



Critical factors on manufacturing processes of natural fibre composites

Mei-po Ho^a, Hao Wang^a, Joong-Hee Lee^b, Chun-kit Ho^c, Kin-tak Lau^{a,d,*}, Jinsong Leng^e, David Hui^f

^a Centre of Excellence in Engineered Fibre Composites, Faculty of Engineering and Surveying, University of Southern Queensland, Toowoomba, Queensland, Australia

^b Department of BIN Fusion Technology, Chonbuk National University, Jeonju, Republic of Korea

^c Department of Physics, The University of Science and Technology, Hong Kong, SAR, China

^d Department of Mechanical Engineering, The Hong Kong Polytechnic University, Kowloon, Hong Kong, SAR, China

^e Smart Materials and Structures Laboratory, Harbin Institute of Technology, China

^f Department of Mechanical Engineering, University of New Orleans, New Orleans, LA 70148, USA

ARTICLE INFO

Article history:

Received 21 September 2011

Accepted 3 October 2011

Available online 17 October 2011

Keywords:

E: Manufacturing process

A: Natural fibre

ABSTRACT

Elevated environmental awareness of the general public in reducing carbon footprints and the use non-naturally decomposed solid wastes has resulted in an increasing use of natural materials, biodegradable and recyclable polymers and their composites for a wide range of engineering applications. The properties of natural fibre reinforced polymer composites are generally governed by the pre-treated process of fibre and the manufacturing process of the composites. These properties can be tailored for various types of applications by properly selecting suitable fibres, matrices, additives and production methods. Besides, due to the complexity of fibre structures, different mechanical performances of the composites are obtained even with the use of the same fibre types with different matrices. Some critical issues like poor wettability, poor bonding and degradation at the fibre/matrix interface (a hydrophilic and hydrophobic effect) and damage of the fibre during the manufacturing process are the main causes of the reduction of the composites' strength. In this paper, different manufacturing processes and their suitability for natural fibre composites, based on the materials, mechanical and thermal properties of the fibres and matrices are discussed in detail.

Crown Copyright © 2011 Published by Elsevier Ltd. All rights reserved.

1. Introduction

Petroleum is a fossil fuel which is estimated to last for only another 50–60 years at the current rate of consumption [1]. Elevated environmental consciousness in the general public and preservation of non-renewable petroleum-based materials especially for petroleum-based plastics have resulted in an extensive use of natural fibre reinforced polymer composites for commercial and medical applications. Excessive use of petroleum-based plastics causes to a serious depletion of landfill capacities. Besides, the severe government's plastic waste control legislations and the growing interest among the customers in sustainable and environmentally friendly products drive the retailers and manufacturers trending towards their investment on the development of sustainable materials with acceptable cost, to alleviate an impact from global warming (including the reduction of carbon footprints). Therefore, the public awareness of increased un-decomposable solid wastes and their impact to the environment has awakened a new interest in the area of developing fully biodegradable polymers (also called

“biocomposites”) with controllable mechanical properties and biodegradation rate.

Recently, biodegradable materials have continued attracting much attention worldwide. Within the period of 2005 and 2009, the global market on the demand of biodegradable polymers was double in size. Among all countries in the World in 2009, Europe had the largest growth in the range of 5–10% on the use of biodegradable polymers as compared with 2008. The total consumption of biodegradable polymers is forecasted to grow at an average annual rate of nearly 13% from 2009 to 2014 in North America, Europe and Asia, which are accounted as the major global markets for materials' consumption [2]. However, high price and limited properties of the fully degradable polymer hinder the diversity of the usage. Therefore, in order to tackle on these problems and retard the exhaustion of natural resources, different projects along the line of developing biodegradable composites have emerged recently and it is general believed that these are one of most key materials in all industries in coming centuries. In aircraft and automotive engineering industries, some new projects have been created on the use of natural fibre (hemp, flax) reinforced biodegradable and fire-proof polymer composites. Natural fibre biodegradable polymer composites are generally defined as a type of materials which are generally composed of natural fibre and biodegradable polymer, as a matrix. The properties of these composites can be tailored for

* Corresponding author at: Centre of Excellence in Engineered Fibre Composites, Faculty of Engineering and Surveying, University of Southern Queensland, Toowoomba, Queensland, Australia.

E-mail addresses: mmktlau@polyu.edu.hk, Kin-tak.Lau@usq.edu.au (K.-t. Lau).

various types of applications by a proper selection of fibres, matrix, additives and manufacturing process. The pre-treatment process of fibre plays a key role it controls the overall interfacial bonding properties and thus, successful stress transfer of resultant composites.

Normally, **natural fibre polymer composites** are fabricated by using traditional manufacturing techniques which are designed for conventional fibre reinforced polymer composites and thermoplastics. These techniques include resin transfer moulding (RTM), vacuum infusion, compression moulding, direct extrusion, compounding and injection moulding. Nevertheless, such techniques have been well developed and accumulated experience has proofed their successability for producing composites with controllable quality. However, their suitability for natural fibre reinforced polymer composites is still unsure due to the materials, geometrical, mechanical, thermal and structural properties of the natural fibres and biodegradable polymers are somehow, different with synthetic fibres and petroleum-based plastics, respectively. For example, chemical treatments on the fibre surface are normally required to compensate its incompatible bonding effect at the interface between the hydrophilic fibre and hydrophobic matrix. Other technical problems such as the uniformity of fibre distributed inside the composites, thermal degradations and weathering effect of fibre and matrix, water absorption of both fibre and matrix, wettability of resin impregnated into spaces between fibrils and breakage of fibres during mechanical stirring/mixing stages during the manufacturing processes also limit the use of natural fibres and biodegradable polymers for new composite development. Recently, seeking for technologies for developing fireproof natural fibre reinforced polymer composites is also one of key topics worldwide to apply them for aircraft interior components. Therefore, the resultant properties of composites in relation to the selections of right materials, pre-processing methods and manufacturing process are inextricably intertwined. In this article, different types of natural fibres and biodegradable polymers, their specific pre-processing techniques and fabrication methods are introduced and discussed in detail.

2. Materials selections

2.1. Natural fibres

Natural fibre is a type of renewable sources and a new generation of reinforcements and supplements for polymer based materials. Briefly grouping different categories of natural fibres, they can be divided based on their origin, derivations of plant, animal and mineral types which are detailedly shown in Fig. 1, [3–6]. These sustainable and eco-efficient fibres have been applied as substitutions for glass fibre and other synthetic polymer fibres for diverse engineering applications. Their remarkable advantages compared with those conventional inorganic man-made fillers enhance their commercial and research potentials. Natural fibres normally are abundantly-renewable resource so that their cost is relatively low as compared with other synthetic fibres. With the consideration of environmental consciousness, natural fibres are biodegradable so as they can alleviate the problem of massive solid wastes produced and relief the pressure of landfills if they are used for replacing other non-degradable materials for product development. Besides, according to their inherent properties, natural fibres are flexible for processing due to their less susceptible to machine tool damage and health hazards during the manufacturing and etc. Moreover, natural fibres possess many advantageous characteristics such as desirable fibre aspect ratio, low density and relatively high tensile and flexural moduli [7]. Table 1 summarizes the mechanical properties of natural and man-made fibres.

