Poly(lactic acid)-silkworm silk fibre/fibroin bio-composites: A review of their processing, properties, and nascent applications

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Abstract. The past few decades have witnessed an upsurge in the utilization of natural fibres in green materials advancement. This rise can be linked to calls from stakeholders, around the world, on the issue of sustainability and eco-friendliness. A shift from the utilization of non-biodegradable sources to renewable sources is a current area of intense research, which also stimulates industrial attention. Amongst the creations of nature, silkworm silk fibres have attracted considerable interest from materials science researchers. Inferable from its amazing biocompatibility, bioresorbability, and biodegradability, silkworm silk strands have been used in the improvement of polylactic acid/silk fibre biocomposites. Hence, with the continued use of these biocomposites in industrial and biomedical applications, it has become necessary to look at the systematic progress made in its processing, overall property improvements, and various applications. This review article also presents the challenges facing the advancement of this biocomposite, the suggested solutions and concludes with anticipated future trends.

Keywords: biocomposites, poly-lactic acid, silkworm/silk fibres, biomedical applications, industrial applications

1. Introduction

The growing environmental and sustainability concerns connected with the utilization of composites reinforced with artificial fibres have prompted a significant spotlight on green materials innovation. Materials researchers have done substantial investigations in the use of natural materials for the development of high-performance materials because of their points of interest, such as easy processability, light-weight, biodegradability and low-cost amongst others

[1]. Some high-quality animal-based fibres, such as silk, wool, and chicken feathers, have been utilized as fibre reinforcements [2–4]. The concern is not only limited to the environment but also bio-engineered materials. The need to develop biocompatible, biodegradable, light-weight and less stiff medical implants, has led to the concept of biomaterials. For example, in bone replacement or fixes, stainless steel and titanium have been used as bone plates for many years because of their exceptional biocompatible

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properties. Be that as it may, the utilization of these materials for a long-term bone repair frequently requires multiple surgical operations to remove the plates and other fasteners, and this often causes pain or inconvenience to the concerned patient. Therefore, it is imperative that stiff materials are utilized for making plates for bone repairs [5]. Composites used in this sense can be based on synthetic and natural materials. Typically, for such biocomposites, a biodegradable polymer (natural or synthetic) and a natural fibre/filler are combined [6].

The silkworm silk fibre (also called silk fibre), which is a reinforcing phase of the bio-composite in the current review, has been traditionally used for decades, as biomedical sutures, tissue scaffolds and in textile production [6–9]. Silk is commonly characterized as protein-based material that is spun into fibres by some lepidoptera larvae, for example silkworms, arachnids, scorpions, bugs, caterpillars, and flies [10]. Silk proteins are usually produced inside specialized glands after biosynthesis in the epithelial cells, trailed by secretion into the lumen of these glands, where the proteins vary broadly in composition, structure, and properties, contingent upon the particular source and where it is cultivated [10]. The silk fibres considered in this review are the *Tussah* silk, originating from the species of wild silkworm called *Antheraea pernyi* (*A. pernyi*) and the *Bombyx mori* silk fibres, artificially cultivated from domesticated mulberry silkworm, which are usually white-toned. The latter is the most broadly characterized silk fibre, and it is obtained from a cocoon, delivered by the domesticated mulberry silkworm, *Bombyx mori* and from spiders (*Nephila clavipes* and *Ara-neus diadematus*) [10, 11]. The production of silk

fibres from the domesticated mulberry silkworm is called *sericulture*.

In sericulture, the silkworms lay hundreds of eggs (between 300–400) at a time, which are carefully stored in hygienic and warm conditions for hatching. A hatched larva is between 60–70 mm long [12]. The subsequent stage is the feeding period, where the larvae become 10 000 times heavier than the weight during the hatching period [13]. In the third step, the silkworm stops eating, and they get ready to spin the cocoons of silk fibres [14]. This is followed closely by a reeling process, where all the cocoons are separated by placing them in hot water, and the silk fibres are obtained by simply unwinding them in the form of threads. [12, 14]. The sericulture process is presented in Figure 1a.

The acquired silk fibre is a natural protein fibre (also called silk fibroin), which is biodegradable and can be either semi or highly crystalline with a well-aligned structure [2, 15]. Average crude silk is composed of 22–25% sericin, 62.5–67% fibroin, water and mineral salts [16]. The silk fibre has a gland with two cores of fibroin appearing as a paired organ and encompassed by a cementing sericin layer in a structure known as ‘bave’ [16, 17]. A SEM micrograph of the cross-section of a silk filament can be seen in Figure 1b. On the one hand, fibroin is a single protein that does not dissolve in water, and it has a fibrillary structure. On the other hand the sericin on the fibre has an amorphous structure, and this gummy protein dissolves in the water more than the fibroin [17]. Its crystallinity, crystalline, and amorphous orientations can be characterized by X-ray and electron scattering techniques. Silk fibre possesses higher tensile strength than some synthetic fibres *e.g.* Kevlar, good ductility

Figure 1. (a) Production of silk fibre from rearing of domesticated silkworm cocoon [14]. (b) A cross-section of a silk fibre filament showing the two fibroin cores surrounded by a sericin layer. Reprinted from [41], with permission from Elsevier.

and excellent fracture toughness [18–20]. Many of its crystalline phase-related parameters correlate with the tensile mechanical characteristics of silkworm silk fibre [15].

The environmental challenges related to the disposal of conventional plastics have prompted the introduction of biodegradable polymers during the 1980s, and it was designed to degrade upon disposal, by the organic activity of microorganisms [21]. Biodegradable polymers offer greater advantages and possibilities due to their good biocompatibility, biodegradability, tailorability, bioresorbability, good mechanical properties, high purity level and easy moldability [22]. Their degradation products have low or negligible toxicity; they are metabolized, and eliminated easily when used *in-vivo* [22]. A commonly used biodegradable polymer is poly (lactic acid) (PLA). Poly (lactic acid) (PLA), also called polylactide are synonymous with the group of aliphatic polyesters, derived from α -hydroxy acids, which is chiefly acquired from starch and sugar. PLA is produced either by microbial means [23] or chemical synthesis [24, 25]. A typical illustration of PLA production by microbial route, utilizing starch obtained from feed-stocks, such as; beet sugar, molasses, and barley as potential starting substrates is presented in Figure 2a [23, 26]. Likewise, chemical synthesis is employed to obtain PLA from lactic acid through polymerization processes such as; polycondensation, ring-opening polymerization, and direct methods (*e.g.* azeotropic dehydration). The direct method and ring-opening polymerization are the most generally used methods [24, 25, 27]. A typical chemical synthesis route is presented in Figure 2b. Since PLA is compostable and derived from sustainable sources, it is viewed as a promising material to decrease environmental and ecological issues [28]. Poly(lactic acid) (PLA) and its copolymers are the most broadly used engineered biodegradable polymers in medicine [6, 21, 29]. It takes months to years for PLA scaffolds to lose their mechanical integrity, either *in-vitro* or *in-vivo* [30]. During biodegradation, PLA degrades into lactic acid, which is finally metabolized and excreted from the host as carbon dioxide and water. It offers, particularly, expanding commercial interest since it is currently conceivable to attain high molecular weight PLA production [5]. Furthermore, PLA can maintain its mechanical properties, even under a humid environment without suffering rapid hydrolysis and thus, PLA can find use in structural applications [5, 30]. Hence, its wide usage

as matrices in the development of PLA/silk fibre biocomposites.

A handful of research works has been conducted in the area of silk fibre-based biocomposites and PLA-based biocomposites. For the former, some works include; silk/chitosan blend [31, 32], silk/poly(butylene succinates) PBS biocomposites [33], and silk fibroin/polysaccharide-sodium alginate blend sponges [34]. In the case of the PLA-based biocomposites, some works include abaca fibre/PLA [35], bamboo fibre/PLA [36], microcrystalline cellulose/PLA [37] and kenaf fibre/PLA [38], composites amongst many others. Several research accomplishments in the development of the two aforementioned composites have provided a conceptual framework for silk-based polymeric composites to be a promising candidate for a wide variety of applications. Past investigations on the effect of silk fibres on polymeric materials, drew the attention of researchers, such as Cheung and coworkers [5, 6, 39], Ho *et al.* [2], Mei *et al.* [40], to the potentials of silk fibres, thereby giving these researchers, the motivation to develop fully, biodegradable PLA/silkworm silk fibre biocomposites. In addition, various studies on their structural, thermal, microstructural, and biodegradation properties have been conducted [2–6, 10, 21, 39]. It is the aim of the present article to present a review of their processing routes, the properties highlighted above, and the nascent areas of applications of PLA/silkworm silk fibre biocomposites. As an addendum, limitations, hindering the large scale development of these biocomposites and proposed solutions, are also discussed.

