexural strengths decreased. This phenomenon is attributed to the disruption of inter- and intra-molecular bonding on the silk fibre with PLA during the mixing process, and consequent reduction of the silk fibre strength. Moreover,

biodegradability tests showed that the hydrophilic properties of the silk may alter the biodegradation properties of the composites compared to that of a pristine PLA sample.

Introduction

Petroleum is a fossil fuel that can only be last for another 50–60 years at the current rate of consumption [2]. Preservation of non-renewable petroleum-based materials especial for petroleum-based plastics is a critical topic because of the increasing environmental consciousness in the society. Excessive use of petroleum-based plastics inducing a huge amount of solid waste disposals would cause a serious depletion of landfill capacities. Besides, the severe government's plastic waste control legislation and the growing interest among the customers in sustainable and environmentally friendly products drive the retailers and manufacturers to trend towards developing more sustainable materials for alleviating the impact of global warming. Therefore, the awareness of soared waste problems and their impact on the environment has awakened a new interest in the area of materials science. To tackle on this problem, different types of fully biodegradable composites are being developed recently, as substitutions for non-biodegradable petroleum-based plastics, and even metallic components.

Recently, 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. In 2009, among all countries in the World, Europe had the largest growth in the market of biodegradable polymers in the range of 5 to 10% as compared with 2008 [1] and this growth has kept continuing. The forecast on the total consumption of biodegradable polymers is to grow at an average annual rate of nearly 13% from 2009 to 2014 in North

America, Europe and Asia, which are accounted as the major global markets for materials' consumption.

Biodegradable composites are generally believed as one of the key materials in coming centuries. They are generally composed of biodegradable fibre (such as nature fibre and synthesized bio-polymer based fibre) and biodegradable polymer matrix, and manufactured by various processes, their properties can be tailor-made to satisfy various product requirements for specific applications. One of the major applications of biodegradable composites is to produce artificial joints and tissues for human body use.

Bioengineering is usually defined as a basic research-oriented activity closely related to biotechnology and genetic engineering which are used for the modification of animal or plant cells, or parts of cells, to (i) restore their function, (ii) repair their damage regions and (iii) develop new microorganisms for beneficial ends [2]. Concerning the implementation of technology in bio-engineering, biomaterials are mainly used in the applications of directing, supplementing, or replacing the functions of living tissues in the human body [3].

The term of "Bio-composite" is a new and advanced bio-material, which is found in use for bone repair and implant application recently as a replacement for traditional metallic materials such as stainless steel and titanium. Although stainless steel and titanium provide sufficient strength and rigidity to align the bone and control motion while healing of bone fracture, they are too stiff as compared with the properties of a natural bone. The Young's modulus of steel typically falls into the range of 150 to 200 GPa while the bone is only 6 to 20 GPa. Therefore, metallic implant plates carry the majority of load which leads to that stress-shielded bone delay bridging. Moreover, the incompletely healed bone is susceptible to refracture after removal of the metallic implant plate. This weaken bone also suffers serious bone loss (osteoporosis) including intracortical porosity, cortical thinning and correspondingly greater loss of mechanical properties. [4-5]

Besides, the need of the second surgery for removing a metallic fixator, corrosion of the fixator inside the human body and bone atrophy associated with rigid metallic fixation devices increase the probably of bone infection [6]. Moreover, the postoperative radiotherapy as well as X-ray for diagnostic imaging on healing bone is interfered by metallic implant plates. It is because the presence of metallic plates changes the local dose distribution and these changes result from backscattering effects which cause overdosage in front of and underdosage behind the plates [7].

To overcome the disadvantages of using traditional metallic bone fixator, silkworm silk fibre reinforced polymer composites, based on their inherent mechanical, biocompatible and bioresorable properties have been found as a desirable versatile bio-material for bone plate fixation. Silk fibers as sutures for human wound dressing have been used for centuries [8]. Recently, regenerated silk solutions have been used to form a variety of biomaterials, such as gels, sponges and films, for medical applications [9]. Moreover, silk has been exploited as a scaffold biomaterial for cell culture and tissue engineering in vitro and in vivo [10]. However, this topic is in need of further study and clarification as no comprehensive study, particularly on the correl0ationship between thermal, mechanical and degradation properties of the silkworm silk fibre reinforced composites have been conducted to date.

Experiment Details

The biodegradable polymer-PLA as a matix under investigation in the current study is a neat grade commercialized by Cargill-Dow under the brand name NatureWorks®PLA Polymer. Silk fibre with the average fibre diameter of 100 µm was supplied by Ocean Verve Ltd., Hong Kong. The inherent body structure of silkworm is composed of two cores of fibroin which exists in a paired of organ. The fibroin fibre itself is a bundle of several fibrils with a diameter of 1µm and one fibril contains 15nm wide microfibrils [11, 12]. As a silk fibre is comprised of many small bundles of filaments, there is no doubt that the wetability of its resultant composites is the key to ensure good bonding/complete chemical bonding between all fibres and matrix is achieved.