2.2. Plant-based fibres

By grinding the bark, the cell walls of most plant-based fibres can be viewed in Fig. 2a. The schematic representation of the cell wall of a natural plant is shown in Fig. 2b and this structure is often called as “macrofibril”. The cell wall consists of a hollow tube, which has four different layers: one primary cell wall and three secondary cell walls and a lumen. The lumen is an open channel in the centre of the macrofibril. Each layer is composed of cellulose embedded in a matrix of hemicellulose and lignin [4]. The microfibril is composed of crystalline and amorphous regions alternately, as is shown in Fig. 2c [4].

The age of the plant, climate conditions and fibre processing techniques would greatly influence the structure of fibres as well as their chemical composition. The primary constituents of plant-based fibres (lignocelluloses) are cellulose, hemicelluloses and lignin. Cellulose contains alcoholic hydroxyl groups so that it is hydrophilic in nature [4]. The moisture content of plant-based fibre could reach to 8–12.6% [8]. Cellulose is a highly crystalline structure which contains as much as 80% of crystalline regions. The microcrystalline structure of cellulose includes crystalline regions (higher packing density) of high order, which are extensively distributed throughout the fibre, and lower order amorphous regions (lower packing density) [4]. Hemicellulose is made up of highly branched polysaccharides including glucose, mannose, galactose, xylose, a group of polysaccharides (excluding pectin) attached to the cellulose after the removal of pectin. Hemicellulose contains different types of sugar units. It is also a highly branched polymer (contrasting with the linear cellulose) and has a degree of polymerisation 10–1000 times lower than that of cellulose [4]. Lignin is amorphous, highly complex, mainly aromatic, polymers of phenyl-propane units [2]. Lignin stiffens the cell walls and acts as a protective barrier for the cellulose. The function of Lignin is a structural support material in plants. During synthesis of plant cell walls, polysaccharides such as cellulose and hemicellulose are laid down first, and lignin fills the spaces between the polysaccharide fibres and cementing them together. This lignification process causes a stiffening of cell walls, and the carbohydrate is protected from chemical and physical damage [8].

The basic chemical structure of cellulose in all plant-based fibres is similar but they have different degrees of polymerisation whereas the cell geometry of each type of celluloses varies with the fibres. These factors contribute to the diverse properties of the green fibre (Fig. 3).

2.3. Animal-based fibre

An animal fibre generally is comprised of proteins such as collagen and keratin. It can be divided into animal hair and silk. Animal hair fibre is defined as the fibre which is taken from animals and hairy mammals. Examples of animal hair are sheep's wool, cashmere, alpaca hair, horse hair. Sheep's Wool is mainly composed of α -keratins, a protein which mainly forms the horny layer of the epidermis and of epidermal appendages such as hair. Wool is a multi-component fibre which consists of about 170 different protein molecules and these protein molecules constitute the morphological components of wool [9]. The diameter of wool fibre is in the range of 20–40 μm and the cross-section is elliptical [10]. The wool fibre is typically divided into three morphological components including cuticle, cortex and cell membrane. The microfibrils in the cortex represent approximately 50–60% by mass of the cortex material, the bonding between the microfibrils and their embedding matrix within the cortex and the presence of the organised helics within the microfibrils dominate the mechanical and water absorption properties of wool fibres [11]. Another type of animal hair is avian fibres, which are feathers and feather fibre. Chicken

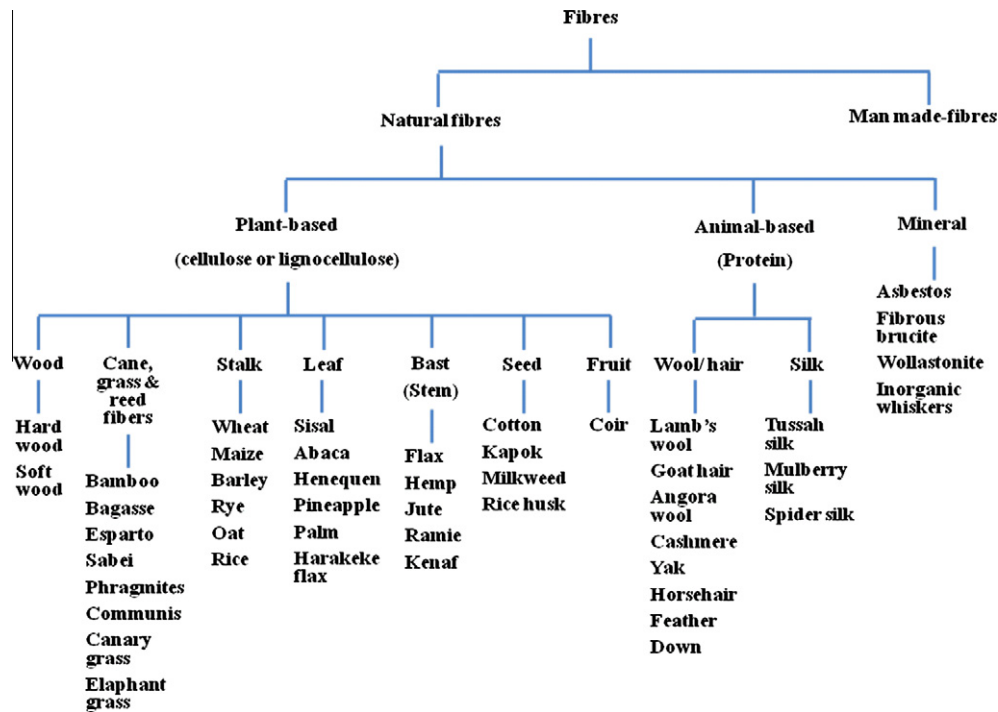


Fig. 1. The classification of different natural fibres.

Table 1
Mechanical properties of natural and man-made fibres.