2. Processing/fabrication techniques

2.1. Criteria for selection of processing techniques

In order to acquire a defect-free product, it is important to choose the most suitable preparation strategies. Factors taken into consideration by product designers include; the area of the intended application, the desired mechanical and thermal properties, the nature of raw materials to be used, the size and shape complexity of the final product (*i.e.* part design), and the manufacturing parameters (including production rate and cost) [41]. The composite size and shape complexity are important factors in selecting the processing techniques. For small-sized materials, injection, compression and melt compounding techniques, can be employed since

they are high-volume moulding methods and can provide high throughput [42–45]. For large non-complex products, open moulding processes (e.g. resin transfer moulding) are usually employed. It is employed for products such as; truck bumpers and fenders, spas, sandwich structures found in boats and modern aircraft [43, 45]. It also includes a vacuum-assisted version, and both processes can combine either hand lay-up or spray-up. Hand lay-up or

spray-up can also be used in isolation for composite fabrication [46–48]. Matrix type, the viscosity of the polymer and processing temperature should be considered when choosing an appropriate composite fabrication technology. Additional processing considerations for enhanced performance of fibre-reinforced composites include; fibre-matrix interaction, fibre-to-resin ratio, fibre form, orientation and architecture [49].

2.2. Silkworm silk fibre preparation

A foremost disadvantage of natural fibre-reinforced polymer composites is the inherent incompatibility between the hydrophilic natural fibres and the hydrophobic polymer matrices. This results in the undesirable properties and performance of the composites. The polymer viscosity is sometimes very high, thereby making it incapable to wet the fibres completely. Consequently, it is important to alter the fibre surface by employing chemical modifications in order to improve the interfacial adhesion between fibre and matrix [37]. In silk fibre composites, the difference in surface characteristics was observed to be the significant reason for poor adhesion between the fibres and matrix. This incompatibility originated from the hydrophilic nature of the silk fibre surface, whereas the polymer surface is often, hydrophobic. On that note, fibres debond and the mechanical strength of the composite decreases. Silk fibres used in this manner could not improve the composite property [50]. Consequently, various interfacial upgrades such as; chemical alkali treatments *e.g.* mercerization [46, 51], physical methods (corona discharge) [52] and silane coupling agents [53], amongst others, have been employed to overcome this difficulty. Also applied, is the environmentally-friendly plasma treatment by Chaivan *et al.* [54] for the improvement of surface of silk fibre and its hydrophobicity without altering its bulk properties. However, the high cost of plasma treatment has so far restricted its wide usage in the industry. Amongst them all, chemical treatment and in particular, degumming is one of the regularly utilized chemical treatments in fibre-reinforced plastics industry. Degumming involves sericin hydrolysis, breaking amino acid groups into small molecules, and final dissolution of the sericin in water [55]. It increases the number of possible adhesion sites since the surface of the fibre is better exposed upon treatment. Following such treatment, the fibre becomes soft and glossy [56].

As mentioned in the introduction, the upper layer of the silk fibres consists of sericin, and this can be removed by degumming without causing any harm to the fibre itself. Sericin removal is done by placing the fibres in a liquid media. It is discovered that the tensile properties of the fibre increase on the removal of the sericin from the fibre. Some degumming processes, such as: water degumming, soap, degumming by soap-alkali boiling, enzymatic processes, boiling in the acidic solutions, and even genetic modifications have been developed. By using boiling

Figure 3. Surface of silk fibres degummed for (a) 0 min (neat sample) (b) 15 minutes, and (c) 60 minutes. Reprinted from [11], with permission from Elsevier.

water, Ho *et al.* [11] studied the effect of degumming time on the tensile properties of silk fibres at different times ranging from 15 to 60 minutes. They discovered that increasing degumming time leads to further fibre damage as the hot distilled water causes the removal of sericin coatings and fibroin loss. For the neat fibre

samples which were not treated with hot distilled water, their surfaces appeared fairly rough due to the presence of sericin coating, as seen in Figure 3a. On the other hand, the fibre sample degummed for 15 minutes exhibited the best tensile property improvements. Its surfaces appeared smooth, and no fibroin damage was found, as observed in Figure 3b. For fibre samples treated after 30, sometimes up to 60 minutes (Figure 3c), though the sericin was removed completely, fibrillation occurred due to longer treatment time.

Strong alkali solutions such as sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) confers relatively harsh irritation to the surfaces of silk fibres [55, 57]. Based on that, Ho [51] utilized a weaker NaHCO_3 alkaline solution to treat silk fibres chemically. When compared with the tensile properties of silk fibres degummed by hot water and strong alkaline solution [19, 55], the NaHCO_3 showed no severe reduction to the tensile properties of the silk fibre. In order to prove the effectiveness of the surface treatment methods on bonding improvement between the fibre and PLA matrix, Ho [51] performed a micro-bond test to measure the interfacial shear strength (*ILSS*) of the composites. The composite with degummed silk fibres exhibited better *ILSS* when compared to the composites with raw fibres, since the treatment led to increased friction and enhanced mechanical interlocking between the fibres and the PLA matrix. Although the fibre treated with hot water exhibited higher *ILSS* (37.8 MPa) when compared to the NaHCO_3 treated fibre (30.1 MPa), the latter still exhibited better tensile strength when compared to the former. In this situation, a conflict arises between higher *ILSS* or tensile strength and the final selection of the best chemical treatment would require a compromise. Describing another degumming process, but using soap-alkali as one of the constituents of the ‘de-gummer’, silk fibre is immersed in a container consisting of a fibre-to-liquor ratio of 1:40. Also, 7 g soap and 1 g soda per liter were added to the solution, which was then boiled for one hour. The fibre was then thoroughly dried in order to remove the residual moisture.

Yukseket al. [56] carried out degumming processes through both the conventional (soap-alkali boiling) and ultrasonic energy methods with three different natural soaps (laurel, olive, and turpentine). With credit to the ultra-sonication process, the authors discovered that the degumming process performed with

turpentine soap, yielded positive outcomes in terms of weight loss, whiteness degree, and mechanical properties. The sericin layer available on the exterior surface was expelled totally in the ultrasonic energy method, where turpentine soap was used as compared to the conventional method. In addition, the fibrillar structure of the silk fibre turned out to be progressively obvious. Overall, they found the ultrasonic energy method to be energy-saving and economical. In present times, when efforts are to diminish the dangers of environmental pollution from such chemical wastes, the ultrasonic method holds promise for the treatment of silk fibres, thus guaranteeing environmental sustainability. Generally, soap-alkali boiling and chemical treatment, previously described, is recommended; however, it is not environmentally-friendly considering the necessary chemical waste disposal. Hence, the enzymatic process and even the ultrasonic method are preferred [56, 58]. The selection of the right silk fibre treatment boils down to a trade-off between the intended properties desired, the fibre source, the availability of the treatment method, costs and environmental considerations.

2.3. Processing/fabrication of PLA/silkworm silk fibre composites

The majority of the PLA/silk fibre composites developed are fabricated by using a process similar to those used for traditional fibre-reinforced polymer matrix composites (FRPMCs). In this regard, there are broad classes, known as the open mould and closed mould processes. The processing of PLA/silk fibre composites, as reported in the literature, is also classified broadly into the open mould process-hand layup, hand spray-up, autoclave, and the closed mould process-the melt compounding-injection moulding combination. The unconventional additive manufacturing route is also discussed to shed light on how it has been implemented in the development of PLA/silk fibre composites

2.3.1. Two-step melt compounding-injection moulding process

The melt compounding-injection moulding process is a combination of two fabrication steps. The initial step is the compounding of the raw material, which is followed by the injection-moulding step in an injection moulding machine. The compounding of a polymer is a common process in which a pre-defined measure of the blend, which contains polymer melt

and fibre is constrained into mould cavities. This system is, likewise, suitable for polymer composites that can not be handled by solution blending, owing to their insolubility in regularly utilized solvents. It, is likewise, a technique free from the use of solvents, and by virtue of that, fibres can be added to polymer matrices in the molten state [59]. Moreover, the operation is environmentally-friendly, direct, industrially and commercially suitable. The equipment which is used in this technique consists of an extruder, two roll mill, and an internal mixer. The polymer matrices used in this process are mostly in the form of pellets, such that with the chopped fibres, they feed individually through a funnel-shaped feed hopper into a heated compression barrel, consisting of rotating single or twin screw. The purpose of the heating the barrel is to transform the pristine polymer pellets into a viscous melt, which can be plunged through a sprue nozzle and forced into closed metal-mould cavities of desired shapes and dimensions. The mould is tightly clamped against the injection pressure, where the polymer solidifies, holding in place, the orientation and initial distribution of fibres. The composite is then removed from the closed mould of the desired shape after it has sufficiently cooled [41].

