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Interfacial bonding and degumming effects on silk fibre/polymer biocomposites

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ABSTRACT

Silk fibre has been popularly used for bio-medical engineering and surgically-operational applications for centuries because of its biocompatible and bioresorbable properties. Using silk fibre as reinforcement for bio-polymers could enhance the stiffness of scaffoldings and bone implants. However, raw silk fibre 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 silk fibre's properties, making the silk fibre possible to be properly used for the development and production of novel bio-composites with specific mechanical and biodegradable properties. Some critical issues such as wettability, bonding efficiency and biodegradability at the fibre/matrix interface are of interesting topics in the study of the degumming process. Therefore, it is a need to detailedly study the effect on different degumming processes to the properties of the silk fibre for real-life applications.

1. Introduction

The silkworm cocoon is built at the end of larval stage and protects the pupa during metamorphosis to be an adult moth. It contains silk protein, known as "silk fibroin" which is stored in the glands of silkworm as an aqueous solution. The silkworm cocoon silk fibre is composed of two cores of fibroin because their gland is a paired organ which is surrounded by a glued-like cementing layer of sericin in a structure known as bave [1]. These malleable silk proteins are usually produced within specialised glands after biosynthesis in epithelial cells, followed by secretion into the lumen of these glands and spin out as fibre and become the cocoon finally [2,3]. The fibre is an inhomogeneously distributed polymer blend of mainly two proteins that is coated with glycol-proteins and lipids [4]. The spinning elongational flow orients the fibroin chains, and the fibroin (liquid) is converted into partly crystalline, insoluble fibrous filaments (solid) [5]. The tussah silk fibre obtained directly from the spinneret of silkworm is free from calcium oxalate crystals at micrometre size but these crystals are usually observed on undegummed cocoon silks. These micrometre-sized calcium oxalate crystals are the type of an excretion by the silkworm and it can be shown in Fig. 1 which is same as the finding from Fu et al. [6].

Shao et al. [7] have found that the speed of spinning controls the mechanical properties of fibre which is depended on the percentages of the amorphous and crystalline regions [3]. Most silkworm silk fibre contains assembled anti-parallel β-pleated sheet crystalline structures. Silks are considered semi-crystalline materials. There is 30–50% crystallinity in spider silks, 62–65% in cocoon silk fibroin from the silkworm *Bombyx mori*, and 50–63% in wild-type silkworm cocoons [5].

A single fibroin comprises of several 1 μm wide fibroin fibrils. Each fibroin fibril contains microfibrils which each 15 nm macrofibril is packed each other together [8]. The whole structure of the silk fibroin is encased by the sericin to form a composite fibre [9]. The sericin is an amorphous structure in nature and acts as binder to ensure the structural integrity of the cocoon [8]. The convenience of reeling long and continuous fibre from the cocoon is to remove the sericin coating layer. Sericin removal requires a thermo-chemical treatment of cocoon in a process conventionally known as degumming [1]. However, the degumming could affect the mechanical properties of silkworm silk fibre because of the change in the microstructure of core fibroins and the bonds between them. It would weaken at least one type of non-covalent interaction of the core fibroin, such as hydrogen bonds and Van der Waal interaction [9].

Silkworm silk fibre is a renewable protein biopolymer which is not only valuable in the textile industry, but also for bio-medical engineering applications because of its superior mechanical properties and biocompatibility. Moreover, this fibre can be easily functionalized, and its structure and morphology can be modulated to match a wide range of working requirements [10]. Two additional

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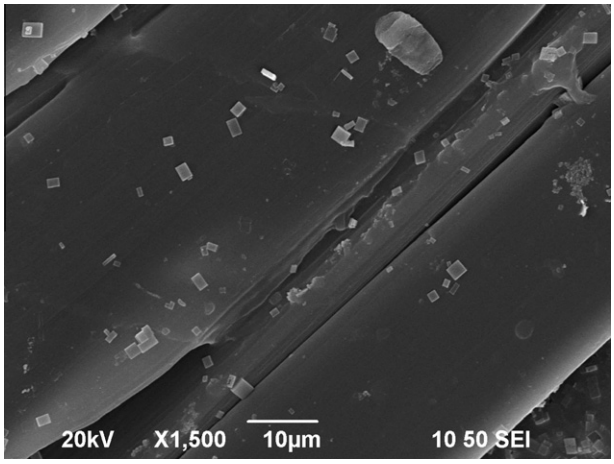

Fig. 1. Micrometre-sized calcium oxalate crystals on the surface of tussah silk fibre.

advantages including excellent handling and knotting characteristics also motivate the silk fibre for implant design and applications [11]. The application potential of using silk fibre is huge including sutures and gauzes for treating skin wounds. Sugihara et al. have found that the healing time of wounds dressed with silk film was 7 days shorter than those dressed with DuoActive dressing [12]. Mandal and Kundu have studied that biospun silk matrices is a natural, inexpensive and alternative substrata for skeletal tissues [13]. Hofmann et al. have investigated in using silk fibroin as biodegradable carries for controlled drug delivery [14]. Besides, biodegradable composites comprising of silk fibre and biodegradable polymer have been studied for tissue engineering applications [15].

2. Hypersensitivity of silk fibre

High tensile strength with a relatively low biodegradation rate of silk fibres makes it a promising candidate for tissue engineering applications [16]. However, almost all biomaterials derived from a non-autologous source would elicit some levels of foreign body response (FBR) following implantation in vivo [10]. Hypersensitivity is a type of FBR which is produced by the normal immune system [10,17]. There are many factors which can influence the level of FBR, including composition, implantation site, size, geometry, surface topography of the biomaterials, etc. Silk fibre has been found to be a potential allergen causing type I hypersensitivity and sericin is considered to be the main inhalant allergen and antigenic properties in silk sensitive persons. Once the patient is sensitised to sericin, plasma cells in the human body secrete antibodies immunoglobulin E (IgE), some antigens binds IgE variable regions, degranulation of cell occurs, histamine and other vasoactive substances are released and It would cause systemic anaphylaxis, localised reactions and asthma [11,16,17]. Therefore, the removal of sericin of silk fibre is a crucial process for it to be applied for real life applications.

3. Amphiphilic characteristic of silk fibre

A noteworthy weakness in natural fibre reinforced thermoplastic composites is their poor interfacial bonding properties between fibre and matrix. The interfacial adhesion between them plays an important role in determining the performance of the composites. As silk proteins are stored in the silk gland and transported down the spinning duct in a lyotropic liquid crystalline state in silkworm silk glands, the molecules of the silk protein must be amphiphilic, which is having a combination of hydrophobic and hydrophilic blocks or groups [18]. When producing silk fibre reinforced composites, hydrophilic characteristic of silk fibre was found to cause poor interfacial bonding with polymer. This is mainly due to their dissimilar hydrophobicity as the surface of fibre is hydrophilic while organic plastics are generally hydrophobic, they are incompatible and prevent efficient fibre–matrix bonding. Therefore, debonded fibres dilute the matrix content and act as flaws which reduce the effective cross sectional area of reinforcement, and finally poor mechanical strength is resulted. Moreover, the formation of fibre agglomeration, due to the inter-fibre hydrogen bonding which prevents thorough dispersion of fibres during the manufacturing process weakens the strength and affects the appearance of the composites [19–22]. In such case, the use of silk fibre could not provide any beneficial advantage to the composites [23]. Besides, the hydrophilic characteristic of natural fibre is responsible for water absorption, it therefore reasonably assumes that high fibre volume fraction would cause more water content in the composites [24].