Fibre	Density (g/cm ³)	Elongation (%)	Tensile strength (MPa)	Young's modulus	Refs.
<i>Natural fibre</i>					
Cotton	1.5–1.6	7.0–8.0	287–597	5.5–12.6	[8]
Jute	1.3	1.5–1.8	393–773	26.5	[8]
Flax	1.5	2.7–3.2	345–1035	27.6	[8]
Hemp		1.6	690		[8]
Ramie		3.6–3.8	400–938	61.4–128	[8]
Sisal	1.5	2.0–2.5	511–635	9.4–22.0	[8]
Coir	1.2	30.0	175	4.0–6.02	[8]
Viscose (cord)		11.4	593	11.0	[8]
Soft wood kraft	1.5		1000	40.0	[8]
Kenaf		1.5	930	53	[10]
Nettle		1.7	650	38	[10]
Abaca			430–760		[10]
Oil palm	0.7–1.55	3.2	248	25	[10]
Pineapple		2.4	170–1627	60–82	[9]
Banna		3	529–914	27–32	[9]
Wool		25–35	120–174	2.3–3.4	[9]
Spider silk		17–18	875–972	11–13	[9]
<i>B. mori</i> silk	1.33	19.55	208.45	6.10	[11]
Twisted <i>B. mori</i> silk		20.57	156.27	3.82	[11]
Tussah silk	1.32	33.48	248.77	5.79	[11]
<i>Man-made fibre</i>					
E-glass	2.5	2.5	2000–3500	70.0	[8]
Aramid	1.4	3.3–3.7	3000–3150	63.0–67.0	[8]
Carbon	1.4	1.4–1.8	4000	230.0–240.0	[8]

feathers are approximately 91% protein (keratin), 1% lipids, and 8% water. Their fibre diameters were found to be in the range of 5–50 μm [12]. Experimental results have showed that the tensile strength varies indirectly with the moisture content. The tensile strength of feather rachis conditioned at 100% relative humidity was 106 MPa. The tensile strength of feather rachis conditioned at 0% relative humidity was 221 MPa [12]. The Young's modulus increased remarkably along the length of the rachis, with the highest values at the feather tip. X-ray diffraction measurements showed more keratin molecule orientation further out along the rachis.

Moreover, the fibre located closer to the bird is smaller in diameter and has lower physical properties compared with the fibre which is far from the rachis [13]. It is obvious that flight feather fibre exists in a hollow form while down fibre is in solid. In terms of the purpose of fibre-reinforcement, the use of down fibre appears much better than that the use of flight fibre [14].

Silk fibre is a type of fibre collected from dried saliva of bugs or insects during the preparation of cocoons. Silks are generally defined as protein polymers that are spun into fibres by some Lepidoptera larvae such as silkworms, spiders, scorpions, mites

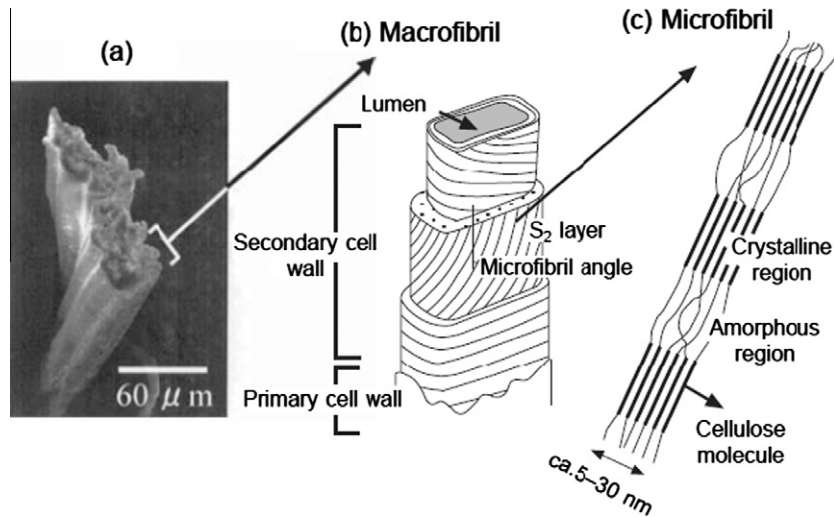


Fig. 2. (a) Scanning electron micrograph of a kenaf bark fibre, and schematic representations of, (b) macrofibril and (c) microfibril of natural plant [4].

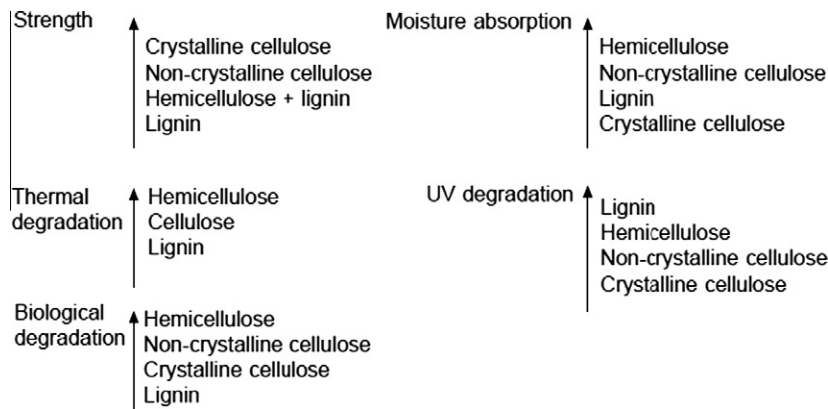


Fig. 3. Properties of cellulose fibres and their dependence on chemical constituents [4].

and flies [15]. Spiders have six or seven sets of glands including major and minor ampullate, flagelliform, aggregate, cylindrical, aciniform and piriform for production of fibres with different amino acid composition. These silks serve as: (1) orb-web Frame, (2) prey capture, (3) wrapping, (4) joint and attachment, (5) reproduction, (6) vibrational sensor and (7) dispersion [16]. The mechanical properties of the dragline silk are highly influenced by the composition of amino acids, insect size, diet conditions, body temperature and drawing speed. [16] Some spider silks exhibit over 200% elongation. Compare with kevlar fibre, the tensile strength of spider silk is a factor of four less than kevlar fibre (3.4–4.1 GPa), but the energy used to break the silk is about three times greater ($1 \times 10^5 \text{ J kg}^{-1}$) [17]. However, the predatory nature of spider silk causes it difficult to handle so that the production of spider silk fibre is relatively low compared to silkworm silk fibre [15].

Arthropods including spider and silkworm have evolved to produce a variety of task-specific silk-protein-based fibre. However, silkworm silk fibre is different to the spider silk fibre as only one type of silk generate by individual silkworm but individual spider can generate 6–7 types of silk for different purposes. Moreover, the dragline produced by spider silk cannot yet be produced in sufficient quantity to support any industrial process. Moreover, the glue-like proteins are generally absent in the spider silk. Therefore, silkworm silk is found to be a higher potential material used for industry and medical application.

The silkworm cocoon is built at the end of the larval stage and protects the pupa during metamorphosis to an adult moth. It

contains silk protein, known as silk fibroin which is stored in the glands of insects and spiders as an aqueous solution. It is understood that the water is acting as a plasticizing agent, keeping the protein malleable [18]. Silk protein is usually produced within specialised glands after biosynthesis in epithelial cells, followed by secretion into the lumen of these glands and prepared to spin out as filament [15]. During the spinning, the concentration of silk in the solution is gradually increased, formation of shear and elongational stresses acting on the fibroin solution in the gland. Elongational flow orients the fibroin chains, and the fibroin (liquid) is converted into partly crystalline, insoluble fibrous filaments (solid) [27]. The bulk of the polymer chains in the crystalline regions are oriented parallel to the fibre axis [18]. Simpson et al. [19] have found that the speed of spinning controls the mechanical properties of fibre.