This technique can be done either on an industrial scale or a laboratory scale by using a Rapra Single-Screw Extruder as demonstrated by Daramola *et al.* [60]. Similarly, Zhao *et al.* [2] fabricated PLA/silk biocomposites by melt compounding with a Thermo Haake MiniLab twin-screw micro extruder at 180 °C. For them to produce dumb-bell specimens, they transferred the mixture to a Thermo Haake, a small scale injection-moulding machine in which the barrel and the mould temperature parameters were pre-selected. A major advantage of this technique is that it is rapid and inexpensive. Silkworm fibres, which are used in this technique, are cut gently into short fibres of a critical length. An example is the work of Zhao *et al.* [2] in which they chose 5 mm as the optimum length for the short silk fibres to be incorporated in the PLA matrix. This critical fibre length criterion is very important since it ensures that stress is fully transferred from the matrix to the silk fibre and that the silk fibre can operate to its full loading capacity, assuming good interfacial bonding is satisfied. Therefore, it is necessary to determine the critical length of the fibre before compounding carefully and injection moulding processes are performed in a 2-step operation. It is entirely expected that loading-up a polymer matrix

with high fibre content would increase the stiffness and strength of the composites developed. However, in practice, the injection moulding process would constrain the amount of fibres that can be injected because of fibre cluttering/attrition, limited gate and sprue of the extruder and increased viscosity of the fibre/polymer mixture [41]. In general, in order to guarantee a seamless injection moulding process, obtain optimal properties of the resulting natural fibre composites and avoid the development of residual stress, which causes warpage, stress cracking and long-term distortion, the process, and geometrical/material parameters should be optimized. Process parameters, such as; the melt temperature, injection and screw speeds, injection pressure, and the mould temperature should be predetermined in order to obtain the best optimum condition for the injection moulding process of PLA/silk fibre composites [51]. A possibility of using a single step injection moulding process has also been explored for PLA/raw continuous long silkworm silk fibre composites [61].

2.3.2. Compression moulding

Compression moulding is a large-scale fabrication method, in which heated hydraulic presses, with precisely matching metal moulds, are used. The matrix and reinforcing materials are at first mixed, and the blending and feeding steps can be automated. Parts with short cycle times in long series are the typical compression moulded products. Examples of products from this manufacturing technique are automotive parts, covers, and insulating parts [45]. Compression moulding offers several advantages, *e.g.* minimal degradation of the resulting composites due to lower shear rate, and a low amount of material waste [62]. Silk fibre composite moulded products with large surface area, good mechanical properties, and performance can be produced by this technique. Unidirectional silk fibre-reinforced PLA composite was prepared by Memon and Nakai [63]. The parallel yarns of the PLA and silk fibres were wound and consolidated. Elastic modulus improvement was achieved, and their study can serve as a recommended manufacturing guide, with respect to the material selection and process optimization for compression moulding of unidirectional bio-composites.

2.3.3. Manual lay-up

Manual or hand-lay up in a suitable metal mould can also be used to prepare these materials, in which the

polymer melt is poured onto the silk fabric inside the mould and a metallic roller is used to aid impregnation, expel trapped air and excess resin. This method can also be combined with a vacuum bagging system, which aids in the removal of air from the polymer melt by using suitable vacuum pressure, thus avoiding subsequent voids that may form in the finished part. Mangat *et al.* [64] utilized the hand-lay manual approach, and they were able to achieve considerable distribution and thickness of the inserts in PLA/silk fibre hybrid composites. However, they recommended the use of an automatic fibre placement system in order to achieve better uniformity and thickness. Casting has also been used for the preparation of silk fibre composites [62].

2.3.4. Additive manufacturing of PLA/silkworm silk fibre composites

The interest in additive manufacturing abilities has risen due to its ability to produce functional finished parts with near-net shape and low material waste. Polymers and metals are considered as the mainstream materials for additive manufacturing (also referred to as 3D printing), with composites as the emerging areas of interest [65]. In spite of the fact that 3D printed parts have so many advantages over the conventional methods, some printed polymeric parts often suffer from poor mechanical characteristics, *e.g.* low strength, which in turn, limits their applications in fully functional and load-bearing components [66]. Be that as it may, the optimization of the operation parameters, such as build orientation and feed rate, has been explored for improving the mechanical properties of thermoplastic parts in a couple of studies [67]. Notwithstanding the parameter optimization, 3D printed thermoplastic parts still exhibit lower properties, when compared to those obtained by conventional polymer processing methods, *e.g.* compression or injection moulding [68]. In addition, the quality of fully printed parts regarding dimensional accuracy and surface finishing is affected by part multi-faceted design, the corresponding print path and the differential cool-down, and solidification of the individual raster, among other variables. These downsides have restricted the wide industrial utilization of 3D printed thermoplastic parts [66]. On that note, improving the mechanical properties of plastic materials would require reinforcement with fibres in order to produce functional and structural properties that are non-attainable in the matrix alone.

For polymer and polymer reinforced components, various techniques, such as; Stereo-lithography (SLA) or Laminated Object Manufacturing (LOM) with photopolymer liquids as feedstock [69], Selective Laser Sintering (SLS) in which polymer powders are used as feed materials [70], and Fused Deposition Modelling (FDM) [71], have been developed.

Fused Deposition Modelling (FDM) is one of the 3D printing innovations that is broadly used for polymer composites [66, 72–75]. It is suitable for producing polymer matrix composites because of the possibility to use multiple nozzles with the loading of different materials, thus leading to short manufacturing times. A criterion for its use requires the feed material to be in filament form. At times, a homogenous dispersion and the removal of formed voids during manufacturing can be a bottleneck. In addition, a compromise in the melt viscosity of the polymer is required, such that it is low enough for extrusion and high enough for structural rigidity [72]. Despite these criteria and constraints, FDM offers the advantages of low cost, high speed, simplicity, and simultaneous deposition of diverse materials [75, 76]. FDM printers operate by controlled extrusion of filaments, as shown in Figure 4a. In this technique, the filaments feed into an extruder and melt into a quasi-liquid state at the nozzle, enabling it to be extruded layer-by-layer onto the build platform, where layers are fused to solidify into final parts. This extruder is normally mounted onto a CNC (Computer Numerical Control) gantry, enabling complex geometrical patterns to be printed. Once a layered pattern is complete, either the printing platform drops down, or the extruding orifice rises by the layer thickness to deposit a subsequent layer. This way, 3D objects can be fabricated through the progressive deposition of layers [72, 77]. A typical example of a 3D printer and the PLA filament formed is shown in Figure 4b.

The introduction of silk fibre/filament into this innovative field is due to the remarkable enhancements and expansion in properties of the subsequent 3D printed materials that exhibit excellent properties with multipurpose applications. Specifically, there is increasing enthusiasm in the development of high-performance composites, suitable for 3D printing that can be achieved via the introduction of fibres with unique properties, *e.g.* silk. Silk fibre possesses excellent mechanical properties, which make it a great candidate for the reinforcement of several polymers [78]. Shubra *et al.* [79] in their study, reported that

Figure 4. (a) Schematic of the FDM technique. Reprinted from [75] with permission from Elsevier (b) FDM printer with a PLA filament (at the Federal Institute of Industrial Research Oshodi, Nigeria).

the mechanical strength of silk/polypropylene materials is greater than that of jute/polypropylene composites. Recent reports revealed that 3D printing had found great industrial applications, especially in biomedical engineering. In all likelihood, PLA/silk composite cannot be used to replace metals, but for bone fracture, it could be the perfect material. Steel plates have been a major medical tool, used by surgeons for fixing fractured bones. However, the challenge encountered in this has been that the steel blocks new bone cells from repairing the fracture [80].

In 2008, Professor Alan Lau's group at the Hong Kong Polytechnic University, combined silk fibres with PLA and found that the polymer became stronger and harder, which was credited to the increase the Young's modulus of the composite due to silk fibre incorporation. They additionally indicated that the material was able to retain its biodegradability and concluded its viability and potential as a tissue engineering material [6]. In orthopedic surgery, 3D printing was chiefly applied in the areas of anatomical models for diagnosis and surgical planning and customized implants and cast [81]. With the 3D printed model, the pre-operative circumstance of complex fractures is clearer to the surgeon. The model also furnishes the surgeons with the information required for effective pre-operative planning and realistic simulation. Furthermore, the 3D printing technique enables

the production of patient-specific implant and cast that precisely matches the patient's body contour, for instance, the reconstruction of a range of bone fractures and pelvic bone resection [82].