4. Wettability of silk fibre

Natural fibre always cannot be wetted completely by following the typical composites manufacturing processes as they are not designed for wetting fibre with tight packing fibrils. The viscosity of resin is normally too high for impregnation. Better resin pre-impregnation allows a better fibre wetting and thus enhances the interfacial bonding properties between fibre and matrix [25].

Surface treatment of natural fibres for adhesion improvement is a critical step in the development of bio-composites. Different treatments such as pre-impregnation, surface modifications, chemical reactions and plasma were studied for improving their interfacial bonding strength of composites [19,20,25–27]. 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. After removing the sericin, the cluster of pearls appears on the surface of silk fibroin and the silk fibre exhibits excellent elasticity [28]. Several degumming processes are developed and under investigated such as extraction with water, boiling off in soap or alkalis, enzymatic degumming, and degumming in boiling acidic solutions.

5. Surface modification

5.1. Alkaline treatment

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 [25]. When the silk fibre is degummed by an alkaline solution, 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 (salts-Donnan membrane effect) [29,30]. Several alkalis such as NaOH (Sodium hydroxide) or Na_2CO_3 (Sodium carbonate) are commonly used nowadays for degumming. However, these strong alkali treatments impose a relatively harsh irritation to silk fibroins [31,32]. Fig. 2 shows the surface of a silk fibre degummed by Na_2CO_3. Individual longitudinal strands are clearly seem, white and black arrows indicate the positions and corrosive dents of the fibre, respectively [33].

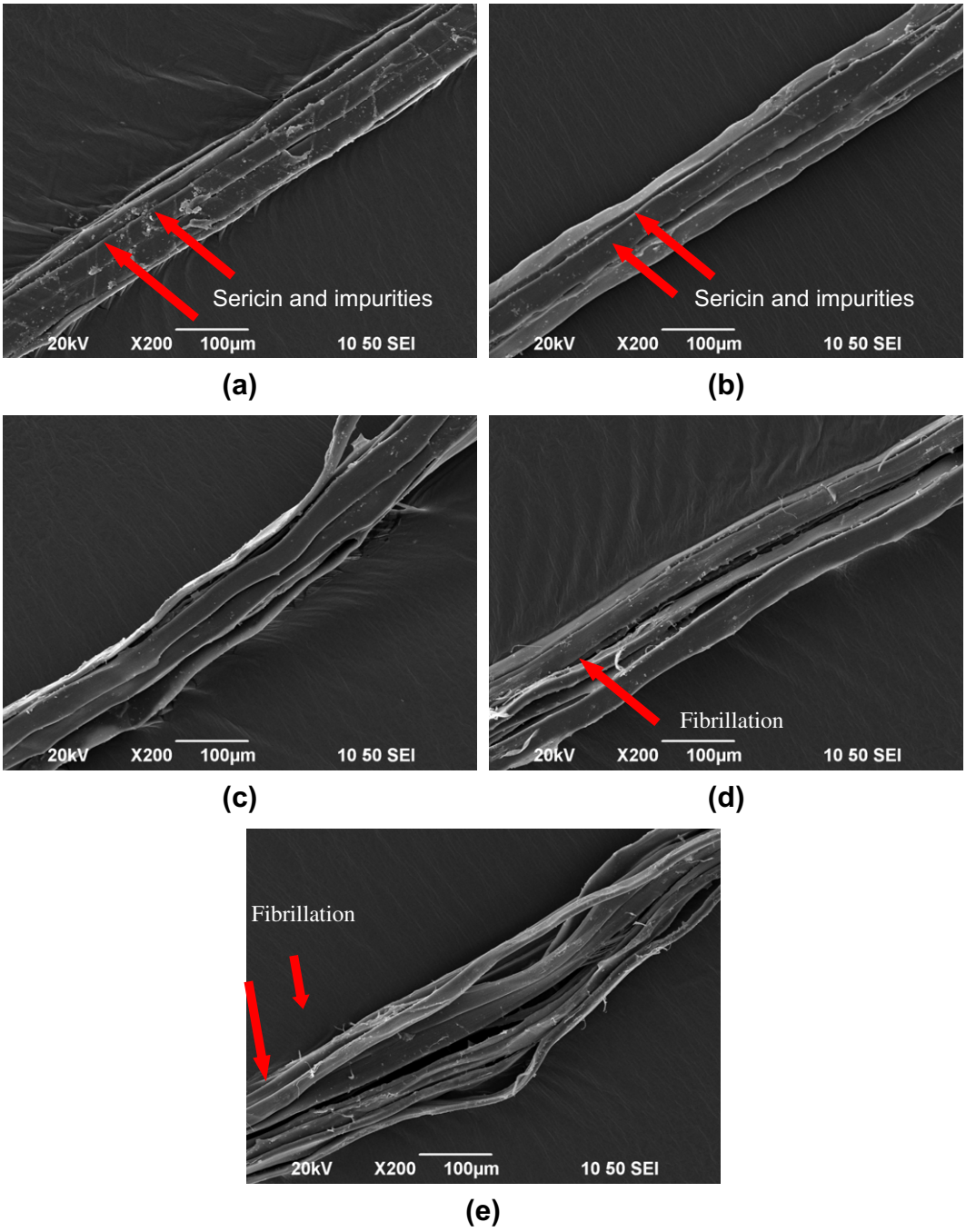

Fig. 2. Surface of tussah silk fibres degummed for (a) 0 min (control sample), (b) 15 min, (c) 30 min, (d) 45 min, and (e) 60 min.

5.2. Distiled boiling water treatment

The amino acid sequence of polypeptides plays an important role in the solubility and crystallization of silk fibroins [34]. In general, Glycine and alanine predominate in the silk fibroin. In particular, the glycine in tussah silk is 26 residue% and alanine is 44.2 residue% [35]. Therefore, tussah silk fibroin is predominantly hydrophobic as alanine is hydrophobic and the glycine is amphiphilic. On the contrary, residues serine, threonine, aspartic acid and glutamic acid are the main components of sericin. Serine and threonine are carbohydrate that can be covalently linked to its hydroxyl (–OH) group. While aspartic acid and glutamic acid contain free carboxyl group making them acidic and hydrophilic. Therefore sericin comprises of more random structures and can be hydrolysed using boiling water [34,36]. However, the level of degumming using boiling water is mainly depended on the treatment time. The surface morphology of heat-treated silk fibres according to different degumming time is illustrated in Fig. 3(a–e).

5.3. Soap–soda method

Traditionally, the recommended degumming method for silk fibre is carried out by soap or soda ash method [Sodium carbonate (also known as washing soda or soda ash), [23, 37–41]. In this degumming method, a weight loss of 25–30% would normally occurred, which indicated a complete removal of sericin [23]. Sericin is swollen and emulsified by the soap and finally, removed from the fibre. Nevertheless, the presence of soap and alkalis in the

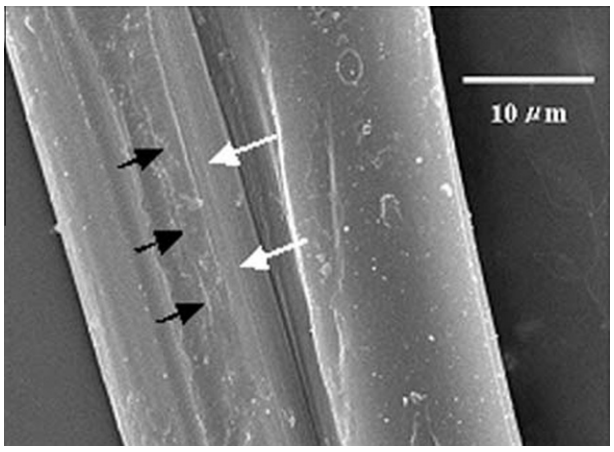

Fig. 3. Surface of *Bombyx mori* silk fibre degummed by Na_2CO_3 [61].

wastewater of degumming process raise an issue of pollution [28]. Besides, the degumming cycles of the soap ash bath is limited because of acidity of sericin hydrolysis products accumulating in the bath [37].