Silkworm silk, the core filament is an inhomogeneously distributed polymer blend of mainly two proteins that is coated with glycoproteins and lipids [20]. The silkworm cocoon silk fibre is composed of two cores of fibroin because their gland is a paired organ which surround by a cementing layer of sericin in a structure known as have shown in Fig. 4 [21]. The core fibres are encased in a sericin coat, a family of glue-like proteins that hold two fibroin fibres together to form the composite fibres of the cocoon case [22]. This glue-like proteins is called sericin which is amorphous in nature and acts as binder to ensure the structural integrity of the cocoon [23]. The fibroin fibre itself is a bundle of several fibrils with a diameter of $1 \mu\text{m}$. A fibril contains 15 nm wide microfibrils.

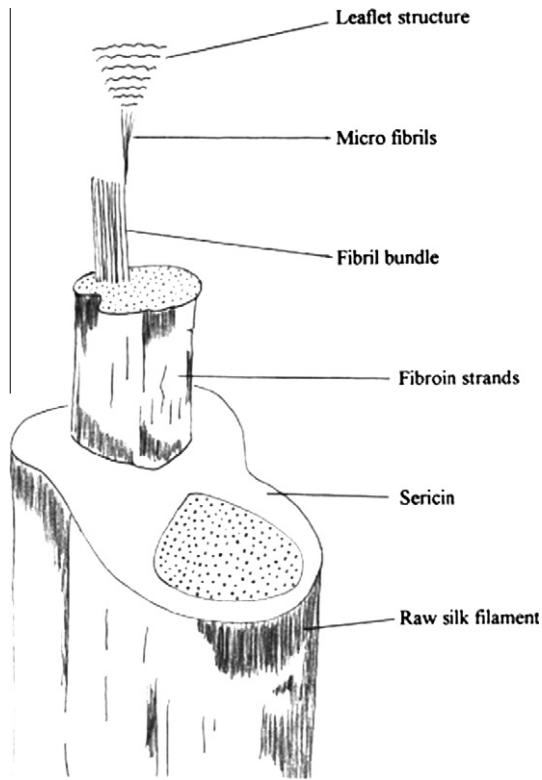


Fig. 4. Structure of silkworm silk fibre [21].

Microfibrils are packed together to form the fibril bundle and several fibril bundles produce a single strand [23,24].

The convenience of reeling long (300–1200) continuous fibre from the cocoon has certainly contributed to its success as a textile fibre. However, a long and continuous fibre can only be reeled from the cocoon after the adhesive sericin coating is removed. Sericin removal requires thermo-chemical treatment of the cocoon in a process conventionally known as degumming [21]. However, degumming would weaken at least one type of non-covalent interaction of core fibroin, such as hydrogen bonds and Van der Waal's bonds. The two important factors associated with degumming could affect the tensile properties of silkworm silk because of the change in the microstructure of two core fibroins [22].

Compared with the commercially Mulberry silkworm silk (*Bombyx mori*), Tussah silk is a textured silk with the brownish toned. It is mainly due to tannin from the variety of trees fed by the caterpillars. Most silkworm cocoon and spider dragline silk fibres contain assembled anti-parallel β -pleated sheet crystalline structures. Silks are considered semi-crystalline materials with 30–50% crystallinity in spider silks, 62–65% in cocoon silk fibroin from the silkworm *B. mori*, and 50–63% in wild-type silkworm cocoons [27]. Fig. 5 shows the cross section, longitudinal view and perspective of silk filaments.

2.4. Biodegradable polymers

Conventional polymers such as polyethylene (PE) and polypropylene (PP) are used for many years and have been developed to be an absolutely necessary part of our life in almost every area nowadays. With time and the rapid development of science and technology, the mechanical property, stability and durability of conventional polymers have been improved continuously. However, these long lasting polymers seem inappropriate in application of the product which has short product life cycle, such as plastic plates and fork for party. These polymers persist for hundred years in a landfill after disposal. Therefore, advantages as disadvantage, high durable property of these polymers increase the environmental burden. Moreover, these polymers are often disposed and stained with food residue; increase the complexity of the plastic recycling. The cost of recycling of plastic is thus so high and so that there is no choose to land filling or incineration of plastic. As the public starts focusing on the huge environmental accumulation of these long lasting polymers and pollution problem caused during and after the life cycle of the polymers (such as manufacturing and disposal process), and fitting the modern society, the study on naturally-degradable polymers with short life cycle is needed.

Biodegradable polymers were first introduced in 1980s [25] which are designed to degrade upon disposal by the action of microorganisms. In general, polymers are solid, non-metallic compounds with high molecular weight. They are comprised of repeated macromolecules, and have varying characteristics. Material usage and final mode of biodegradation are dependent on the composition and processing method employed [26]. These polymers means capable of undergoing decomposition into carbon dioxide, methane water, inorganic compounds or biomass in which the predominant mechanisms is the enzymatic action of micro-organisms that can be measured by standard tests, over a specific period of time, reflecting available disposal conditions.

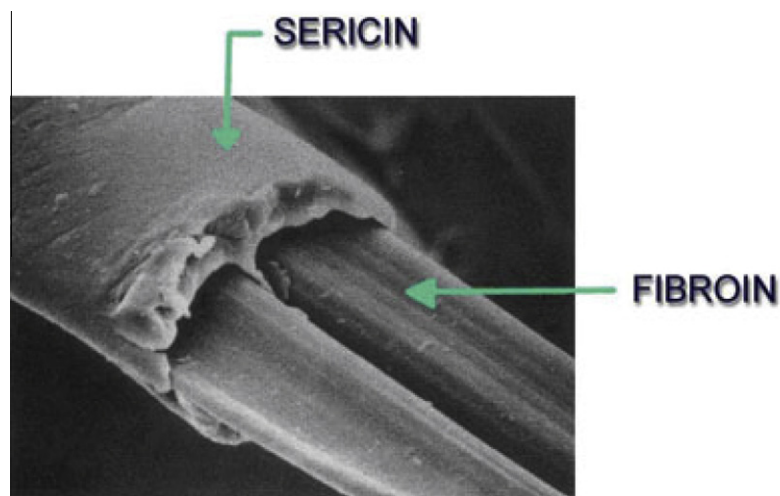


Fig. 5. Cross section, longitudinal view and perspective of silk filaments.

These polymers can be also classified on the basis of the origin, that is, naturally occurring or synthetic in Fig. 6 [27]. Natural polymers are available in large quantities from renewable sources, while synthetic polymers are produced from non-renewable petroleum-based resources. Nowadays, degradable polymers used in various forms including films, moulded articles, sheet, etc. The potential applications of biodegradable applications include: (1) film such as plastic shopping bags and bin bags, (2) cling wrap, (3) flushable sanitary products, (4) sheet and non-woven packaging, (5) bottles and container, (6) loose fill foam and (7) medical application. Among these biodegradable polymers, aliphatic polyesters

constitute the most attractive family have been extensively studied. Table 2 summarizes the properties of aliphatic polyesters. Polyesters play a predominant role as biodegradable plastics due to their potentially hydrolysable ester bonds.