Yeon *et al.* [74] were able to use 3D printed (silk/PLA filament) parts for the treatment of bone fracture without drilling a hole in the bone. Given their evaluation of the characteristics of each bone clip, they developed a PLA/Hydroxyapatite(HA)/silk composite bone clip, which showed similar mechanical property, but with superior biocompatibility when compared to PLA and PLA/HA clip and they concluded that the 3D printed part improved the regeneration capacity with high biocompatibility. Current research in this area was reported in an article titled 'A soft touch for mending broken bones' as found in the 2017 Swinburne Research Impact Magazine, where the team of Professor Alan Lau, who is now at Swinburne University of Technology, Australia is looking to creating surgical pins and cages from PLA/silk composite [80]. Future research is envisaged to encompass the fabrication of 3D printed PLA/silk implants and the necessary clinical trials of these parts. If successful, it could become a good substitute as medical implants in humans [83]. A summary of the various fabrication techniques for PLA/silkworm fibre biocomposites and their key property findings is presented in Table 1.

Table 1. Summary of various fabrication methods of PLA/silkworm silk composites and their key properties findings.

PLA/silk fibre composites	Fabrication method	Key findings	Ref.
PLA/silk fibre	Two step*	Optimal fibre length and weight content selected for better properties are 5 mm and 5 wt% respectively leading to a maximum hardness of 19 HV. Increasing fibre length and content led to poor mechanical properties.	[6]
PLA/5 wt% silk fibre	Two step*	Melt compounding at 180 °C and the injection mould and barrel temperatures maintained at 200 and 45 °C respectively. Maximum tensile strength of 70.6 MPa.	[2]
PLA/unidirectional silk fibre	Compression moulding	Optimum compression temperature (185–195 °C). At high temperature, strength decrease as silk fibres deteriorate and the melt resins flow out from unidirectional composite due to the macroscopic flow of low viscosity resin.	[63]
PLA/5 wt% tussah silk	Two step*	Elastic Modulus in the range of 1.833–2.439 GPa. Strain and peak stress decreased from neat PLA to the reinforced sample with values of 4.575% and 61.25 MPa respectively.	[39]
PLA/5 wt% tussah silk	Two step*	Fibres in chopped form of 5 mm average length to prevent coiling with screws or plastic stretching during injection. Modulus ranges between 3.21–4.08 GPa. Tensile strength (70.73 MPa) and strain (5.5%) decreases by 0.2 and 30% respectively from the neat PLA to the PLA/silk fibre composite sample	[87]
PLA/waste silk laminate	Hand-layup and fused deposition modelling	Waste silk fibre layers manually inserted in PLA and laminated structures are 3D-printed. 2-laminates formed with infill density of 20 and raster angle of 0/90°. Hand layup led to non-uniform inserts. Flexural peak strength (16.03–24.58 MPa) and Shore-D hardness (68.83–79 HD)	[64]
PLA/silk/ hydroxyapatite	3D printing	Printed in form of bone clips of 0.1 mm layer thickness at 170 °C nozzle temperature and printing speed of 20 mm/s. No significant effect of silk on compressive strength of the composite as it was similar to the neat PLA.	[74]

*Two step refers to the melt compounding-injection moulding process

3. Mechanical properties of PLA/silkworm silk fibre composites

Over the years, certain polymers, *e.g.* poly(lactic acid) (PLA) have been designed to undergo controllable degradation as well as having the option to provide appropriate mechanical strength for implant applications. These polymers have been proposed in lieu of metals for orthopedic fixators, but their mechanical properties are inferior to bones [6, 84, 85]. Hence, there is a quest to improve these properties via reinforcing.

3.1. Tensile properties

The properties of the starting material (pristine PLA) during manufacture, usually play a crucial role in the final properties of the composite after fabrication. Cheng *et al.* [84] reported that when PLA is fabricated as a porous scaffold, its mechanical properties drop significantly and may not provide sufficient strength for load-bearing applications. Likewise, the pre-treatment of the silk fibre plays a role in the final mechanical properties of the composites part where it would be employed. As stated in the section on silk fibre preparation, degumming is a surface modification process, which allows a wide control of the silk fibre's properties, thus allowing their application in the production of novel bio-composites with unique/specific mechanical properties. Suesat and Ujjin [86]

investigated the effect of degumming conditions on the mechanical properties of PLA/silk blended fabrics. The fabric was designed with the silk yarn in the warp direction and PLA yarn in the weave direction. After initially treating the PLA and silk fabrics in a bath at varying degumming temperatures and pH, they recommended a bath containing 10 g/l Sera Wash (wetting agent) at pH 10, liquor ratio of 20:1, and a temperature of 70 °C for 15 min as the optimum conditions to prepare PLA and silk fibres to be used for the development PLA/silk blended fabric. Following the drying of the degummed composite fabric at room temperature, a measurement of the tensile strength and stiffness was performed. In each of the composite fabric tested, an improvement in tensile strength after degumming was evident. The density of each fabric also increased due to shrinkage, causing a more compact structure to be obtained. The authors also attributed the increase in stiffness to the improved density of the composite fabric. Several researches have employed silk fibre as reinforcement to enhance PLA. Table 2 shows that silk fibres have better strength and modulus when compared with some selected natural fibres. Some of the findings of the use of silk fibre as reinforcement for PLA, gave better stiffness and ductility when compared to the pure PLA sample, but did not significantly improve the tensile strength [84]. Factors such as; the

Table 2. Mechanical and physical characteristics of selected natural fibres.

Fibre	Modulus [GPa]	Strength [MPa]	Density [g/cm ³]	Elongation [%]	References
Bamboo	35.9	441	0.80	9.5	[120]
Vetiver grass	12.0–49.8	247–723	1.50	3.8	[120]
Coconut	4.0–6.0	131–175	1.10	16.0	[120]
Silk	9.4–22	511–690	1.17	1.5–2.5	[120, 121]
Coir	4.0–6.0	131–593	1.2	15–40	[122, 123]
Jute	10–30	393–773	1.3	1.16–1.8	[123, 124]
Hemp	70	600	1.47	2.0–4.0	[125]
Cotton	12	400	1.5–1.6	3.0–10.0	[124]

length of the fibre, weight content, fibre orientation, and fibre-matrix interface, have been reported by Cheung and coworkers [6, 85] to have influenced the mechanical properties of the resulting PLA/silk biocomposite.

The strength and stiffness of the composite, as an orthopedic fixator, is imperative because inadequate stiffness at the repair site can lead to gross motion and retardation of the bone healing process. The tensile strength and the percentage strain-at-break of the pure PLA samples were reported by Cheung and Lau [39] to be ~65 MPa and ~4.7%, respectively, while the 5 wt% PLA/silk biocomposites recorded ~61 MPa and ~4.6%, respectively. This shows that the pure PLA sample has better ductility. The elastic modulus of the same weight of silk fibre in PLA was also reported to be ~2.439 GPa, which was ~33% (1.833 GPa) higher than the pristine PLA. However, it is imperative also to consider the impact of the fibre length on these properties. Some researchers, Ho *et al.* [87] chopped the silk fibre into 5 mm length to avoid coiling with screws and extending the fibres plastically, during the injection process. The modulus was reported to have increased by over 27% with 5 mm silk fibre, but there was no increase in the tensile strength. This phenomenon was attributed to the disturbance of both inter and intra-bonding on the silk fibre with PLA, during the blending process. The investigation concluded that the use of silk fibre, as reinforcement, can improve the modulus of PLA as well as modify its pace of bio-degradability, which are significant properties for the design of implants for bone fixation.

In order to ascertain the optimal amount and length of silk fibre to be used to improve these properties, Cheung *et al.* [6] prepared a PLA/silk biocomposite by cutting the fibre into (between 3–6 mm) and then mixed the fibre and PLA at various ratios of; 1:99, 3:97, 5:95 and 7:93. The sample with 5 mm fibre

Figure 5. Stress–strain curves of (a) pure PLA sample and (b) 5 wt% PLA/silk fibre biocomposite. Reprinted from [6], with permission from Elsevier.

length and 5 wt% of silk fibre showed interesting behavior. In spite of the fact that it did not improve the tensile strength, however, it increased the strain-at-break by 53%, as shown in Figure 5. When compared to the modulus reported by Cheung and Lau [39], the reinforced composite of 5 mm and 5 wt% improved by 4%. This was attributed to the silk fibres acting as micro-pins inside the matrix, thereby generating an interlocking mechanism that prolonged the fracture process. This infers that the ductility of

Figure 6. Micro-hardness test results on different fibre length and content of PLA/silk fibre biocomposites. Reprinted from [6], with permission from Elsevier.

the silk fibre/ PLA biocomposite was higher than that of the pristine PLA.