Besides, a sericin layer also plays a critical role as it may isolate the physical contact or direct chemical bonding between the fibre and matrix. This layer is mainly made by protein as a coating and adhesive of the silkworm silk fibre. In this study, the coating was pre-removed by the supplier and the fibre received as in a form of reeling. As mentioned in a previous literature [13], this layer would affect the bonding between the fibre and polymer-based matrix, and thus worsen the mechanical properties of silk fibre composites.

For the tensile and flexural strength tests, all samples were made by using Hakke MiniLab twin-screw micro-extruder. Before mixing the fibre with PLA, degummed fibre were chopped into 5 mm in length in order to avoid coiling with the screws and stretching the fibres plastically either co- or counter rotating during injection process. These fibres were pre-placed inside an oven for drying to minimise excessive water/moisture content into them before the process. The optimal fibre content, in terms of mouldability inside the PLA environment was 5 wt% based on our preliminary study. A uniform temperature of 180°C was maintained at all zones inside the machine so as to ensure that PLA was in a processing temperature condition, and also this temperature is below the degradation temperature of the fibre. The screwing speed and the mixing duration were set as 100 rpm and 10 mins, respectively. The first run of the extrusion was discarded and the strands of an extrusion mixture were then directly collected by a pre-heated injection cylinder for further injection moulding. The mixture was then transferred to a Thermo Hakke small scale injection moulding machine. The injection cylinder and the mould were pre-heated to desirable temperatures of 200°C and 45°C, respectively, silk fibre/PLA samples were made in a dumbbell shape according to ASTM D3039 and in regular plates with the size of 90 mm x 10 mm for the tensile property and flexural strength tests, respectively.

Afterwards, the samples were mounted onto a MTS testing machine [Alliance RT/50] with tailor-made supporting fixtures for conducting the test; the crosshead speed of the tensile property and flexural strength tests were 1.5 mm/min and 0.946 mm/min, respectively. An extensometer was used to measure any small change in linear dimension during the tensile test. Table 1 shows the tensile and flexural properties obtained from the tests for PLA and silk fibre/PLA samples.

In terms of biodegradability test (in vitro), PLA and silk fibre/PLA samples were placed into separated tanks contained Phosphate Buffered Saline (PBS) solution. White dry powder of PBS was diluted with 1L of deionised water with ultimately the pH level of 7.4 being achieved. Two types of samples were stored into the tanks with 500 ml of solution each. The tanks were then stored in a humidified, thermostable and orbital-shaking incubator at 37 °C with 100rpm. In order to investigate the changes in mechanical properties of the samples, the samples were characterized by weight change, tensile test, bending test and morphology study at different stages during the biodegradation process.

Results and Discussion

According to the results shown, the Young's modulus and flexural modulus of the silk fibre/PLA samples increase by 27% and 2%, respectively as compared with a pristine PLA sample (Table 1). It can be seen that the chopped silk fibres can play a role of effectively enhancing the tensile modulus of PLA. However, the enhancement in flexural modulus is small. Figures 1(a) & (b) show the stress-strain curves obtained from the experiments. In these figures, they show that the tensile and flexural strengths as well as ductility of the silk fibre/PLA samples as compared with the pristine PLA.

The major factors affecting the mechanical performance of short fibre reinforced composites include fibre-matrix interface, fibre length, fibre content and fibre orientation. In our pervious study, 5mm is the most optimal silk fibre length for injection moulding which can prevent the fibre from being coiled with the screws or stressed plastically. Fibre content is another factor in influencing the tensile strength but it is limited by the restriction of the injection molding and the sample size. At low fibre content (5%) of silk fibre/PLA composite sample, the matrix is not restrained by enough fibres and highly localized strain occurs in the matrix, causing the bond between matrix and fibre to break. Therefore, the debonded fibres dilute the matrix content and act as flaws which reduce the effective cross sectional area and, finally poor mechanical strength is resulted.

Fibres, due to their surface contour can provide mechanical interlocking, if they align along the loading direction, to the surrounding matrix to allow good stress transfer when the composite is under tensile loading. To assess the alignment of fibres during the manufacturing process, small and thin dumbbell shaped composite samples were made by injection moulding [14]. A microscopy was used accordingly to observe the fibre orientation through the image analysis technique. According to Figure 3, most of the fibres are well aligned along the sample's axis (i.e. the loading direction), only a small amount of obliqued fibres.

Notwithstanding fibre length, fibre content and fibre orientation affect the properties of the composites, interfacial bonding between silk fibre and PLA plays a decisive role on expressing the phenomenon on the increment in the modulus but decrement in the strength. In order to illustrate the relation between the mechanical properties and fibre-matrix interfacial bonding of the composite, the sequences of the loading of fibre and surrounding matrix of the composite with the interfacial bonding are discussed.