Poly (lactic acid) (PLA) belongs to the family of aliphatic polyesters derived from α -hydroxy acids. PLA is a compostable polymer derived from renewable sources which is mainly from starch and sugar. Since PLA is compostable and derived from sustainable sources, it has been viewed as a promising material to reduce societal solid waste disposal problems [28]. A high-molecular PLA cannot be directly synthesised from the molecule of lactic acid, mainly

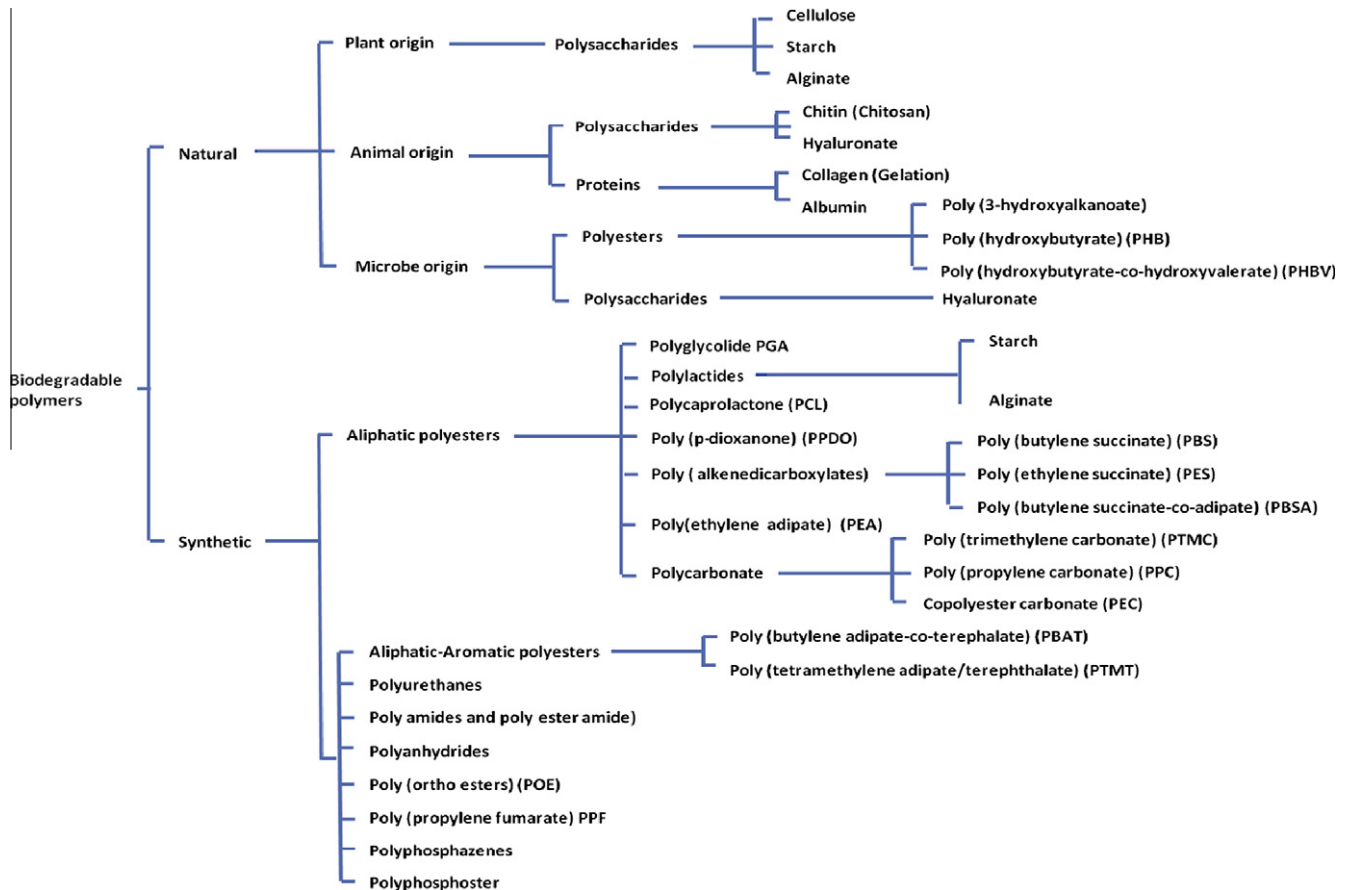


Fig. 6. Natural and synthetic biodegradable polymers [27].

Table 2
The properties of aliphatic polyesters.

Examples	Crystallinity	Glass transition temp.	Melting point	Modulus	Loss strength (month)	Loss mass (month)	Processing temp.	Refs.
Poly (butylene succinate) (PBS)		−45 to −10	90–120	0.4–0.6			160–200	[32,38]
Poly(ethylene succinate) (PES)		−45 to −10	90–120				160–200	
Polyglycolide (PGA)	45–55%	35–40	200	12.5 Gpa	1–2	6–12		[38]
Polycaprolactone (PCL)	67	−60	55–60	0.19		24–36		[38–40]
<i>Poly lactides</i>								
Poly L-lactide (PLLA)	~37	60–65	170–180	4.8	~6	12–24		[38,39]
Poly D-lactide (PDLA)								
Poly DL-lactide (PDLA)		55–60		1.9	1–2	12–16		[38]
Polydioxanone PDS, PPDO	High	<20	2.1	1.5	1–2	6–12		[38,35,42]
<i>Poly hydroxyalkanoates PHA</i>								
Poly(3-hydroxybutyrate) (PHB)	80	5	173–180	0.9–4				[40,41]
PHV								
PHH								
Poly(trimethylene carbonate) PTMC						3–4		[38]

because of the generation of water during the condensation process (leading to the degradation of the PLA formed and formation of only low-molecular oligomer). In general, three different ways can be followed to solve this problem:

- (1) Addition of chain-coupling agents during the condensation process.
- (2) Dimerization of the oligomer into cyclic lactide (see above), distillation of solution to take out the water condensed and then production of the PLA by ring-opening polymerisation.
- (3) Azeotropic dehydration during the condensation process, removing the water during the process by change of pressure.