3.2. Micro-hardness indentation response

The length and weight fraction of the fibre also play important roles on its hardness property. The hardness of pure PLA sample was reported to have increased by ~12% after reinforcement with silk fibre [39]. It was also observed, as shown in Figure 6 that the hardness value increases for fibre length from 3 to 5 mm, yet decreases beyond 5 mm for all biocomposite samples with various fibre weight contents (from 1 to 6 wt%) [6]. It was observed from this work that the maximum viable measure of fibre weight content, needed to make the biocomposite was 6 wt% (Figure 6) because the trial to produce samples with 7 wt%, resulted in a relatively brittle and hard to demould sample.

3.3. Impact strength

Ho [51] tested PLA and their composites samples and found the pristine PLA sample to be ~156.3 J/m, higher than the average impact strength of the PLA/ 5 wt% silk composite, which was 110.7 J/m. The reduction of the impact strength was because silkworm silk fibres in the polymer matrix acted as stress

Figure 7. Fracture energy against fibre content of neat PLA specimen and 5–15 vol% PLA/silk fibre biocomposites [61].

concentrators, which decreased the crack initiation energy [51]. Similarly, Cheung *et al.* [61] reported an increment of ~70% of both the fractured energy and energy loss, when 10 vol% of silk fibre (Figure 7) was added to the composite. However, a significant drop in the fracture energy was observed when more than 10 vol% of silk fibre was added to the composite. This was attributed to the high volume percentage of fibre embedded in the matrix, resulting in weak interfacial bonding. A summary of the mechanical properties of some reported PLA and their silk reinforced counterparts, is presented in Table 3.

The reviewed result demonstrates that fibre and matrix bonding is a significant factor required to obtain good mechanical properties. Therefore, there is a direct linkage between the strength of composites and the interfacial bonds, since the applied stress is more effectively transferred through the interface [3, 6]. The decrease in the tensile strength of the composite in the work of Cheung *et al.* [6], can be traced to the weak bonding that exists between the fibre and the matrix. Further clarification was given by Ho *et al.* [87], stating that despite the mechanical interlocking, as a result of the fibre surface roughing, the hydrophilic natural silk fibre and the hydrophobic PLA matrix were not chemically bonded together. Due to this characteristic poor compatibility, the load transfer through the interface is constrained. Another factor contributing to the reduced strength can occur when the fibre breakage happens earlier than the failure of the surrounding [89].

4. Thermo-mechanical and thermal properties of PLA/silkworm silk fibre composites

4.1. Dynamic mechanical response

Dynamic mechanical analysis (DMA) is a procedure used to study the viscoelastic (elastic and viscous) responses of a sample under oscillating load against

Table 3. Summary of mechanical properties of pristine PLA and PLA/silk fibre biocomposites.

Sample	Properties							References
	Hardness [HV]	Tensile properties			Flexural properties		Impact strength [J/m]	
		UTS [MPa]	Elongation [%]	Stiffness [GPa]	Flexural strength [MPa]	Stiffness [GPa]		
Pure PLA	17	65.19	4.675	1.83	–	–	–	[39]
5 wt% silk/PLA	19	61.25	4.575	2.439	–	–	–	
Pure PLA	17	65.19	6.73	3.75	107.37	3.58	–	[6, 90]
5 mm/5 wt% silk/PLA	19	62.08	10.29	4.99	71.71	4.01	–	
Pure PLA	–	70.73	5.5	3.21	109.4	3.98	–	[51, 87, 126]
5 wt% silk/PLA	–	70.60	3.8	4.08	97.41	4.06	–	

temperature, time or frequency, where the frequency of oscillation is proportional to the modulus of the material. The significant properties obtained during a DMA analysis, as a function of temperature are the storage modulus (E'), which refers to the energy stored in the sample elastically after the stress has been applied (associated with the elastic part of the material), and the loss modulus (E'') which describes the energy dissipated during deformation (associated with the viscous part of the material). Another commonly used quantity is the damping coefficient ($\tan \delta$) given as the ratio of the loss modulus to the storage modulus ($\tan \delta = E''/E'$), which is identified with material's capacity to dissipate energy in the form of heat [41, 85, 90].

Ho [51] designed a PLA/silk composite for bone fixator, which requires high storage modulus (E') and loss modulus (E'') to enhance its ability to absorb and dissipate energy, respectively, in a pre-determined time, *i.e.* during an acceptable duration when the fixator is in the process of degradation. The result showed that the E' of the composite is higher than that of the pristine PLA. This was ascribed to the existence of silkworm silk fibre, which formed as physical cross-linkage and permitted stress transfer between the silkworm silk fibre and the PLA. A similar result was reported by Cheung and Lau [91], where the increase in storage modulus in PLA/silk was attributed to the effect of the fibre in the viscoelastic matrix, hence, allowing for the transfer of stress and reducing the mobility and deformation of the matrix. The high value of $\tan \delta$ implies that once the deformation is prompted, the material will not recover to its initial dimension. The decrease in $\tan \delta$ also signifies an improvement in the hysteresis of the system and a decrease in the internal friction [92]. At 37 °C,

Figure 8. $\tan \delta$ as a function of the temperature of; (a) pure PLA sample and (b) 5 wt% PLA/silk biocomposite. Reprinted from [93], with permission from Elsevier.

which is the normal human body temperature, there was no considerable contrast in $\tan \delta$ for both the composite and the pristine PLA, as shown in Figure 8.

4.2. Crystallization and melting behaviour

The differential scanning calorimetry (DSC), a versatile thermal analysis technique for polymer, is typically embraced to study the thermodynamic processes (glass transition, specific heat capacity) and kinetic events, such as cure and enthalpic relaxations that are related with physical aging or stress. In other words, it allows for the measurements of changes in the polymer thermal properties due to the alteration of temperature. Usually, polymers are not 100% crystalline materials, making them amorphous or semi-crystalline. Generally, the greater the crystallinity of a polymer the more noteworthy are its stiffness and density. The glass transition temperature (T_g) is the temperature where the polymer changes from a hard and relatively brittle state to a soft or rubbery state [92, 93]. The T_g and the crystallinity of polymers have additional indirect effects on the degradation rates because degradation first occurs in the amorphous regions and later in the crystalline zones [61, 88]. The T_g of PLA is above the physiological human body temperature of 37 °C; hence it is glassy in nature and can be applied to the biomedical domain. The T_g of pure PLA and PLA/5 wt% silk composite was reported by Cheung [90] to be 60.2 and 64.4 °C respectively, with an increment of 7% from the neat to the composite sample. However, a 14 °C drop in the crystallization temperature from 114 °C and a slight change in the melting temperature (T_m) of the PLA were experienced following the addition of 5 wt% silk fibres [90].

There are two fundamental factors that control the crystallization of the polymeric composite systems in relation to additives added to the composites. The first is related to the nucleating effect from the added additives, which result in an augmentation of crystallization temperature and a beneficial effect on the degree of crystallization. The second is the restriction of the migration and diffusion of polymer chains to the surface of the developing polymer crystal in the composite, thereby, leading to a reduction in the crystallization temperature (T_c) and hence, a negative impact on the degree of crystallization [61, 89]. The latter was observed by Ho [51], where there was a reduction in crystallization temperature (by ~4.68 °C) after the addition of the silk fibre, leading to an

Table 4. Comparison of the thermal properties of pristine PLA and PLA/silk fibre biocomposites at different weight fraction proportions. Silk in wt%.

Sample	T_g [°C]	T_c [°C]	T_m [°C]	ΔH_c [J/g]	ΔH_m [J/g]	X [%]	References
Pure PLA	60.2	114.0	166.5	34.5	35.4	38.1	[6, 39]
	53.7	94.86	163.44	29.46	48.0	51.2	[51]
	62.0	104.0	168.0				[95]
PLA/silk (95/3)	59.6	112.5	163.0	39.0	40.9	–	[2]
PLA/silk (95/5)	64.4	100.5	168.4	19.9	35.7	38.4	[6, 39]
	59.6	111.2	162.3	48.8	48.4	–	[2]
	53.7	90.18	162.71	29.50	48.4	51.7	[51]

 ΔH_c = crystallization enthalpy ΔH_m = measured melting enthalpy

increased rate of degradation. Over 3 wt% of silk fibre incorporation in PLA decreased the crystallization temperature, as reported by Zhao *et al.* [2] and the enthalpy of crystallization of all the PLA/silk composites was reported to be higher than the pristine PLA. The finding by Zhao *et al.* [2] demonstrates that the crystallization ability of PLA can be enhanced as a result of silk fibre addition, which may act as a nucleating agent. The molecular chemistry and chain structure play a major role in the degree of crystallinity (X). This is because of the side-branches and cross-linking upset the mobility of chains. In addition, monomer units with complex species render crystalline order difficult [93]. Since these polymers are not 100% crystalline, it explains the degree of crystallization summarized in Table 4. Similar factors, such as; chain flexibility, molecular weight, branching/crosslinking, intermolecular attraction, and steric effects additionally influence the T_g [94, 95].