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 fibres and matrix to share the load and fibres take higher load subsequently through the stress transfer by surface friction of the fibres. Modulus is determined at low strain levels where the fibre-matrix interfaces under very low shear force. Therefore, as the modulus is a property of material at low strain and is not very sensitive to the fibre-matrix interface, thus the modulus of composites is higher than that of a pure PLA. At the certain level of load applied at that time the strain increases into the non-elastic region, debonding between the fibre and matrix happens as the shear force with the normal force at the bonding region may overcome the surface frictional force. The strength of composites is a direct indicator of the strength of interfacial bonds since the applied stress is more efficiently transferred through the interface [14, 15].The interfacial debonding limits the stress transfer through the interface and thereby, as all fibres are debonded, areas with the fibres exist like a cavity without any reinforcement which cause the ultimate strength decreases consequently.

Therefore, poor bonding between the fibre and the matrix would dominate over other factors of strength reduction. Sericin and the hydrophilic characteristic of the silk fibre as the reasons for poor bonding are discussed as follows. A small gap is observed between the fibre and the matrix on the fracture surface of the composite (Figure 2). Silk fibre used for this project was collected as in an "as-it-Is" form, which was degummed by boiling water from the supplier. This degumming procedure removes the more soluble components of sericin, but does not clean all the sericin as both sericin and fibroin core are protein. Thus partial sericin would remain on the surface. [16]. Sericin hinders the bonding between the fibre and matrix, and the efficiency of stress transferred between resin and fibre decreased from the weak interfacial regions thus. Moreover, the fibre used in this project was not undergone any chemical treatment with compatilizer, modifier and/or other bonding agencies due to our target application is for the development of bone implants (no excessive chemical treatment of natural materials is allowed), it is therefore expected that a weak bonding between them was still the case here.

Natural silkworm silk fibre contains hydroxyl groups which is called hydrophilic. In this composite system, one (fibre) is in hydrophilic while another is hydrophobic (matrix) properties, their interface cannot be assumed to be securely (chemically) bonded together due to the inherently poor compatibility and thus induce poor bonding and limit the load transfer through the interface. Therefore, the tensile strength of the composites would not be improved by the addition of silk fibre. However, mechanical interlocking still existed due to the roughness of the fibre and this kind of weak bonding dominates the reasons for diminished strength and strain The roughness of the fibre is basically formed during the spinning process of cocoon, two fibroin fibres which contain numerous silk filaments with different diameters bundled together to form the fibre.

Clearly, for most biodegradable materials, especially artificial polymers, passive hydrolysis is the most important mode of degradation [17]. Silk fibre dominates in the water uptake behaviour, which initiates the degradation of the composite. The mechanism of moisture absorption is owing to the involvement of hydrophilic natural fibre and hydrophobic matrix by water molecule diffusion in the following steps [18]:

(1) The diffusion of water molecules inside the micro-gaps between polymer chains,
(2) Capillary transports into the gaps and flaws at the fibre-matrix interface,
(3) The transportation through matrix micro-cracks formed during the compounding process

Based on the experimental results, the weight of the silk fibre/PLA sample increased with the increase of immersion time. For the silk fibre/PLA sample submerged into the solution for 4 months, it was found that the weight increases by 2.4% as shown in Table 2. For the pristine PLA sample, there is no change in weight with time at all. This result may be due to the hydrophilic effect of silk fibre. In general, silk fibre has comparatively high moisture absorption which leads to swelling within the silk fibre/PLA sample. Although most of the fibres are encapsulated, the equilibrium of water in the composites induces PLA of the composite absorbing water faster than pure PLA. Therefore, the silk fibre/ PLA composite would absorb water more quickly for water penetration into interfacial bonding until silk fibres get saturated.

Besides, it has been found that the Young's modulus, tensile strength, flexural modulus and flexural strength decrease as shown in Figures 4 to 7, of both PLA and silk fibre/PLA samples after being immerged into water. Nevertheless, the properties of the silk fibre/PLA samples are worse as compared to those the neat PLA sample in general. Therefore, the mechanical properties of pure PLA and silk fibre/ PLA composite were weakened because of the effects of water absorption. Water absorption of the samples has been associated with micromechanical damage in the resin and at the fibre-matrix interface as well as reduction of dimensional stability, development of internal stresses. Moreover, water molecules act as a plasticizer and penetrate into the polymer chains. These polymer chains are forced apart and become more mobile and consequently poor mechanical properties and faster degradation are resulted [18][19][20]. Besides, Yutaka et al. have found that silk fibroin is one of the proteinous materials which stimulate the production of enzymes from PLA-degrading microorganisms and consequently speed up the degradation [21]. Silk fibre comprises numerous of micro-fibrils. After the degumming of silk fibre, they can be divided into two triangular of fibrils (brins) and furthermore, a fibril can be separated into individual micro-fibrils shown in figure 8 by the screws during injection moulding. These micro-fibrils may connect together from one end to another end, so the moisture can be easily penetrate into the silk fibre/PLA composites.