PLA belongs to the family of the polyester and is generally linear (without strong entanglement, branching between the chains). The structure of the molecule influences its mechanical and thermal properties (for PLA 3051D: T_g is 55–65 °C, T_c 150–165 °C and tensile strength ~48 MPa [29]), which are quite similar to other polyesters (such as PET). The thermal properties are however a bit lower, due to the absence of the benzene ring (chain more free to move). Its chemical properties and water resistance are weakened by the presence of the carbonyl group (C=O), which allows hydrolysis degradation. Like most of the polymers, the different macromolecules (chains) are bonded together by hydrogen bonds (Van de Waals forces). Most important mechanical and thermal properties (crystallinity rate, T_g and T_m) are then influenced by the concentration and disposition of different enantiomers (L- and/or D-lactic acid). Indeed, the chains made of a unique basic element can align each other easier in a configuration favoring inter chain bonds. Thus the lowest T_g is found in racemic mixing of L- and D-enantiomers while the highest properties are obtained by stereo complex PDLA and PLLA blends (respectively using the D- and L-enantiomers) and reach a maximum with a ratio of 50:50. Like most polymers, PLA is hydrophobic. It can only absorb 1% water content and undergo hydrolytic degradation, making it biodegradable and environmentally friendly. PLA normally undergoes three main degradation processes: (i) chemical hydrolysis, (ii) enzymatic degradation and/or (iii) microbial degradation [30]. During chemical hydrolysis, the water molecule attacks the double bonding C=O of the PLA, like shown below:

The enzymatic degradation occurs mainly in the amorphous region of the polymer and seems to attack preferentially the ester bonds of L-lactic acid (cleaving the polymer). The PLA-degrading and the silk fibroin-degrading enzymes belong roughly to the same groups and it seems that the L-lactic acid unit of PLA is recognised as similar to the L-alanine unit of silk fibroin. The same conclusion can be made for the microbial degradation, where the bacteria's ability to degrade the PLA and silk are linkable. One can moreover note that the bacteria able to degrade PLA are more scarce than the ones able to degrade most of others polyesters [15].

In order for PLA to be processed on large-scale production lines in applications such as injection moulding, blow moulding, thermoforming, and extrusion, the polymer must possess adequate thermal stability to prevent degradation and maintain molecular weight and properties. PLA undergoes thermal degradation at temperatures above 200 °C (392.8 °F) by hydrolysis, lactide reformation, oxidative main chain scission, and inter- or intra-molecular transesterification reactions. PLA homopolymers have a glass transition and melt temperature at about 55 °C and 175 °C, respectively. They require processing temperatures over 180 °C. At this temperature, unzipping and chain scission reactions leading to loss of molecular weight, as well as thermal degradations, are known to occur. Consequently, PLA homopolymers have a very narrow processing window. The rheological properties of PLA, especially the

shear viscosity, have important effects on thermal processes, such as injection moulding, extrusion, film blowing, sheet forming, fibre spinning, and thermoforming. Poly-Lactide melts are shear thinning, similar to polystyrene. Its working temperature is dependent on the melt viscosity, which is, in turn, dependent on the weight-average molecular weight of PLA, the amount of plasticizer, the shear rate, the type of melt processing, and the amount of work put into the polymer. Under the same processing conditions, semi-crystalline PLA had a higher shear viscosity than amorphous PLA. As the temperature increased, the shear viscosity decreased for both types of PLA. The PLA melt was characterised as a pseudo plastic, non-Newtonian fluid [31].

3. Processing of raw materials

3.1. Selection criteria

Suitable manufacturing processes must be utilised to transform the materials to the final shape without causing any defect of products. For the selection a suitable process to fabricate biodegradable polymer-related composites, design and manufacturing engineers would mainly focus on numbers of criteria including desired properties, size and shape of resultant composites, processing characteristics of raw materials, the production speed and the manufacturing cost. The size of the composites is a dominating factor for the preliminary assessment on a suitable type of manufacturing processes to be used. For small to medium sized components, injection and compression mouldings are preferred due to their simplicity and fast processing cycle. However, for large structures, they are typically manufactured by open moulding and autoclave processes. Similar to other plastic products, the complexity of shape of a product also influences the type of manufacturing processes to be used. For example, filament winding is the most suitable method for manufacturing composites pressure vessels and cylinders. Recent development has also used carbon fibre wrapped on the surface of forged Aluminium cylinders to form ultra-high pressure tanks.

Pultrusion is mainly used for producing long and uniform cross-section parts. In some extent, optic fibre can be integrated into the pultrusion process to produce self-structural-health monitored composite structures. The shape of the parts being made is highly dependent on the shape of the die. Somehow, several stages of heat control are needed to cure the composite parts. Depending on the performance of composites products, suitable raw materials (thermosets/thermoplastics, high/low viscosity, processing temperature) should be chosen with an appropriate composite fabrication technology.

However, in certain extent, the criteria of selecting the right manufacturing processes for natural fibre composites are different with that to be used for traditional polymers. The properties of natural fibre composites are highly dependent on the length, orientation, diameter and content of fibre. The surface condition of the fibre also plays a key role as it would affect the bonding interface between the fibre and surrounding matrix. Removal of a surface coating of fibre (like silk and coir fibres) or pretreatment of fibre (like hemp) by using chemical process may be needed to ensure a good bonding is resulted. Theoretically, high tensile strength could be achieved by increasing the amount of fibre used. However, it may not be done by using injection moulding process as the expansion of fibre in wet condition could cause a sucking effect. Therefore, compression moulding may be used for a simple form of composites products.

Natural fibres extracted from wool and cocoon silks are comprised of numerous of micro-fibrils. It has been reported that these fibres after degumming, only two triangular fibrils (brins) would be remained, and these fibrils are formed by several thousands of

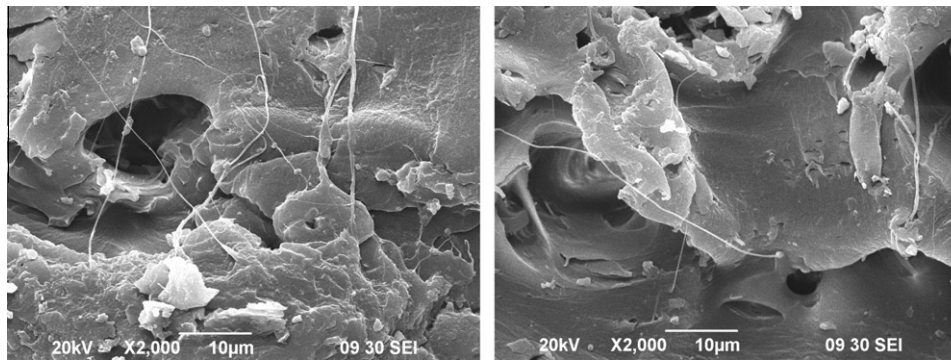


Fig. 7. Scanning electron micrographs showing the micro fibrils of the silk inside the composites.

micro-fibrils as shown in Fig. 7. A noteworthy weakness in the natural fibre reinforced thermoplastic composites is the poor interfacial bonding between the fibre and matrix. The interfacial adhesion between them plays an important role in determining the performance of the composites. 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. The incorporation of hydrophilic fibres in polymers leads to heterogeneous systems whose properties are inferior due to poor adhesion between the fibres and the matrix [32–34]. Therefore, these debonded fibres dilute the matrix content and act as flaws which reduce the effective cross sectional area and, finally poor mechanical strength is resulted. Moreover, the formation of fibres agglomeration, due to the inter-fibre hydrogen bonding which prevents thorough dispersion of fibres during the manufacturing process and thus weakens the strength and affects the appearance of the composites [32,35].