5.4. Enzyme treatment

The application of enzymes in textile industries has been increased recently. Various studies have been dealt with the removal of sericin by using different types of enzymes including protease and lipase as degumming agents [28,37,39]. Enzyme degumming involves the proteolytic degradation of sericin, using the specific proteins with minimum effect on fibroin. When the substrate molecule fits into the active sites of the enzyme's molecular structure to form an enzyme–substrate complex, this complex then is broken and yields an end product and the original enzyme molecule is reproduced. Enzymes treatment operates under mild conditions and low temperatures which can reduce the energy consumption [28,41]. However, the lower performance of enzyme degummed silk including difficult to handle and high cost have limited the application of enzymes on the silk industry [41].

5.5. Acidic treatment

Using acidic agents such as tartaric acid and citric acid for silk fibre degumming and finishing was approved for physical property enhancement [42–44]. It has been pointed out that the action of organic acids is generally milder and less aggressive than that of an action by alkali solution. Freddi et al. have found that the high performance on degumming is achieved by tartaric acid in terms of sericin removal efficiency and of intrinsic physico-mechanical characteristics of silk fibres [42]. Yang et al. have studied critic acid for degumming and found that the dry and wet resiliency of finished silk was remarkably increased with citric acid treatment [46]. However, same as alkaline treatment, acid also causes the damage on the fibroin surface [45]. Fig. 4 shows that there is a non-uniform removal of gum from interlacing regions of fibres degummed by succinic acid [33].

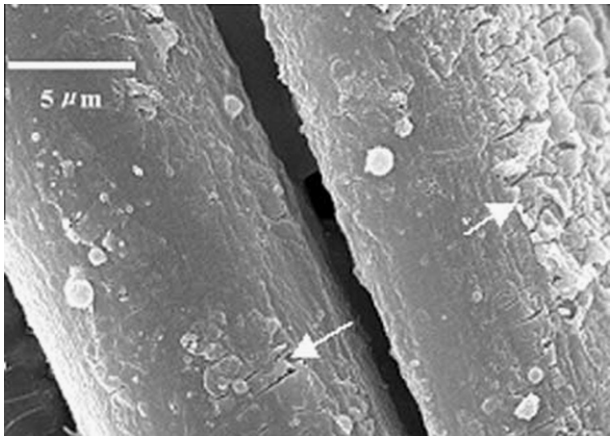

Fig. 4. Scanning electron micrographs illustrating silk fibre degummed by succinic acid [61].

6. Mechanical properties of degummed silkworm silk fibre

The effect of degumming directly influences the properties of silk fibre. One of the disadvantages of degumming procedure is that it would cause detrimental changes in the mechanical properties of the fibre [47,48]. The mechanical performance of the silk fibre using different degumming agents is shown in Table 1. Significantly, the degumming processes using soap, succinic acid and enzymes may cause undesirable degradation of fibroins [49]. Chemically treated fibres showed a considerable decrease of the tensile strength and this decrease is attributed to the dimensional change, substantial bond breakage, degradation of protein chain and partial harmful damages of silk molecules during the treatments [50]. However, the extent of these properties being affected are depended upon the method and the duration of degumming [41]. As succinic acid is a strong acid (pH = 2.88) [33] while citric acid is a weak acid, succinic solution may attack the fibroin after removing the sericin but citric acid would only have a little or no effect on it. Besides, the strain of silk fibres degumming by different methods except enzyme treatment was noticeably increased. The decrement in the tensile properties of enzyme degummed silk fibre confirmed that silk fibre is susceptible to proteolytic attack [39]. The initial modulus of silk fibre was decreased and the elongation at break was increased after it was degummed by different treatments [50].

The tensile parameters do not reproduce the actual mechanical properties of two core fibroin fibres, they require considering the fact that different levels of degradation in sericin may occurs [33]. Besides, the removal of sericin layer on the fibre surface would contribute significantly to the change of cross sectional area and subsequently the tensile properties of the fibres. At the beginning of degumming process, the degumming agent starts dissolving the sericin on the fibre surface and causing the decrement to the diameter of fibre.

The reasons of the strength increment of degummed tussah silk fibre using distiled water is that their microfibroins are twisted in nature. The removal of the binding agent (i.e. sericin) would potentially align the fibroins towards the loading direction. Thus, the friction in-between the fibres is reduced substantially and the load bearing capacity increases. Nevertheless, this scenario is totally reverted when the degumming time increases or use of other types of irritant chemicals such as strong alkali and acid solutions. After the removal of sericin coating, hydrophilic and amorphous structures start being attacked at the first place. In the silk fibre, strong crystalline regions which support strong tensile strength are interspersed by, the soft and more flexible amorphous peptide chains which are responsible for the elasticity of silk and also help with the distribution of stress [51,52]. Under a tensile load, the amorphous chains are extended, and the crystalline networks are rotated during the stretching and shrinking processes to produce a strongly preferred molecular orientation which is parallel to the fibre's axis. Moreover, once the fibre is extended physically, partly

Table 1
Lists the change of the mechanical properties of silkworm silk fibre degummed by different degumming solutions compared to its raw silk fibre.

Degummed samples	Tensile strength (%)	Young's modulus (%)	Elongation at break (%)	Ref.
Bombyx mori silk fibre				
Distiled boiling water	−44	−50	44	[61]
Succinic acid	−38	−28	39	[61]
Sodium carbonate	−18	−34	28	[61]
Urea	0	−44	33	[61]
15% soap	−41	−13	33	[63]
15% citric acid	20	−11	47	[63]
30% citric acid	0	−17	28	[63]
Protease	−20	–	−34	[7]
Tussah silk fibre				
Enzymes	−16.1	–	–	[64]
Acid	−34.6	–	–	[64]
Distiled boiling water	3	9	21	
$NaHCO_3$	9	–	−34	

amorphous chains in the fibroins would be crystallized as a rigid and highly oriented network [53]. Therefore, the amorphous structure also contributes the strength improvement because of the crystallized-amorphous region.

As most natural fibres owe their strength from hydrogen bonds, these bonds play an important role in the secondary, tertiary, and quaternary structures of proteins [54]. However, the degumming process weakens at least one type of non-covalent interaction. Water acts as a plasticizer and penetrates into the amorphous regions and this interrupts the inter- and intra- molecular hydrogen bonds. It increases the displacements of protein chain segments and stress relaxation making it easier to respond any driving force for a microstructural change. Consequently, the elongation at break of silk fibre degummed by different agents is increased [55,56].

7. Other treatments

7.1. Treatments using compatibilizer or coupling agent

The surface modifications of fibres by using compatibilizer or coupling agent for effective stress transfer across the interface were explored [19]. The compatibilizer is a kind of polymeric interfacial agent or polymers with functional groups that graft onto the chain of polymers. Besides, coupling agent is a chemical substance which is able to react chemically on both natural fibre and polymer matrix during processing to form or promote a stronger bond at the interface as bridges in order to improve the mechanical properties of resultant composites. The nature of bond formed between a specific coupling agent and fibre depends strongly on the characteristics of fibre surface to which the coupling agent is adhered [19]. The coupling agents are tetrafunctional organometallic compounds which are commonly known as silane coupling agents [20]. These coupling agents are usually used to bind organic and inorganic materials together. Cyanuric chloride is one of the most effective and widely applicable coupling agents to attach synthetic or natural polymers such as polysaccharides to proteins [57] Gotoh et al. have found that cyanuri chloride as coupling agent improved the interaction between silk fibroin and Polyethylene glycol (PEG) and the result indicated that PEG molecules covalently bonding to SF narrowed the spacing of inter-chain periodicity and promoted the formation of inter-chain β-sheets [58]. Furuzone et al. used coupling agent to prepare a covalent linkage between silk fibroin and hydroxyapatite (HAp) [59].