4.3. Thermal degradation

Thermogravimetric analysis (TGA) is an effective methodology for evaluating the thermal stability of polymeric materials. In order to study the thermal stability, TGA provides information on the decomposition temperature (T_d) of the composite. This is important to know the thermal behavior and the changes the developed composite would experience in service. It is also a significant factor in the manufacturing and functioning of biodegradable and bioresorbable composite bone fixators because the material can experience volume or length variations, owing to changes in moisture content, curing, stress release and phase changes during heating [51, 96]. Huda *et al.* [92] reported that the thermal degradation of PLA/recycled newspaper cellulose fibre (RNCF) composite occurred in three stages; majorly due to

release of absorbed moisture in the fibres (40–130 °C), degradation of cellulosic substances (195–360 °C) and non-cellulosic materials (360–469 °C). However, reports from PLA/silk composite shows different behavior.

In the study by Zhao *et al.* [2], a major degradation was observed between 265–390 °C, which was the differential region between the composite and pristine PLA because no difference in thermal stability was observed before 265 °C. This result can be validated because silk fibre has been reported to undergo degradation between 250–350 °C and then starts to decompose at 350 °C [90]. Therefore, the degradation of the composite at the onset of the fibre degradation embedded in the matrix can be easily traced. The summary of the TG and Derivative Thermogravimetric (DTG) curves of PLA/silk composite studied by Zhao *et al.* [2] is presented in Table 5, indicating the different temperatures of weight loss with increasing silk fibre composition.

From the results (Table 5), it can be clearly observed that the values of all the PLA/silk composites are lower than the pristine PLA. This could be attributed to a reduced interaction between the silk fibre and

Table 5. TGA results of the neat PLA and PLA/silk fibre biocomposites [2]. Silk in wt%.

Sample	T_p [°C]	T_D^1 [°C]	$T_D^{0.5}$ [°C]	w_g^{600} [%]
Neat PLA	370.3	331.9	365.3	1.3
PLA/1 silk	367.2	326.4	361.5	3.0
PLA/3 silk	356.4	319.5	353.6	3.3
PLA/5 silk	354.5	312.2	349.6	3.3
PLA/7 silk	351.2	304.6	346.3	5.1

* T_p : The temperature at which there is the maximum of the DTG curves.

T_D^1 : The temperature corresponds to 5% (initial) weight loss.

$T_D^{0.5}$: The temperature at which 50% of the sample weight is lost.

w_g^{600} : Weight percentage of the residue at 600 °C.

the PLA matrix as higher difference was observed with the inclusion of 7 wt% silk. However, Cheung [90] reported that the thermal stability of the PLA/silk biocomposite was improved with 5 mm length and 5 wt% of silk fibre. It was reported that the silk fibres act as obstacles for better heat insulation and decrease the permeation of the products of volatile degradation into the biocomposite. Generally, it is recommended that the use of silk fibres in a polymer matrix during fabrication processes or in an application, should be utilized below its minimum degradation temperature of 250 °C. This is because above this temperature, the property of the proposed composite would be significantly affected.

5. Microstructural analysis of PLA/silkworm silk fibre composites in relation to biodegradation properties

Fibre composites have quite a number of microstructural characteristics that are special, and when adequately documented, they can serve as a springboard for further development of these materials. The discussion on the microstructural observations as they relate to biodegradation properties of composite, is centered on the fibres, matrix and the fibre/matrix interfacial adhesion. As earlier mentioned, the demand for biodegradability, renewability, and recyclability of materials, especially natural fibres (because of their lightweight and cost) is growing amongst manufacturers and consumers. There is a paradigm shift towards ‘greenness’ and environmentally-friendly materials. The biodegradable and renewable characteristics of silkworm silk fibres are mainly important for the disposal of their components at end-of-life, thus, enabling the easy conversion of these materials into the production of thermal energy into thermal energy through combustion without leaving behind any residue [9]. The use of natural fibre, mixed with biodegradable polymers/matrix, *e.g.* PLA can produce composites that are biodegradable and environmentally-friendly. In this regard, the use of silkworm silk fibre as a form of reinforcement for fabricating PLA-based environmental biocomposites, have been reported [5, 9].

PLA/silk fibres fall under the class of natural protein fibre as they are known to be biodegradable and crystalline, having structures that are well aligned, thereby making these fibres suitable potential materials for biomedical and bioengineering applications [39]. In the biomedical application of these materials,

biodegradability is an important factor to reduce any extra discomfort the patients may experience as a result the removal of non-biodegradable implants after multiple surgeries. The biodegradability property of this fibre also ensures the smooth transfer of load from a damaging implant to neo-tissue. Biomaterials that slowly degrade also aids in sustaining the reliability of tissues in an implantation site, thus making the transfer of load-bearing burden to the regeneration of biologically functional tissues, easy [84].

Cheung *et al.* [84] carried out a biodegradable test on both samples of PLA and PLA/silk biocomposites in order to study the pH condition of the surrounding fluid. Twenty neat PLA samples and twenty PLA/silk fibre biocomposites were fabricated into dumb-bell shapes, and *in-vitro* biodegradation test was done by using Dulbecco’s Phosphate Buffered Saline (PBS) at a temperature of 99 °F (~37.222 °C) for 4, 8, 12 and 16 weeks in a shaking incubator. The samples were monitored on a weekly basis by using a pH meter; the result showed that the pH value in the range between 7.37 and 7.41 was the same for both the pure PLA and the PLA/silk samples. This possibly indicates that degradation does not affect the pH values, hence points to the likelihood of biocompatibility and biodegradability of PLA and PLA/silk. It is pertinent to state that the control of the rate of biodegradation is also an important factor in ensuring that the structural integrity is maintained until loaded cells are able to acclimate to the environment before implants are eventually replaced by new tissues. The presence of silk fibre in the PLA matrix increases the mechanical properties, *e.g.* stiffness, thermal stability and considerably, improves the degradation capacity of the PLA matrix [2]. Thus, increasing the silk fibre content could cause stress shielding of the bone and consequently leading to bone loss [88]. The relationship between the silk content and degradation in the PLA matrix was found to be direct. Zhao *et al.* [2] investigated the biodegradable properties of PLA/silk. Enzymatic degradation tests were carried out on fabricated test samples, and changes in the surfaces of the samples were also examined by using the scanning electron microscope (SEM). Results as observed in Figure 9, showed that several pores were formed on the surface of the samples after degradation, and these pores were found to increase in diameter with incubation time, indicating a well-pronounced degradation.

From the biodegradation test, also conducted by Zhao *et al.* [2], the SEM micrographs in Figures 9,

Figure 9. Scanning electron micrograph of neat PLA after an incubation time of (a) 0 (b) 24 hrs (c) 72 hrs and (d) 120 hrs enzymatic degradation. Reprinted from [2], with permission from Elsevier.

10 and 11, showed that there were changes in the surface of the composite after the enzymatic degradation test of the PLA/silk and PLA. Before degradation, the surface of the pristine PLA was seen to be smooth, but after degradation (at different times), there were appearances of pores and cavities, which increased in diameter as incubation time increased, hence, indicating further degradation. The surfaces of the PLA/silk composites for the different weight percents of silk fibre, showed rougher surfaces when compared with the neat PLA before degradation (Figure 9). The rougher fibres have been proven to increase the degradation process, a clear indication that the incorporation of more silk fibre to the PLA (increasing the fibre content), will accelerate the degradation process because more silk fibres will be exposed on the surface of the composites, prior to degradation. The enzymatic degradation, which leads to loss of weight is an important factor that can be used in the description of the degradability of a material. This happens as a result of a hydrolytic process, which takes place in

both the surface of the composites and at the interfacial zone between the fibre and the matrix. There was no report on the delamination/debonding of the fibre from the matrix during the degradation process. On the nature of the fracture surface, only the surface crack, along the silk fibre, was reported (as shown in Figure 10c with the sample containing 3 wt% fibre content and Figure 11b with 7 wt% fibre content). Fracture surface characterization was carried out on pure PLA and PLA/silk biocomposite samples by Cheung *et al.* [84]. This was done at different times in order to examine the samples after the biodegradation test. The result showed that the fracture surface of both test samples before the biodegradation test was relatively rough, and no void was found when related to the fracture surfaces during the biodegradation test [6, 84]. Cheung *et al.* [6] also examined the fractured surface of the silk fibre/PLA biocomposite by using the SEM. The micrographs (Figure 12a) showed that pure PLA was smooth, and no void was found, indicating the

Figure 10. Scanning electron micrograph of PLA/silk fibre biocomposite with 3 wt% respectively silk after an incubation time of (a) 0 (b) 24 hrs (c) 72 hrs and (d) 120 hrs enzymatic degradation. Reprinted from [2], with permission from Elsevier.

fact that there was no moisture absorption in the sample during manufacturing. Figure 12b shows a good interfacial adhesion between the silk fibre and the PLA matrix, forming a network that is able to create some sort of reinforcement in the biocomposite during loading and also stopping crack propagation.