Thus the treatment of natural fibres for adhesion improvement is a critical step in the development of the composites. Different treatments such as pre-impregnation, surface modifications, chemical reactions and plasma have been studied for interfacial shear strength improvement in order to develop composites with better mechanical properties [32,33,36–38]. Natural fibre always cannot be wetted completely by following the general manufacturing processes as they are not designed for wetting fibre with tight-packing fibrils. The viscosity of polymers is normally too high for impregnation. Better fibre pre-impregnation allows a better fibre wetting and thus enhances the mechanical interlocking between fibre and matrix [36].

The surface modifications of fibres by using compatibilizer or coupling agent for effective stress transfer across the interface were explored. 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 the both natural fibre and the 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 fibres depends strongly on the characteristics of the fibre surface to which the coupling agent is adhered [32]. The coupling agents are tetrafunctional organometallic compounds which are commonly known as silane, zirconate, or titanate coupling agents [33]. Rozli Zulkifli et al. [38] have found that the silk/epoxy composite with fibre surfaces which treated by silane-based coupling agent shown an improvement of the adhesion. Keener and Stuart [34] used polyethylene couplers and the results indicated that the tensile strength and impact property of the coupled composites were improved as compared with non-coupled blend composites. Kazayawoko et al. [35] used Maleated

polypropylene (MAPP) as a coupling agent and the effectiveness of MAPP has been attributed to its ability to wet and disperse the wood fibre efficiently.

Chemical treatments such as dewaxing, delignification, acetylation, and chemical grafting are used to modify the surface properties of the fibres and enhance the performance of composites [33]. Alkaline processing is one of the most common chemical treatments in the industry which are not only used for increasing the surface roughness of the natural fibre that results in a better mechanical interlocking, but also for the increments of the amount of cellulose exposed on the plant fibre surface, thus increasing the number of possible reaction sites. Valadez-Gonzaleza et al. [36] have explored the fibre–matrix interphase physicochemical interactions of the natural fibre reinforced plastic. They have found that the fibre surface area was increased by the means of alkaline treatment.

Plasma treatment is an environmentally-friendly new technology which can alter the surface properties of the materials without interfering their bulk properties. Chaivan et al. [36] have studied the utilisation of SF₆ plasma treatment for improvement in hydrophobic property of silk fibre. A reproducible and significant increase in the hydrophobic property compared with the untreated sample was obtained.

4. Moulding processes

4.1. Injection moulding

Injection moulding of composites is a process that forces a measured amount of mixture which contains molten polymer and fibre into mould cavities. Many studies have been conducted on the potential of using natural fibres as reinforcement for renewable polymers to make a composite through injection moulding [40–45]. The original thermoplastic polymer used by this process was designed for plastic pellets. For fibre reinforced composites, the pellets with chopped fibres are fed individually through a funnel-shaped feed hopper into a heated compression barrel with a rotating screw (“screws” for twin-screw extruder). The purpose of heating the barrel is to transform the solid pellets into viscous liquid which can be drove through the sprue nozzle and finally forced into the matched-metal closed mould cavities. The mould is tightly clamped against injection pressure where the polymer solidifies, freezing the orientation and distribution of fibres. The composite is then removed from the closed mould after it is sufficiently cooled to be ejected to form a part of desired shape. As the mixture is required to move toward to the sprue nozzle, polymer is pressurised because of the screw mechanism. The function of the screw is to (1) generate heat by viscous shearing to melt the

polymer, some heat that is used for melting pellets evolved from the friction in between pellets, barrel and screw [45], (2) apply the shear force to mix the polymer and fibre and (3) act as a piston to force the mixture of fibres and molten polymer through sprue nozzle into a matched-metal closed mould. It has been reported that as the temperature increases, the shear viscosity of biodegradable polymers would decrease which makes the flow easier. Besides, as the shear rate increases, the viscosity of the polymer melts would also be decreased significantly. This change of viscosity is caused mainly by the breaking of PLA molecule chains due to the strong shear forces and temperature [46].

Fibre that is used in the injection moulding is usually chopped into short fibre according to the critical fibre length criterion in which the stress should be fully transferred from the matrix to the fibre and the fibre can be loaded to its full capacity assuming a good interfacial bonding is resulted. However, the traditional injection moulding process limits the fibre length that solidifies in the final part since the high shear rates in the barrel and the passage of fibres through narrow gates and openings in the mould which cause significant fibre attrition. Therefore, the fibre length in practice is normally shorter than the predicted fibre length because of the fibre attrition. This fibre attrition causes the fibre length below the critical length as expected, the fibres shorter than the critical length would not be able to carry their maximum load effectively. In an extreme case, the fibre rather acts as a defect in the material not only because of its length effect, but also on the poor bonding properties. Nevertheless, if the fibre length is beyond the pre-determined critical length, it will carry an increasing fraction of the applied load and may fracture prior to the failure of the matrix. Therefore, it is necessary to carefully determine the critical length of the fibre before injection moulding is performed. On the other hand, increasing fibre content would theoretically improve the stiffness and the strength of resultant composites. However, in practice, the traditional injection modelling process would limit the amount of fibres to be injected because of the fibre cluttering, narrow gate and sprue and, viscosity of the fibre/polymer mixture. Another main issue is the volume expansion of the fibre after mixing with the liquid form of matrix.

Residual stress and fibre orientation with respect to the depth are also the critical issues which affect the modulus distribution of the injection moulded composites. Residual stress is an internal stress which occurs as a result of the rapidly cooling of molten polymer in the absence of external forces. In general, the residual stress distribution shows tensile stresses at the surface and core regions and compressive stress at the intermediate region, which is well-known as the characteristic residual stress distribution in injection-moulded parts [47]. Numerous of researches have therefore studied the residual stress distribution of composites made by the injection moulding process [46–49]. (1) High pressure gradient, (2) non-uniform temperature profile caused by inhomogeneous cooling of the polymer melt, (3) orientation of polymer chains and (4) the difference in thermal expansion coefficient between matrix and fibres are the common phenomena which residual stresses may be introduced in injection moulded polymers or composites during filling, packing, and cooling stages.

When the flow is ceased, the molecule orientation starts to relax while solidification process subsequently occurs before this process is completed. It would impede the relaxation of the molecular orientation which is then frozen in, the residual stress is therefore formed inside the part. Residual stress in a pure thermoplastic polymer and its fibre composites cause an earlier fracture of the composites which affect the quality of products seriously. Stress distribution along the flow path is influenced by the pressure history of the molten mixture at the beginning of the injection moulding process to the end of filling up the mould cavity. The various features of the stress profiles are explained by the influence of

the pressure decay rate in the injection-moulding process [49]. These residual stresses also result in warpage and shrinkage of the final products and may induce reduction of mechanical properties. Therefore, the dimensional accuracy and properties of the final products are highly related to the residual stress distribution in the moulded part [47]. For natural fibres, as their moisture absorption characteristics, impurities and voids formation inside injection moulded composites may be resulted as high temperature is used during the process and cause water molecules trapped inside micro-fibrils to be gasified.