7.2. Plasma treatment

Plasma treatment is a new environmentally-friendly technology which can alter the surface properties of polymers and textile materials, without interfering in their bulk properties. Chaivan et al. have studied the utilisation of SF_6 plasma treatment for improving in hydrophobic property of silk fibre. A reproducible and significant increase in the hydrophobic property compared with the untreated sample was obtained [25]. Fang et al. have found a numerous of advantages of oxygen plasma for silk fibre surface modification. It includes enhanced colour yields, excellent pattern sharpness and more grooved surface. Besides, the hydrophilicity of silk fibre was remarkably improved after being treated with plasma [60]. CF_4, CHF_3, C_2F_6, and their mixtures in plasma modification of polymers and textiles have been reported to be effective in imparting water repellency to fibres efficiency of the surface treatment [61]. However, the cost of the plasma treatment restricts the usage of the technique in the industries widely.

8. Stress transferability

As aforementioned, a silk fibre consists of fibroins that are bound together by a sericin layer, Zhao et al. has found that the diameter of a *B.* mori silk fibre is in the range of 2–4 μm [62]. The thickness of this layer is highly affected by the degumming process and the solutions such as NaOH, water or citric acid used. However, certain amount of sericin may purposely or accidentally remain on the surface of the core fibre because of incomplete degumming [4]. The intrinsic condensed structure of sericin is mainly amorphous and contains few β-structure [5]. More amorphous regions of sericin bestow extensibility because the high energy absorption. Therefore, the existence of sericin layer would absorb part of energy when a composite is under loading. The strain experienced by a host biopolymer is not transferred completely to the core fibre. However, very few available theoretical analyses pertain to silk fibre reinforced biopolymer composites and most of these analyses do not take into account on the effect of sericin. Therefore, a linear, elastic and isotropic theoretical model with the consideration of sericin thickness to evaluate the differential stress between the core fibre and surrounding sericin layer is introduced. Besides, the influence on moisture absorption in relation to the shear stress between the core fibre and the layer is also discussed as below.

8.1. Constant load applied along the core fibre the fibre's direction

The sericin layer in the composite would potentially absorb part the energy and affect the deformations of each material. Besides, the length of the core fibre, in the case of short fibre is used, is also important for the accuracy of the result because a shear stress concentration exists at the fibre ends. Fig. 3 depicts a three-cylinder model for analysing the stress transfer properties of a single fibre

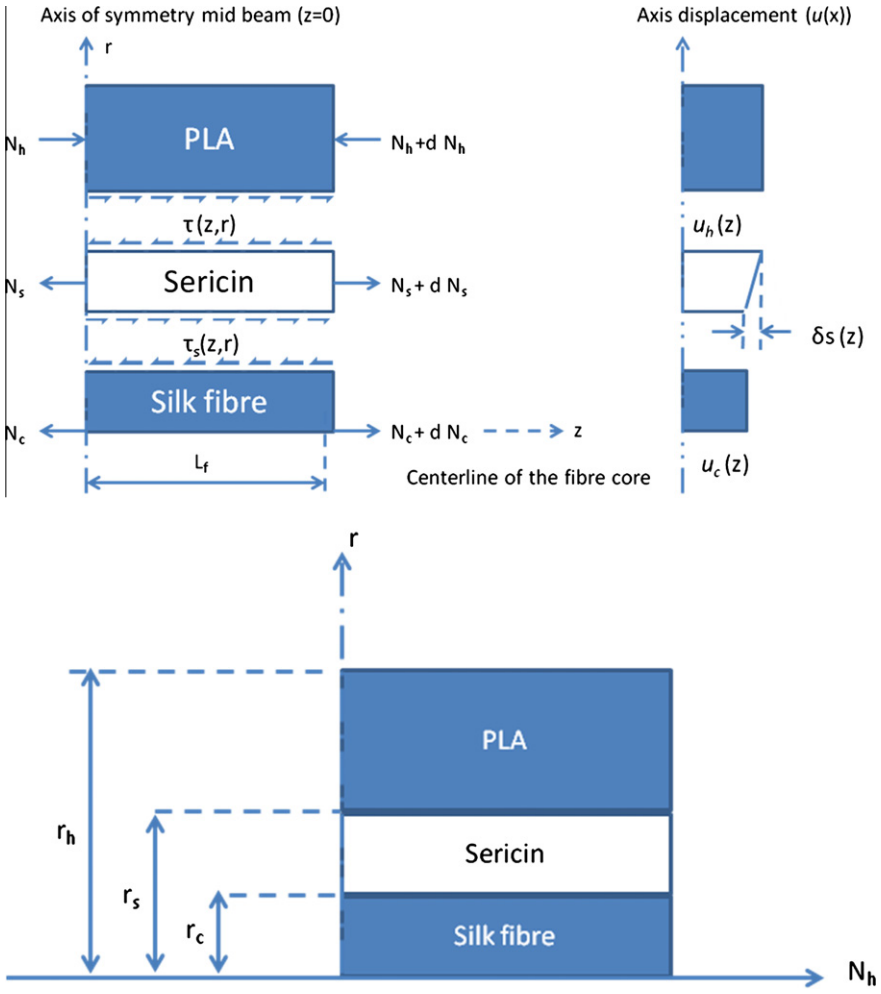

Fig. 5. Three-cylinder model for the present study.

reinforcement system. As two core fibre are stuck closely together and maintain an elliptical shape in its aspect ratio less than 2, it therefore reasonably assumes that the core fibre can be modeled as a single fibre with the radius of r_c.

The longitudinal axis z represents the direction of the applied load. Transverse direction r represents the distance measured from the centre ($r = 0$) of the core fibre. In Fig. 5, the subscripts c, s and h denote the core fibre, sericin coating and surrounding host polymer material, respectively. Tensile and shear moduli are given by E and G, respectively. $\tau_h(z, r)$ and $\tau_s(z, r)$ denote the shear stresses along the axial direction (i.e. fibre's direction) at the interfaces between the polymer material and sericin layer, and between the sericin layer and the core fibre respectively. r_h, r_s, and r_c represent the outer radii of the host polymer material, sericin layer and the core fibre respectively.

In the case when the composite is under an axial load, the loads are applied to the host polymer material, sericin layer and the core fibre are denoted by N_h, N_s and N_c, respectively. Because of the symmetry about both r- and z-axes, only a quarter section of the system is considered.

The following basic assumptions are made to simplify the case of current study:

1. The theory is applicable as long as all the material involved including host polymer material, sericin layer and the core fibre are linear, elastic and isotropic. This assumption is not entirely match the truth as the mentioned materials behave in a nonlinear viscoelastic manner.
2. The core fibre, sericin layer and the host polymer material are assumed to be free of voids.
3. All interfaces are perfectly bonded.