Conclusion

As the use of silk fibre reinforced PLA composites is aimed at developing a suitable material for bone fixation, their moduli and biodegradation rate are the leading parameters for the design of implant plates. Before the degradation test, the Young's modulus and flexural modulus of PLA increased over 27% and 2 % respectively, with the use of 5 wt% of silk fibre as reinforcement. The reduction of strength is mainly because of the poor interfacial bonding. However, the limited fibre content in injection molding process and the poor fibre-matrix interface are the significant factors for strength decrement. After immersing samples into PBS solution to simulate their exposure in a liquidised environment, like human body, their mechanical properties were altered with immersion time. The declining rate of mechanical properties of the samples was demonstrated faster than that of pure PLA. It further proves that the hydrophilic effect of the silk fibre does affect the water absorbability in its related composites.

In the current study, it is found that the use of silk fibre, as reinforcement can enhance the modulus of PLA as well as alter its rate of bio-degradability, in which these properties are the primary parameters for the design of implants for bone fixation. The biodegradation rate is crucial in which it have to be compromised with the cell growth rate of bone inside the human body. Besides, for the successful use of silk fibre/ PLA composites in bone implant applications, the mechanical properties of the composite should withstand the loads which human bone suffered daily. Nevertheless, too stiff bone implant plant causes stress shielding of the bone and consequently the bone may become osteoporosis. Therefore, it should require further investigation of the bone plate with desirable biodegradation rate while at the same time possess proper mechanical properties (high modulus ~ 20 GPA, close to natural bone properties) with moderate strength) for supporting a load that an un-damaged bone should withstand.

Acknowledgement

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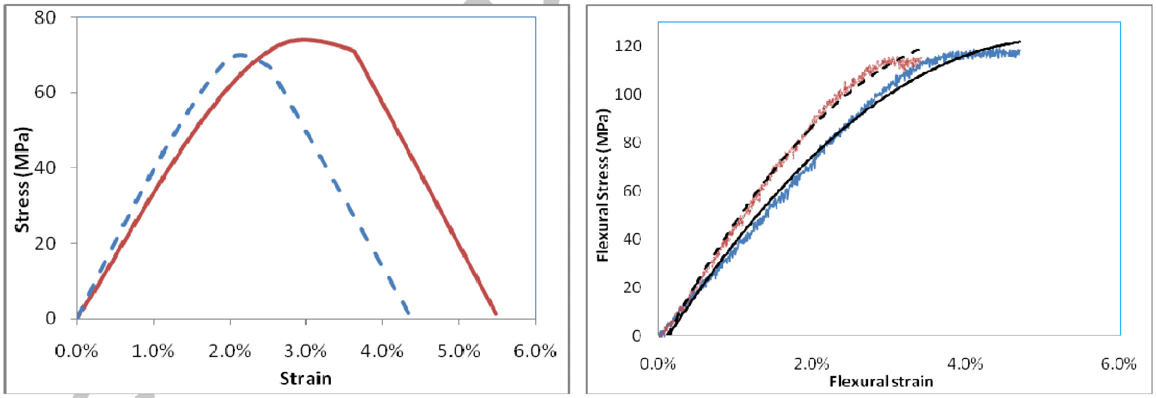
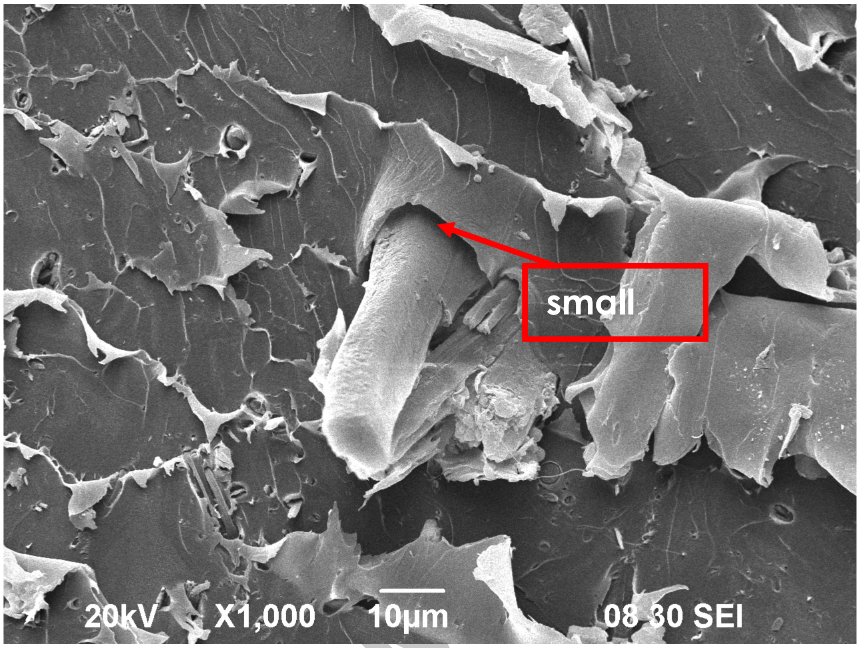
	Young's Modulus (GPa)	Tensile Strength (MPa)	Strain at Break (%)	Flexural Modulus (GPa)	Flexural strength (MPa)	Maximum strain (Flexural) (%)
PLA	3.21±0.08	70.73±2.4	5.5±1.7	3.98±0.23	109.4±14.5	4.1±0.75
5 wt% Silk fibre/PLA	4.08±0.05	70.6±1.1	3.8±0.5	4.06±0.20	97.41±21.8	2.9±0.99
Percentage increase	27%	-0.18%	-31%	2%	-11%	-29%