6. Antibacterial properties of PLA/silkworm silk fibre composites

Despite the unending quest of researchers for a paradigm shift from petroleum-based polymers to the greener types in the different fields of applications, the high susceptibility of some biopolymers such as PLA and silk fibre, to microbial attack questions the rationale behind this quest [100]. Microbial invasion of natural materials used for biomedical and food packaging applications and the consequent infections can be very chronic and at the worst terminal, especially for victims with a low level of neutrophils and immunocompromised body systems [100].

As PLA, silkworm silk fibres and their composites are extensively used for the foregoing applications; hence, this review considers it noteworthy to highlight the ongoing progress in this research territory. With reference to the literature data pool, very limited research findings are available on the antibacterial properties/activities of PLA/silk fibre composites. To date, only the work of Li *et al.* [101] is the most relevant reference (based on google scholar search) for the antibacterial activity of PLA/silk fibre composite. Although, the PLA/silk fibre composites used in their investigation contained nano-hydroxyapatite and silver nanoparticles. The *in vitro* antibacterial activity of the porous scaffold developed from the above-mentioned materials was assessed against *S.aureus* and *E.coli* bacterial strains. Their result revealed that the developed scaffold was able to inhibit the growth of both bacterial strains [101]. Some interesting research findings are also available on the antimicrobial properties of PLA films functionalized with

Figure 11. Scanning electron micrograph of PLA/silk fibre biocomposite with 7 wt% respectively silk after an incubation time of (a) 0 (b) 24 hrs (c) 72 hrs and (d) 120 hrs enzymatic degradation. Reprinted from [2], with permission from Elsevier.

Figure 12. Scanning electron micrograph of (a) pure PLA and (b) PLA/silk fibre biocomposite fracture surfaces. Reprinted from [6], with permission from Elsevier.

chitosan, zinc oxide, glycerol and polyethylene glycol against the above-mentioned bacterial strains [100–102]. In the case of silk fibres, their antibacterial properties significantly improved by genetic modification [97] with functionalization with leaf extract [98], chitosan blending [99], silver nanoparticles

[100], gentamicin [101], tannic acid [102] and sericin-copper [103]. Similarly, the resultant modified silk fibres showed strong bactericidal effects on *S.aureus* and *E.coli*.

From the above information, it is envisaged that the adaptation of the techniques used to confer

antibacterial properties to PLA and silk fibres will yield the same results for PLA/silk fibre composites. Thus, biomaterials scientists, biomedical engineers and microbiologists with keen interest in the antimicrobial properties of the PLA/silk fibre composites are encouraged to consolidate their research efforts towards this area as the authors of the present work strongly believe it will be a remarkable expansion of the frontiers of existing knowledge on the preceding subject matter.

7. Applications of PLA/silkworm silk fibre composites

During the conceptual design phase of novel materials, it is expected that the materials scientist/engineer envisages solutions to particular problem or problems, reliant on the applications of the proposed materials, *i.e.* the primary goal of developing a new material should be inclined towards problem-solving activities. Interestingly, the development and characterization of PLA/silkworm-based materials have shown that these materials might be perfect candidates for solving some of the challenging problems, invariably encountered in the biomedical, textile and plastic industries [61, 64, 84, 86, 96, 104, 105]. The following section gives a succinct account of the recent progress that has been made in the last decade, regarding the applications of PLA/silkworm-based materials as effective solutions-provider in the above-mentioned fields.

7.1. An overview of PLA/silkworm silk fibre composites proposed for biomedical applications

In tissue engineering and regenerative medicine, the issues of acceptable biocompatibility level and time-dependent structural integrity of manmade biomaterials are of primary concern. Several attempts have been made by researchers to break this barrier. One of these attempts is the exploitation of PLA-silkworm-based materials for biomedical applications as they possess excellent biocompatible and biore-sorbable properties that are desired of implantable biomaterials. In one study, Yin *et al.* [104] were able to develop PLA-silk fibroin-gelatin scaffold via electrospinning. After three months of subcutaneous implantation test, the developed composites were found to exhibit preferred porous structure, strong and pliable properties, capacity to support cell growth *in-vitro* and superb biocompatibility *in-vivo* [104].

These observations clearly translate to their confident suggestion of the developed materials as scaffolds for tissue engineering applications. In a conference report presented by Cheung *et al.* [61] at the European Conference on Composite Materials in Venice, Italy, these researchers documented improvement in the ductility, stiffness, and toughness of PLA composites reinforced with between 5–15 vol% silkworm fibre. Hence, based on these findings and other positive results from their spectroscopic and microstructural characterizations, they proposed the composites developed for prosthetic applications [61].

A novel insight into the dynamic mechanical performance and thermal degradation of PLA-silk fibre composites, in line with their potential applications as scaffolds and implants, has been reported by Ho *et al.* [40]. In their work, they found that silk fibre can improve the mechanical integrity of PLA for the above-mentioned biomedical applications. However, appreciable research effort is needed to make the materials suitable for a thermomechanical-based biomedical application [40]. Another work by Ho *et al.* [96] investigated the *in-vitro* biodegradation of PLA/silk fibre composites for 16 weeks. A mild acidity of the degradation material was observed for the composites. Both the degradation rate and mechanical properties (stiffness and ductility) of the composites were also found to improve with the addition of silk fibre to PLA. From their observations, they concluded that the regeneration duration of neo-tissues at the implantation site could be successfully controlled by reinforcing PLA with silkworm fibres [84]. Similarly, Mangat *et al.* [64] proposed PLA/silk composites for scaffolds development. This resulted from their positive findings, which revealed enhancements in the flexural strength, hardness, as well as biodegradation and antibacterial properties of porous biodegradable PLA/silk laminates.

In summary, it is evident that the last decade has experienced a rise in the interest of researchers in the synthesis and biomedical applications of PLA-silk composites. However, it is noteworthy to mention that most of the previous studies did not go beyond the proposition of their developed PLA-silk composites as promising materials for biomedical applications. One prominent exception to this was the bold step taken by Professor Alan Lau and his team at Swinburne University of Technology, to create surgical pins and cages from PLA-silk composites [80]. This was inspired by the significant enhancement of PLA's

elastic modulus from 3.21 to 4.08 GPa, following the addition of silk fibres to PLA. In addition, the resultant composite retained its biodegradability [6]. Further research inputs are still needed to promote the clinical trials for successful *in-vivo* biomedical applications of PLA-silk composites.

7.2. An overview of PLA/silkworm silk composites proposed for textile applications

In the textile industry, customer's satisfaction is very crucial, which in turn makes the textile market highly competitive since customers must always be provided with multiple choices. Thus, it is mandatory for textile manufacturers to present outstanding fabrics in terms of texture, aesthetics, affordability, comfortability, re-usability, durability and in recent times, their environmental friendliness. Judging by recent research findings, PLA-silk blend seems to exhibit most of the above-mentioned desirable properties [86, 105, 106]. On the one hand, popularity is a hallmark of pure silk fabric in the textile industry. This is attributed to its shining appearance, soft texture, superb draping quality, washability, good tensile strength and appreciable resistance to abrasion [86, 106]. However, its high cost, coupled with its high susceptibility to pollution, wrinkles, and discoloration, has called for research attention. On the other hand, the eco-friendliness, sustainability, inexpensiveness and other attractive characteristics of PLA can be conferred to silk fabric in order to compensate for its foregoing deficiencies to meet modern-day textile applications [86, 105, 106]. Interestingly, pertinent researches on this subject matter have begun to emerge. Zhu and Pan [105] studied the properties of PLA/silk mixed fabrics. They found that the mixed fabrics exhibited better wearability, anti-pilling resistance and gas permeability than the pure silk fabric. Based on these findings, they confidently suggested mixed fabrics for textile application [105].