The axial displacement conditions are described by

$$u(z) = \begin{cases} u_h(r,z) = u_s(r_s,z) \\ u_s(r_c,z) = u_c(r,z) \end{cases} \quad (1)$$

The relative displacement (δs) of the sericin layer due to the shear deformation is given by

$$\delta_s(z) = u_h(r_s,z) - u_c(r_c,z) \quad (2)$$

At the mid-beam region ($z = 0$), the strains for all elements are mathematically identical, i.e.,

$$\epsilon_h(r,0) = \varepsilon_s(r,0) = \varepsilon_c(r,0) \quad (3)$$

4. Thermal load is not applied in the system. The strain evaluated at the core fibre only responds to the strain induced by the load applied axially.

By considering the force equilibrium for an element of sericin layer in the loading direction as shown in Fig. 5, the shear stress in this layer can be approximately obtained by using the following relationship:

$$\pi(r^2 - r_c^2)\sigma_s + 2\pi r_c \int_0^{L_f} \tau_c(z,r_c)dz - 2\pi r \int_0^{L_f} \tau(z,r)dz = 0 \quad (4)$$

where σ_s is the axial stress in the sericin layer in the z direction, Eq. (4) can then be rewritten in the following form:

$$\frac{1}{L_f}\int_0^{L_f}(r^2-r_c^2)\sigma_c dz + 2r_c\int_0^{L_f}\tau_c(z,r_c)dz - 2r\int_0^{L_f}\tau(z,r)dz = 0 \quad (5)$$

Hence, Eq. (5) is alternatively written as the following:

$$\frac{1}{L_f}(r^2-r_c^2)\sigma_c + 2r_c\tau_c(z,r_c) - 2r\tau(z,r) = 0 \quad (6)$$

In general case, the length of the core fibre is greater than its diameter i.e., $L \gg r$, so that the first term appeared in Eq. (6) becomes very small as compared to other terms in the equation, and thus this term can be neglected in the current analysis. The relationship, in term of the shear stress in the sericin layer and the shear stress at the surface of the core fibre at any section z can be expressed by:

$$\tau(z,r) = \frac{r_c}{r}\tau_c(z,r), \quad r_c \leqslant r \leqslant r_s \quad (7)$$

The axial displacement of the host polymer material can be obtained by considering the condition of compatibility for all elements shown in Fig. 5.

$$u_h(z) = \delta_s(z) + u_c(z) \quad (8)$$

in which the relative displacement of the sericin layer is determined by

$$\delta_s(z) = \frac{1}{G_s}\int_{r_c}^{r_s}\tau_c(z,r_c)\,dr \quad (9)$$

For the host polymer material and the core fibre, the axial displacements are given by

$$u_h(z) = \int_0^z \frac{\sigma_h(z)}{E_h}dz \quad (10)$$

and

$$u_c(z) = \int_0^z \frac{\sigma_c(z)}{E_c}dz \quad (11)$$

The tensile force of the core fibroin fibre is thus expressed as

$$N_c(z) = \pi r_c^2\sigma_c - 2\pi r_c\int_0^z \tau_c(r_c,z)dz \quad (12)$$

where σ_c is the axial stress of the core fibre at mid-beam section ($z = 0$). Substituting Eqs. (9)–(11) into Eq. (12) yields the following integral equation:

$$\int_0^z \frac{\sigma_h}{E_h}dz = \frac{1}{G_s}\int_{r_c}^{r_s}\frac{r_c}{r}\tau_c(z,r_c)dr + \int_0^z\frac{\sigma_c(z)}{E_c}dz$$

$$\int_0^z \frac{\sigma_h}{E_h}dz = \frac{1}{G_s}\int_{r_c}^{r_s}\frac{r_c}{r}\tau_c(z,r_c)dr + \int_0^z\frac{N_c(z)}{E_c\pi r_c^2}dz$$

$$\int_0^z \frac{\sigma_h}{E_h}dz = \frac{r_c}{G_s}\tau_c(z,r_c)\ln\left(\frac{r_s}{r_c}\right) + \frac{1}{E_c\pi r_c^2}\times\int_0^z\left[\pi r_c^2\sigma_c - 2\pi r_s\int_0^\xi\tau_c(\xi,r_c)d\xi\right]dz \quad (13)$$

By differentiating Eq. (13) and combining the compatibility condition (3), the equation is simplified as

$$\frac{-2}{E_c r_c}\int_0^z\tau_c(\xi,c)d\xi + \left\{\frac{r_c}{G_s}\ln\left(\frac{r_s}{r_c}\right)\right\}\frac{\partial\tau_s(z,r_s)}{\partial z} = 0 \quad (14)$$

Further, differentiating Eq. (14) gives

$$\frac{\partial^2\tau_c(z,r_c)}{\partial z^2} - \lambda^2\tau_c(z,r_c) = 0 \quad (15)$$

where

$$\lambda = \sqrt{\frac{2G_s}{E_c r_c^2\ln(r_s/r_c)}} \quad (16)$$

The solution to Eq. (20) is given by

$$\tau_c(z,r_c) = C_1\cosh(\lambda z) + C_2\sinh(\lambda z) \quad (17)$$

Two unknowns C_1 and C_2 are determined using two boundary conditions. The first boundary condition is evaluated at $z = 0$. The axial load (N_c) at the core fibre is determined by the compatibility condition (Eq. (3)). The strain of the core fibre at the mid-beam region is equal to the strain of the host polymer material. The second boundary condition is evaluated at the point, where the axial load of the core fibre core is zero, i.e.

$$N_c(0) = \sigma_h\pi r_c^2\frac{E_c}{E_h} \quad \text{and} \quad N_c(L_f) = 0 \quad (18)$$

in which L_f is the distance measured from the mid-beam ($z = 0$) to the point of zero axial load of the core fibre. Using above boundary conditions, the constraints C_1 and C_2 are obtained by

$$C_1 = \frac{\sigma_c r_c\lambda}{2\sin h(\lambda L_f)} \quad \text{and} \quad C_2 = 0 \quad (19)$$

Combining Eqs. (17) and (19) yields the final form of shear stress distribution at the interface between the sericin layer

$$\tau_c(z,r_c) = \frac{\sigma_m r_c\lambda}{2\sinh(\lambda L_f)}\cosh(\lambda z) \quad (20)$$

Tensile force in the core fibre is determined by substituting Eq. (20) into Eq. (12)

$$N_c(z) = \pi r_c^2 E_C\frac{\sigma_m}{E_m}\left[1 - \frac{\sinh(\lambda z)}{\sinh(\lambda L_f)}\right] \quad (21)$$

Further, distribution of stress along the core fibre is given by,

$$\sigma_c(z) = \frac{1}{\pi r_c^2}\left[\sigma_c\pi r_c^2 - 2\pi r_c\left(\frac{C_1}{\lambda}\sinh(\lambda z)\right)\right] \quad (22)$$

$$\sigma_c(z) = \frac{E_c\sigma_m}{E_m}\left[1 - \left(\frac{\sinh(\lambda z)}{\sinh(\lambda L_f)}\right)\right] \quad (23)$$

And the corresponding strain along the core fibre is

$$\varepsilon_c(z) = \frac{\sigma_m}{E_m}\left[1 - \left(\frac{\sinh(\lambda z)}{\sinh(\lambda L_f)}\right)\right] \quad (24)$$

Therefore, the shear stress, axial stress and the axial strain of the core fibre can be obtained through Eqs. (23), (24). The axial stress's

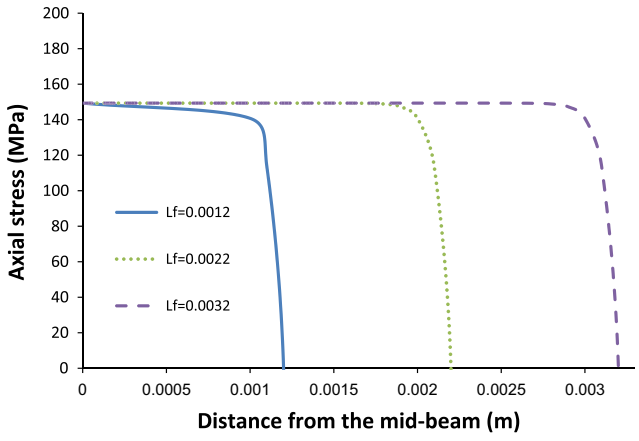

Fig. 6. Axial stress of the core fibre against the distance measured from the mid-beam ($z = 0$) with different embedding lengths.