Table 1. Experimental results extracted from the tensile property and flexural strength tests.



(a) *(b)*

Fig.1.(a) Tensile stress-strain curves of (i) pure PLA – solid line and (ii) silk/PLA composite – dashed line.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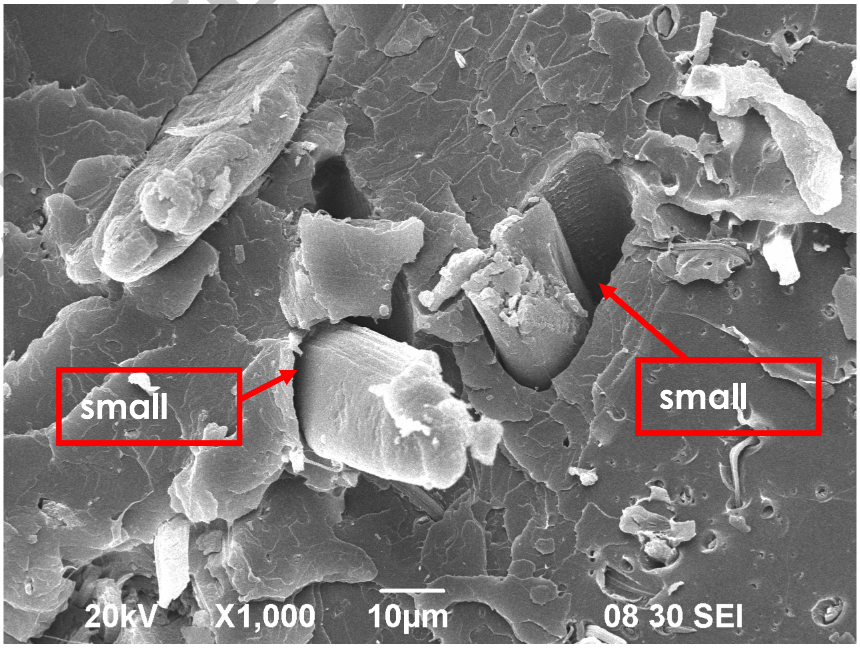
(a)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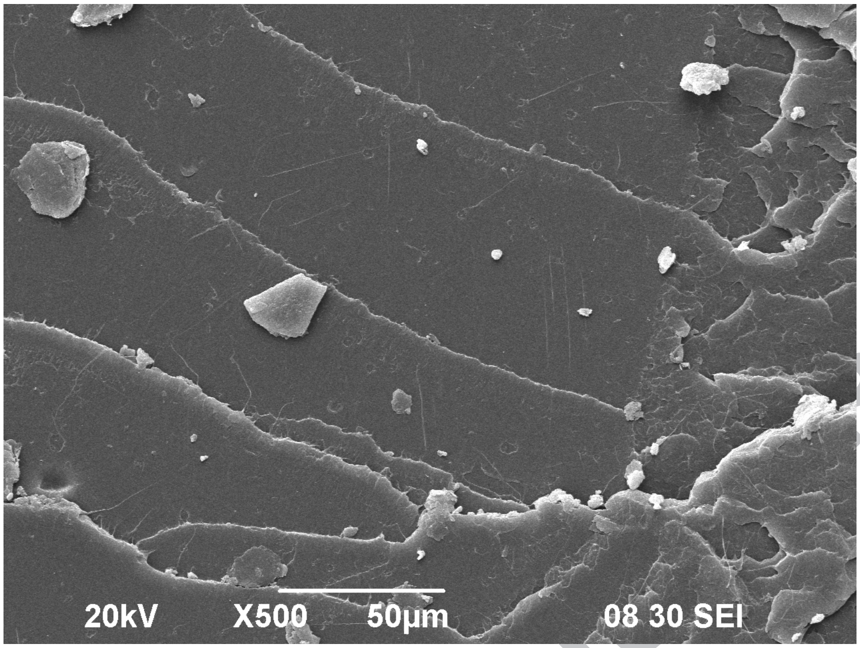
(b)