Suesat and Ujjin [86] reported that PLA-silk blend could successfully undergo the degumming process needed for silk pre-treatment to remove sericin at an elevated temperature of 70 °C and a pH of 10 and a pH of 10. Thus, the process has no negative effect on the structure and mechanical integrity of the fabric. They encouraged the industrial production of this blend for textile applications. Feng *et al.* [106] have also investigated the wearable performance of PHA/PLA fibre/spun silk blended fabrics. Their results

revealed that while the pilling resistance of the blended fabrics improved with weft density, the wrinkle recovery performance, air permeability and moisture permeability of the blended fabrics were not enhanced. Making reference to previous studies [86, 105, 106], this is a clear indication that PLA-silk fabrics exhibit better textile properties than PHA/PLA/silk fabrics. Thus, further investigations are recommended to improve the textile applications of PLA-silk blend/composites.

7.3. An overview of the prospects of PLA/silkworm silk fibre composites as promising materials for disposable/edible food packaging applications (DFPAs/EFPAs)

Food packaging is a dynamic and an integral part of the food production line, where different types of materials, such as; papers, polymers (plastics, bioplastics and bio-based plastics), metals, glasses, and leaves are currently being employed as packaging materials, based on the types and properties of the food to be packaged [107]. Due to their low cost, lightweight, associated packaging aesthetics and relatively high compatibility with most food products, papers and polymers are typically the most widely used food packaging materials [108]. However, considerable emphasis is placed on polymers in this work in order not to digress from the key concept of the present review. According to the United States of America Food and Drug Administration, plastics are recognized as 'indirect food additives'. Therefore, they must conform to the requirements stated in Title 21 of the Code of Federal Regulations for food packaging applications [109]. As a matter of fact, to ascertain guaranteed preservation, containment and protection of food, a fundamental understanding of the properties of any material to be used as a disposable food packaging material is essential [110].

To date, synthetic/petroleum-based plastics such as; polyethylene, polystyrene, polypropylene and nylon are still dominating the market as food packaging materials. However environmental issues concerning their disposal, which contribute a large percentage to municipal solid wastes, has called for a rethink [111]. Although these materials have stood the test of time with reference to desirable properties (chemical resistance, microbial resistance, moisture impermeability, gas barrier property, abrasion resistance, mechanical performance, thermal stability, etc.) and

field-proven reliability required of standard food packaging materials. However, there is still rising demand for a paradigm shift to disposable bioplastics and bio-based plastics that are biodegradable, compostable and edible, while maintaining the above-mentioned qualities [112]. This proposition is considered to be highly far-reaching and tremendously beneficial to global environmental welfare and the sustainability of the food supply chain [112, 113]. Interestingly, research findings have revealed PLA bioplastic and silk fibre biopolymer, combined with other materials, as suitable materials for DFPAs.

Previous studies have shown PLA to be the most commercially exploitable biopolymer for DFPAs. More so, it is easy to modify its physical and mechanical properties by simply changing its chemical composition and processing conditions [100, 114, 115]. Different investigations on PLA films have revealed that these films are very suitable for DFPAs because, in addition to the fact that they are biodegradable, transparent, compostable, and produced from renewable resources, they exhibit the same behavior that is comparable to the mechanical, thermal, and barrier properties of most used synthetic polymers such as polystyrene and polyethylene [99]. However, the major drawbacks currently hindering their long-term deployment as materials for DFPAs in the food packaging industries include their low resistance to thermal stress, low stiffness, high water vapour transmission rate and high oxygen permeability [116]. Detailed and impressive information on the applications, delimitations, and suggestions for improvement of PLA and PLA-based materials for DFPAs can be found in the works of Öz *et al.* [117], Siracusa *et al.* [118], and Tawakkal *et al.* [110]. On the other hand, in a quest to curb the huge waste of perishable foods and its associated loss of economic values and resources, as reported by the Food and Agricultural Organization of the United Nations, new investigations into the suitability and efficiency of silk fibroin as edible food packaging materials (EFPs), have begun to emerge [115]. Marelli *et al.* [115] conducted an experiment, wherein they used water-based processed silk fibroin as edible coatings for the preservation of strawberry and banana fruits. From their results, they found out that micrometer-thin silk fibroin membranes around the fruits, enhanced the fruits' shelf life at ambient conditions. They attributed this occurrence to the silk fibroin-induced phenomenon, which reduced cell respiration rate and

water evaporation. Although limited to the knowledge of the authors of the present review, based on open literature search, to date, there exists no record of PLA/silk fibre/fibroin composites developed for DFPAs and/or Edible Food Packaging Applications (EFPAs). Thus, researchers are strongly encouraged to explore this untapped avenue for novel and innovative ideas with great prospects that can facilitate the postharvest treatments of foods and equally promote their sustainable and bio-friendly packaging. In addition, the fact that silk fibres are readily biodegradable and compostable translates to their plausible ability to confer these properties to PLA/silk fibre composites, with reference to DFPAs and EFPAs specifications.

8. Challenges and suggested solutions

Manufacturing challenges are encountered in the development of these composites, particularly with the pristine constituents. In order to fabricate them by using large scale operations, such as injection moulding and extrusion, the polymer matrix must possess sufficient thermal stability, needed to prevent degradation and maintain appropriate molecular weight, and properties needed for good performance while in use [41]. PLA matrix still suffers some thermal degradation at certain processing temperatures due to its chemistry, rheology and physical properties. When PLA is in the filament form to be 3D-printed, it experiences shape deformation due to high-temperature exposure [119]. Likewise, there have been reports on certain the disadvantages by using PLA/silk filament in 3D printing, such as: low heat resistance, low glass transition temperature, and softening at elevated temperatures [119]. On that note, research on physical, thermal and rheological properties improvements of pristine materials or feedstock, such as PLA and PLA/silk filament would be apt.

Despite the reports of silk fibres enhancing some mechanical and thermal properties of PLA/silk composite, there are still more grounds to conquer in order to ensure the increased utilization of the composite in other applications that do not restrict it as a biocomposite. This is because, composite application or the means/routes of fabrication, has been limited to temperatures below 250 °C and in addition, the composites still exhibit a relatively low tensile strength, needed for its usage in some other applications. Major progress envisaged to further develop PLA/silk composite, would be to improve

the degradation temperature and strength, thereby providing a wider range of applications.

Without a doubt, PLA/silk-materials are excellent biodegradable, sustainable, lightweight and green materials with great prospects and potentials for biomedical and textile applications. Although their biomedical applications are yet to pass clinical trials, it is predicted that in the near future, their use for *in-vivo* biomedical applications in tissue/cellular engineering and regenerative medicine, would transit from an embryonic phase to common practice. In addition, it is somewhat puzzling that the above-mentioned attractive properties of these materials have not been notably exploited for Disposable/Edible Food Packaging Applications (DFPAs/EFPAs). Thus, researchers are tremendously enjoined and equally encouraged to beam their searchlight in this direction. Such involvement will reduce the environmental pollution and carbon footprint, constituted by synthetic polymers, *e.g.*, the polyolefins that are currently and extensively used for packaging applications. Moreover, both PLA and silk have been singularly and successfully combined with other materials for DFPAs. This is a clear indication that their combination with each other will result in a reliable, low-cost and green material for DFPAs. In addition, more and concerted research effort is currently needed to significantly improve the antibacterial properties of PLA/silkworm silk fibre composites against different bacterial strains. This will likely mitigate the invasion of the service environments where the composites have potential applications. Significant much

emphasis should be concentrated on *in-vivo* environment due to its liable nature.

9. Conclusions

The development of natural fibre reinforced composites continues to attract considerable attention due to its role in promoting sustainable materials development. On that note, the progress made in research and development efforts of PLA/silkworm silk fibre composite has been considered in the current review, keeping in mind the United Nations sustainable development goals (SDGs) in developing advanced materials with good service performance and minimal impact on the environment. Their fabrication routes, including the transformative additive manufacturing approach, were discussed. Prior to that, effective and environmentally-benign fibre treatment strategies were considered. The mechanical, thermal and biodegradation properties of this composite were also compared with neat PLA in a bid to assess the reinforcing effect of silk fibres. Reviewed results and data indicated that silk reinforced PLA composites fared better. In addition, the structure-property relationships were brought to light by microstructural evidences, which revealed all forms of defects arising from processing routes and parameters employed. An overview of the process steps for the development of PLA/silkworm silk fibre biocomposites, right from processing to the application areas, is presented in Figure 13.

The review further contains an overview of some specific application fields of this material, *via* textile,

Figure 13. Graphical overview of the development, properties, and nascent applications of PLA/silkworm silk fibre biocomposites.

food packaging applications (DFPAs/EFPAs), and biomedical, looking into its current state of the application in the biomedical context, where further development of surgical pins, made from 3D printed PLA/silk fibre composites, and implementation of clinical trials are upon us. Challenges faced in the advancement of this material and possible solutions were proffered. If such solutions are adopted and researched upon, the large scale application of this material in areas, such as DFPAs and EFPAs could be achieved.

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