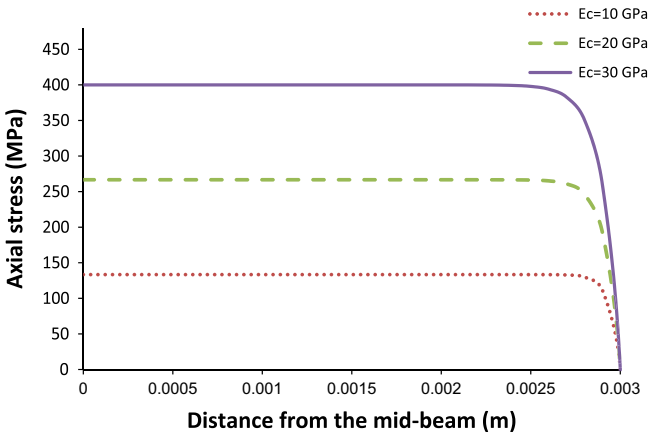

Fig. 7. Axial stress of the core fibre against the distance measured from the mid-beam ($z = 0$) with different Young's modulus of the core fibre.

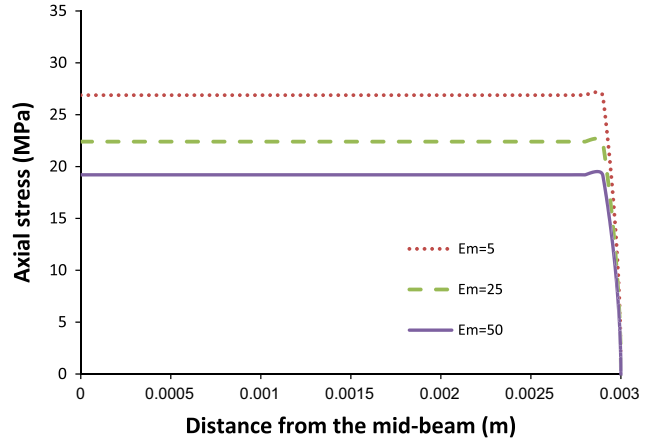

Fig. 8. Axial stress of the core fibre against the distance measured from the mid-beam ($z = 0$) with different Young's modulus of the host polymer material.

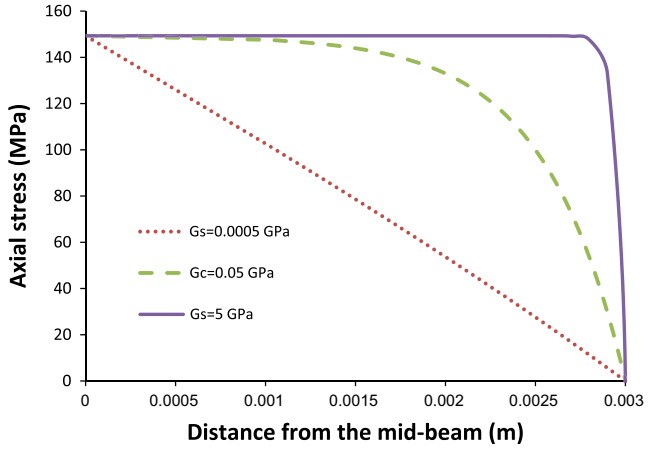

Fig. 9. Axial stress of the core fibre against the distance measured from the mid-beam ($z = 0$) with different shear modulus of the sericin.

curves of the core fibre obtained with different bonded lengths are shown in Fig. 6. Among three fibre with different fibre lengths, the length of the shortest fibre is smaller than the critical length (l_c) so that the stress cannot be transferred completely.

The axial stress of the core fibre obtained through Eq. (23) with different parameters (Young's modulus of the core fibre and host

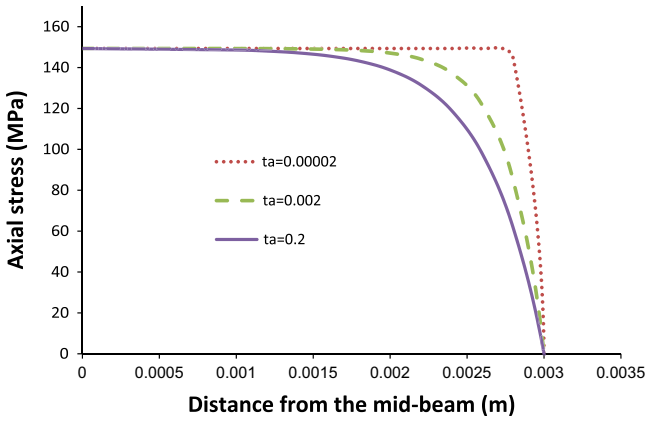

Fig. 10. Axial stress of the core fibre against the distance measured from the mid-beam ($z = 0$) with different thickness of sericin.

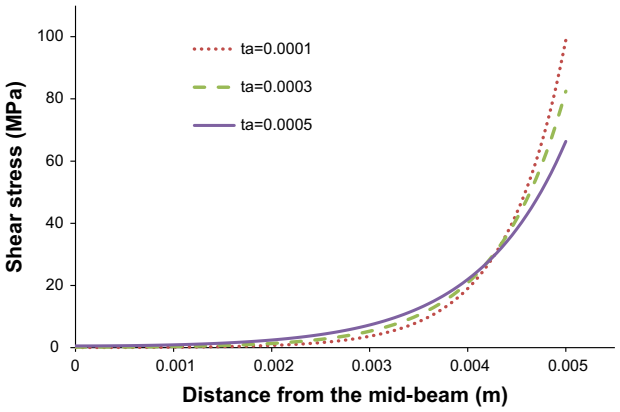

Fig. 11. Shear stress of the core fibre against the distance measured from the mid-beam ($z = 0$) with different thickness of sericin.

polymer material, shear modulus and thickness of the sericin layer) along the mid-beam are plotted in Figs. 7–11 separately. In Fig. 7, it shows that the use of lower value of Young's modulus of core fibre, longer fibre length is needed for complete stress transfer and, the axial stress is also increased. However, it can be seen that the increment in either the Young's modulus of the host polymer material or the shear modulus of the matrix, the length for stress transfer is reduced (Figs. 8 and 9). Therefore, the critical length is reduced as the young's modulus of the host polymer material or shear modulus increase. Fig. 10 shows that thicker sericin layer requires longer stress transfer length. Fig. 11 shows the interfacial shear stress against the length of the fibre with different sericin thicknesses. In the figure, it shows that the maximum shear stress of thinner sericin is higher than that of thicker ones. Besides, the fibre which coated by thicker sericin requires longer stress transfer length for complete stress transfer from the host polymer material to the core fibre through sericin. It is because much of energy is converted into shear deformation at the sericin.