(c)

Fig.2. Scanning electron micrographs showing the fractured surfaces of (a) & (b) silk/PLA composites with the fibre pull out compare with (c) pure PLA

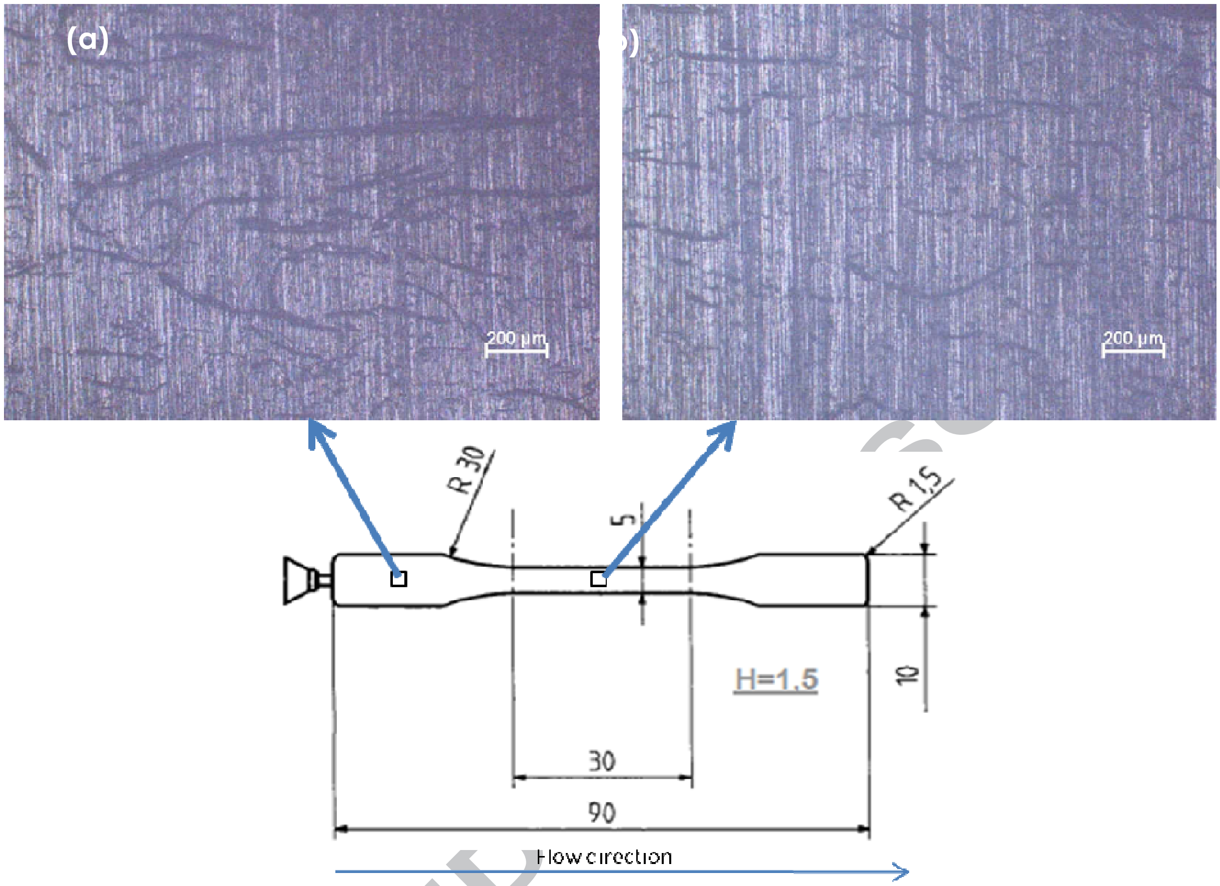


Fig.3. Micro graphs of cut-off view (along the longitudinal direction of the sample)of the silk fibre/PLA composite with 5 vol% silk fibre: (a) wide section and (b) narrow section.

	Duration of the degradation Test (Week)								
	0 Before Test	2	4	6	8	10	12	14	16
PLA (g)	1.22	1.22	1.23	1.22	1.22	1.23	1.22	1.23	1.23
5 wt% Silk fibre/PLA (g)	1.22	1.25	1.24	1.24	1.25	1.25	1.24	1.24	1.25

Table 2. The weight of pure PLA samples and silk/PLA biocomposites during biodegradation test.