8.2. Influence of moisture absorption on load transfer

In general, the degradation process can be divided into 4 steps:

1. water absorption,
2. reduction of mechanical properties,
3. reduction of molar mass,
4. weight loss,

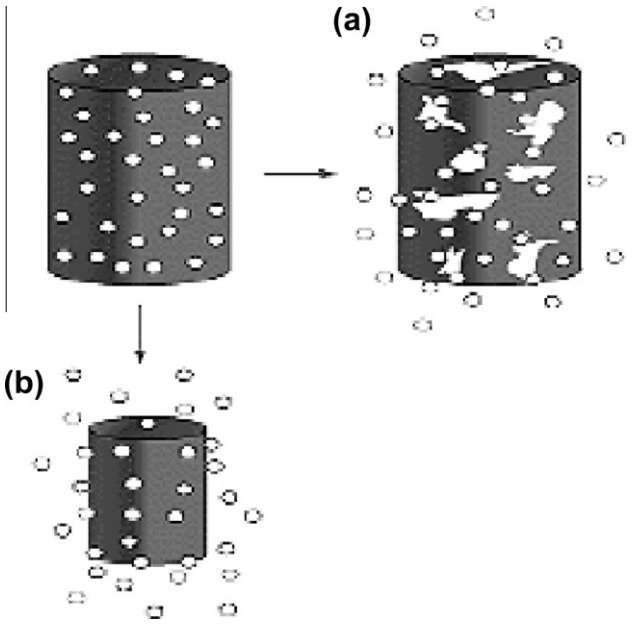

Fig. 12. The scheme of (a) bulk erosion and (b) surface erosion [1].

Different types of erosion for degradation are illustrated in Fig. 12. Bulk erosion is the process in which hydrolysis takes place at the same time throughout an entire material. During the bulk erosion, the diffusion process is instantaneous which means the ingress of water is faster than that of the rate of degradation. Hence, the simultaneous decrease in molecular weight, the reduction in mechanical properties, and the loss of mass also occur throughout the material [1]. The polymers which process the bulk erosion include PLA, PGA, PLGA and PCL. Another type of erosion is called "heterogeneous" or "surface erosion", in which mass loss is faster than the ingress of water into the bulk. Therefore, hydrolysis occurs in the region near the surface. As the surface is eroded and removed, the hydrolysis front moves through the material core. The examples of surface erosion's material include poly(ortho)esters and polyanhydrides.

Surface and bulk erosions can be classified through the comparison between the characteristic time of hydrolysis and the diffusion coefficient of water. Time of hydrolysis (τ_H) is expressed as [1]

$$\tau_H = \frac{1}{kEw} = \frac{1}{u_m} \tag{25}$$

where E and w are the concentrations of ester groups and water in the material, respectively, k is the hydrolysis kinetic constant and, u_m is the hydrolysis rate, assuming that E and w are constants in the early stage of the reaction.

Besides, if D is the diffusion coefficient of water in the polymer and L is the sample thickness, the characteristic time of diffusion (τ_D) is:

$$\tau_D = \frac{L^2}{D} \tag{26}$$

When $\tau_H \gg \tau_D$, water reaches the core of the material before it reacts, and the degradation starts homogenously. When $\tau_H \ll \tau_D$, water reacts totally in the superficial layer before reaching the core of the material. It can be assumed that $\tau_H \gg \tau_D$ is in the case of both PLA and silk fibre. Accordingly, it can be classified as the totally bulk erosion.

The effect of degradation on the strength of the material is significance. However, the constant slope of a linear elastic stage indicates that no significant variation in Young's modulus occurred during the degradation process [1]. Therefore, the change in Young's modulus during the process of a silk fibre reinforced PLA composite shown in an experimental result is assumed as mainly dependence on the moisture content. Besides, diffusion is assumed to occur instantaneously which means the moisture content in the composites is constant throughout the whole entire.

In general, moisture absorption is depended on several parameters such as temperature, diffusion rate, applied load, materials properties, system of the composite, and type of media and time. When the composite is immersed into water, the water absorption is processed, water molecules can attach on hydrophilic materials and form hydrogen bonds. In the case of load transfer analysis, moisture absorption can alter the Young's moduli of constituents of the composite, so as the axial stress and strain in a fibre. The Nissan's model [2] represents that the elastic modulus is as a function of moisture

$$E = E_0 e^{(a-bm)} \tag{27}$$

where a and b are material constants and m is the moisture content.

As the change of moisture content is depended on time, it can be measured by the change of weight of the composite. Two cases are discussed on the moisture absorption at different situations,

1. Moisture absorption affects the Young's modulus of a host polymer material (Only the Young's modulus of host polymer material is changed).
2. Moisture absorption affects the properties of host polymer material and core (Young's moduli of host polymer material and core fibre are changed based on the moisture absorption).

8.3. Moisture absorption affects the Young's modulus of a host polymer material

In order to specify the effect on the moisture absorption in relation to the axial stress between the sericin and the core fibre during the degradation process, certain assumptions must be addressed. The changes of the Young's modulus either of the host polymer material or host polymer material and core fibre with time are considered until the moisture content is saturated. Degradation can be classified into a four step process as mentioned previously. In this section, only the step 1 of degradation (moisture absorption) is concerned. Therefore, the weight change of the material is assumed dependent on the amount of moisture in the material. Besides, moisture saturation is regarded as the maximum amount of water particles that can be contained within the composite. The levels of saturation for any given type of material can be varied because of different voids content. These voids would contain water and speed up the moisture diffusion and degradation. Therefore, it is assumed that there is no predictable contrived void exists in the composite.

The process of the water absorption is under the condition that a composite is immersed into the water bath. As the atmosphere contain water which diffuse into the composite before immersing it into the water, the initial moisture content is set to be non-zero. Fig. 13 shows the change of Young's modulus of the host polymer material measured from (a) the change of moisture content of host polymer material and (b) time. The results show that the Young's modulus increases with time. This result may reflect the ability of bounded water to enhance chain mobility. The effect of the change in the Young's modulus of host polymer material induced by the increase of moisture content on the axial stress depending on time is shown in Fig. 14. Fig. 15 shows the effect on the axial stress to the Young's modulus of host polymer material. The figures indicate that the increment in the axial stresses depends on an

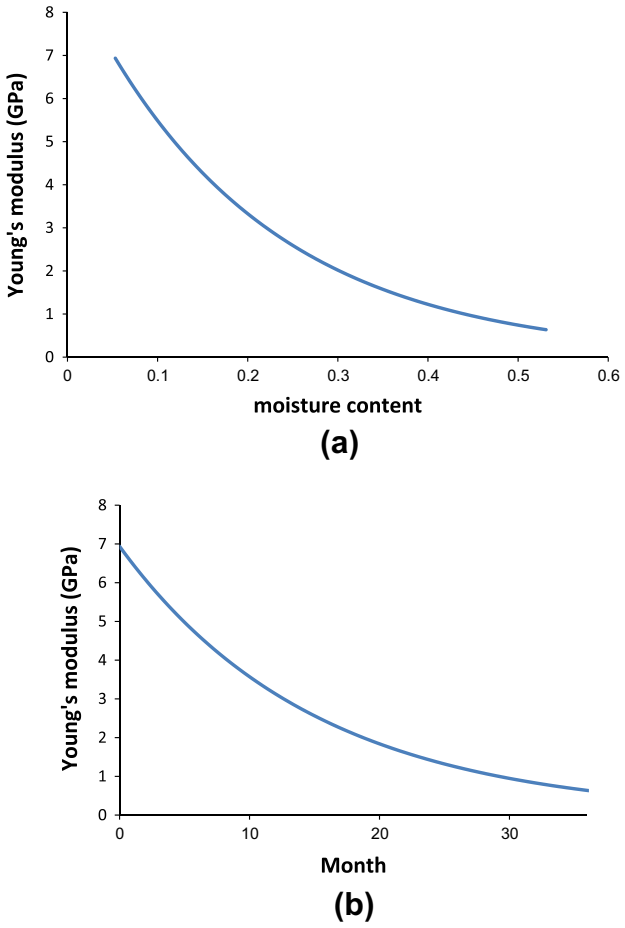

Fig. 13. The Young's modulus of host polymer material calculated from (a) the change of moisture content and (b) time.

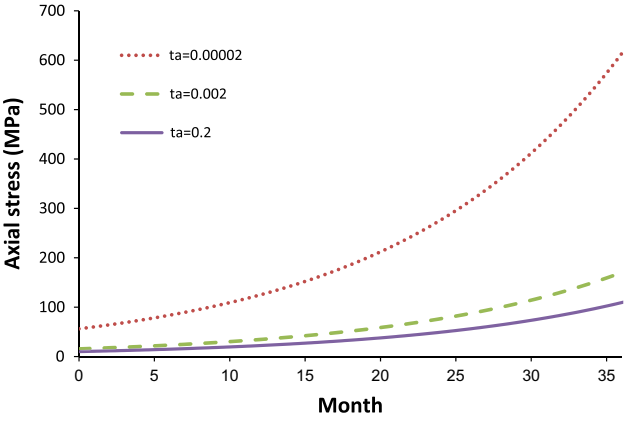

Fig. 14. Axial stress between the sericin and the core fibre calculated from (a) the increase in moisture content based on time with different thickness of the sericin.

increase in immersion time of the composite as the Young's modulus of host polymer material is changed.

8.4. Moisture absorption affects the properties of host polymer material and core fibre

In the case of both host polymer material and core fibre absorb moisture and thus change their Young's modulus. It is assumed that their dimensional change (swelling) is not significant. Fig. 16

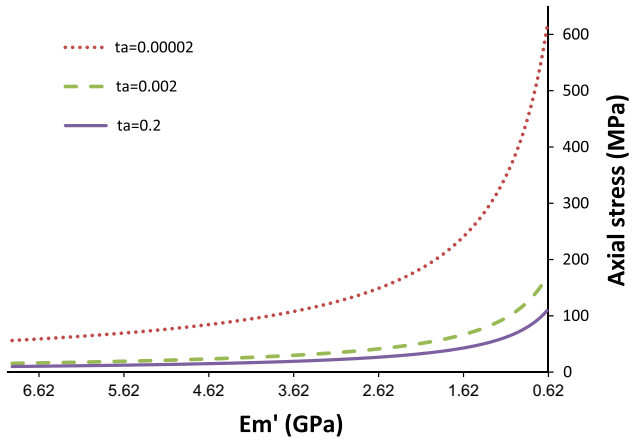

Fig. 15. Axial stress between the sericin and the core fibre calculated from (a) the change of Young's modulus of host polymer material based on the increase in moisture content with different thickness of the sericin.

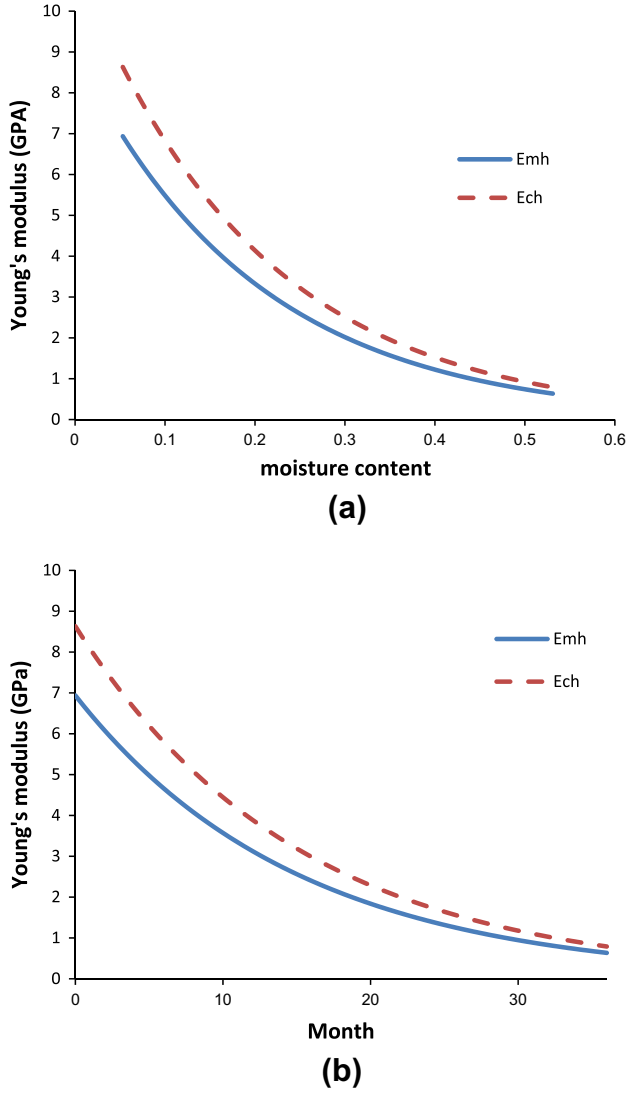

Fig. 16. The Young's modulus of host polymer material and core fibre measured from (a) the change of moisture content of host polymer material and (b) time.

shows the Young's modulus of host polymer material and core fibre measured from (a) the change of moisture content of host

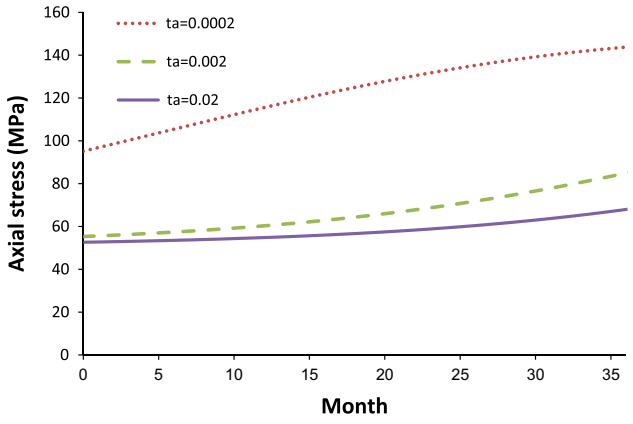

Fig. 17. The effect of the moisture content of host polymer material and core fibre on the axial stress in the fibre depending on time.

polymer material and the core fibre and (b) time. Fig. 17 exhibits the effect of the moisture content of host polymer material and core fibre on the axial stress depending on time. Fig. 17 shows the rate of increment in the axial stress with time is smaller than the result shown in Fig. 14. In Fig. 17, as both of the host polymer material and core fibre absorb moisture, the effects on the axial stress by the change in Young's moduli of both host polymer material and the core fibre are compensated.

9. Conclusion

Silkworm silk fibre is a renewable protein biopolymer which is not only valuable in the textile industry, but also for the medical application because of its superior mechanical properties and biocompatibility. Preprocessing of silk commonly known as degumming is an essential process to obtain an ideal fibre because of its fibre structure. Silk degumming process scours the sericin and some impurities from silk fibres. This paper addresses a comprehensive review on different types of degumming process and their effects to the silkworm silk fibre. Theoretical analysis also retrieves that the stress transfer properties is also affected by the effectiveness of the degumming process. Degradation of the surrounding matrix (biodegradable polymer) would also influence the result properties of silk fibre reinforced polymer composites.

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