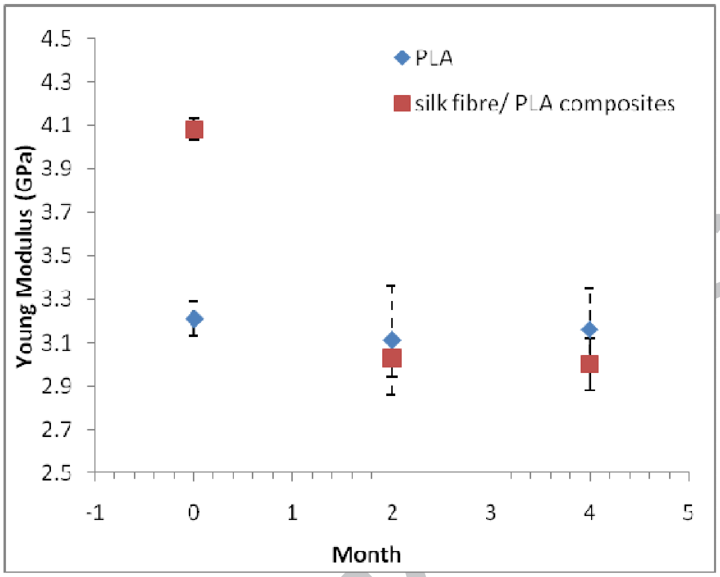


Fig.4. Young modulus as a function of time for (a) Pure PLA and (b) silk fibre/PLA composite

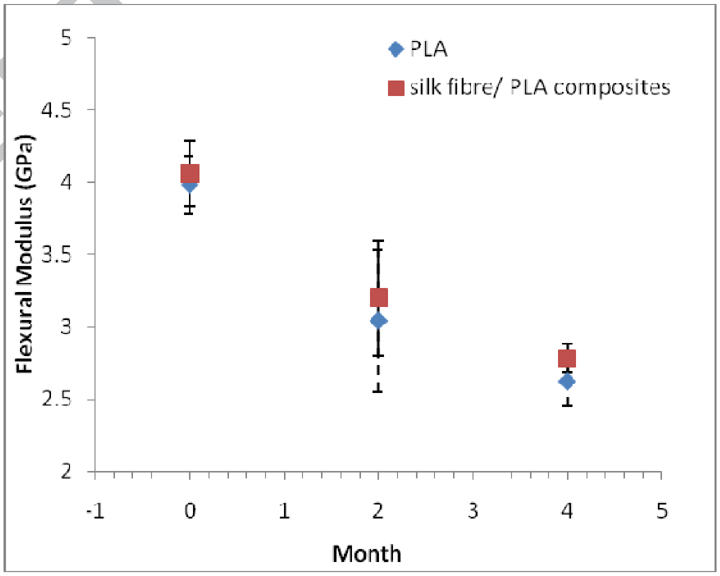


Fig.5. Flexural modulus as a function of time for (a) Pure PLA and (b) silk fibre/PLA composite

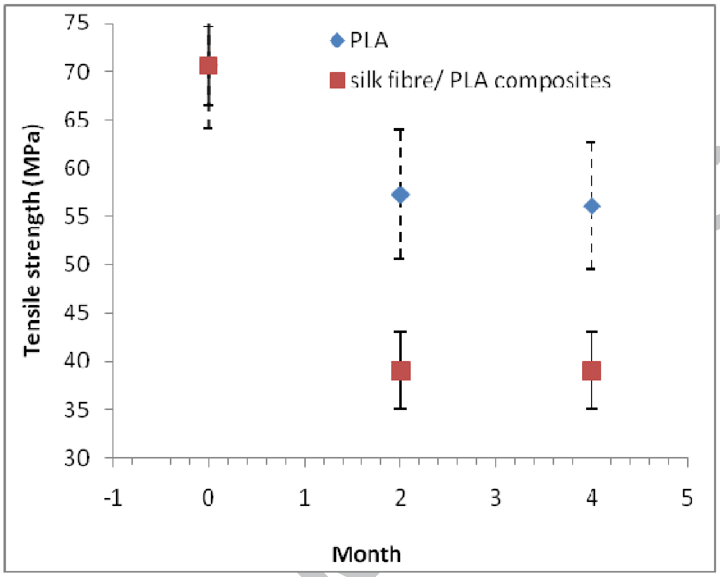


Fig.6. Tensile strength as a function of time for (a) Pure PLA and (b) silk fibre/PLA composite

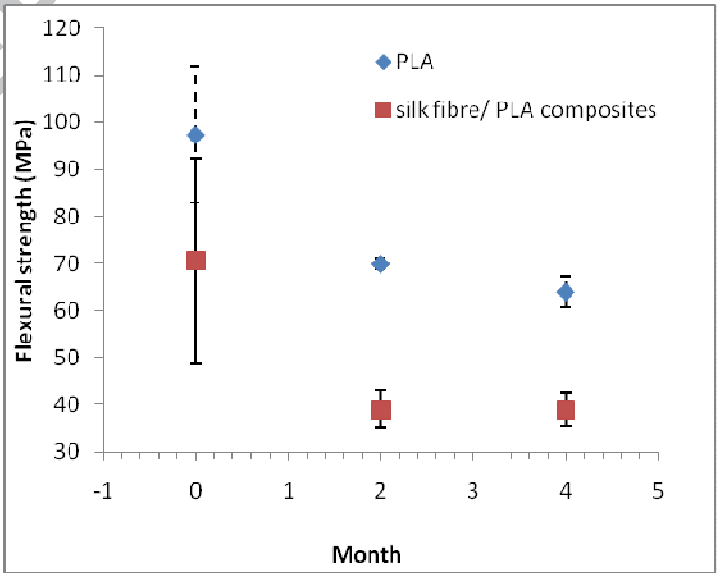
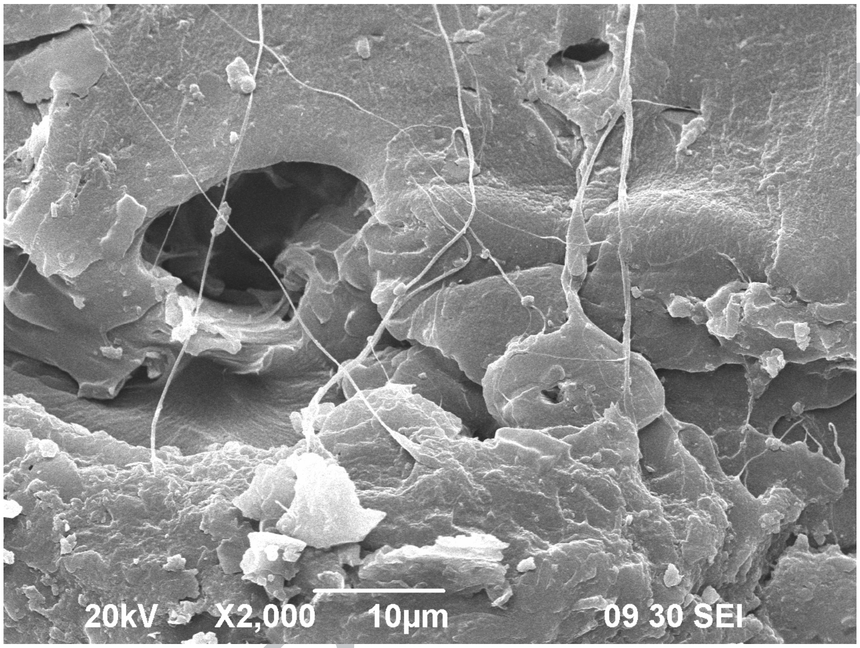
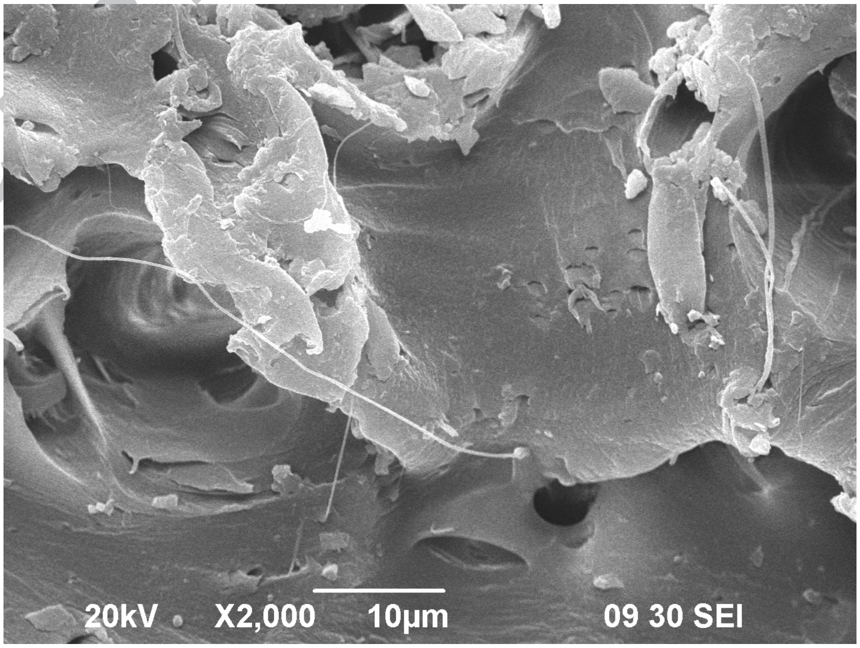


Fig.7. Flexural tensile strength as a function of time for (a) Pure PLA and (b) silk fibre/PLA composite



(a)



(b)

Fig.8 (a) & (b). Scanning electron micrographs showing the micro fibrils of the silk inside the composites.

Keywords: B. Mechanical properties; A. Natural Fibre Composites