Fibre orientation in an injection moulded short fibre composite is experienced variation with respect to the thickness direction as well as the in-plane direction. It induces the mechanical properties of the composite such as modulus and tensile strength may vary in the thickness direction according to the corresponding orientation status. For the range of fibre concentrations encountered commercially, fibres do not appear to have any direct effect on the matrix orientation. As the fibre concentration increases, however, the matrix orientation becomes dominated by the orientation of the fibres [50]. During the injection moulding process for composites, a complex molten polymer flow field is generated and fibres are therefore oriented. The orientation of fibres will be fixed until the matrix is solidified. Convergent flow results in high fibre alignment along the flow direction, whereas diverging flow causes the fibres to align at 90° to the major flow direction. Shear flow produces a decrease in alignment parallel to the flow direction and the effect is pronounced at low flow rates. In generally, the fibres align in the direction of shearing and also in the direction of stretching. The shear flow near the mould walls aligns the fibres in the direction of the injection flow and this layer is called the skin. Below the skin layer, the molten mixture continues to experience shear and fibres orient along the shear lines. Finally, the core layer is formed as the fibres are swayed by the bulk deformation of the flow in the mould which usually has an elongated component, causing the material to stretch in and out of the paper direction aligning the fibres. This skin core structure shown in Fig. 8 is a common microstructural observation [48,51]. However, the skin core structure is less significant in the small sample with low fibre volume fraction. To assess the alignment of fibres during the manufacturing process in a small sample, small and thin dumbbell shaped composite samples were made by injection moulding. A microscopy was used accordingly to observe the fibre orientation through the image analysis technique. According to Fig. 9, most of the fibres are well aligned along the sample's axis (i.e. the loading direction), only a small amount of obliqued fibres.

There are numerous issues that should be concern during the injection moulding process to obtain the optimal properties of the resulting natural fibre composites and avoid development of residual stress which cause warpage, stress cracking, and long-term deformation. Process, material and geometric parameters should be optimised to minimise these problems happen. Process parameters include the melt temperature, injection and screw speeds, injection pressure and the mould temperature that can be controlled on the injection units. Increasing mould temperature results in a decreasing overall stress level, while the compressive stress region is shifted onto the surface [49]. According to recent research investigations, for biocomposites, the machine temperature of biodegradable polymer, such as Poly-lactic-acid (PLA) composites was made by using injection moulding process should be restricted in the range of 150–210 °C depending on the type of PLAs and their crystallinity from diverse manufacturers.

Molten polymer rheology, and fibre type and content are the material parameters which affect the manufacturing process and the properties of resultant composites. Under the same processing conditions, semicrystalline PLA had a higher shear viscosity than that of amorphous PLA [46]. The geometric parameters also play

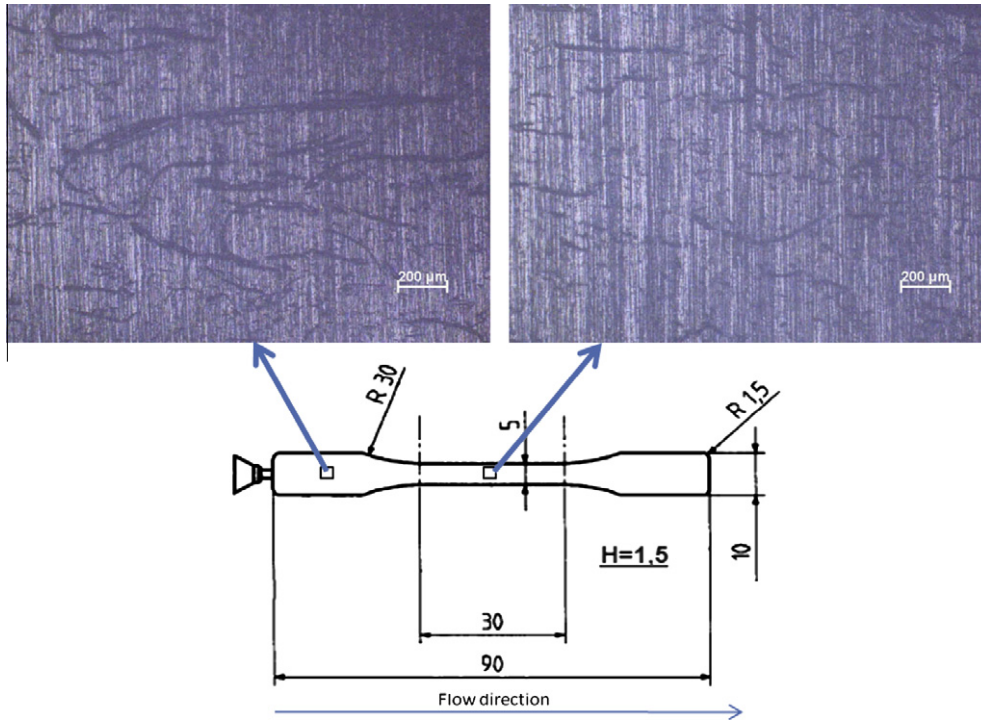


Fig. 8. Micro graphs of cut-off view (along the longitudinal direction of the sample) of the silk fibre/PLA composite with 5 vol.% silk fibre: (a) wide section and (b) narrow section.

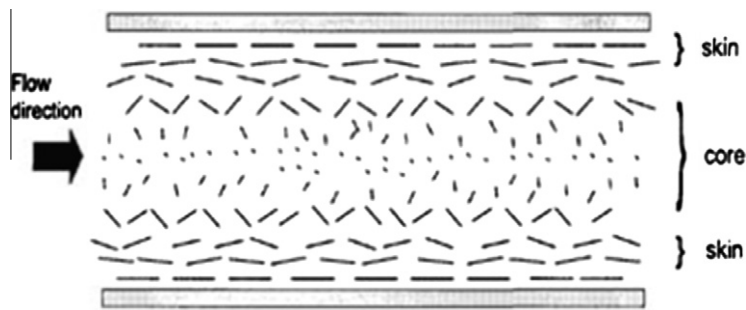


Fig. 9. Influence of flow on fibre orientation: Skin-fibres are mostly aligned along the flow direction; Core-fibres are mostly aligned perpendicular to the flow direction.

a key role on the residual stress elimination. The mould cavity shape and size, the locations of injection gates and the vents that allow the air to escape are the examples of geometric parameter which not only affect the residual stress, but also the air trapping and stress concentration.

4.2. Compression moulding

Many studies have been conducted on the feasibility of using natural fibres as reinforcement mixed with renewable polymers to form a new class of biocomposites through compression moulding process [40–44]. This process is a combination of hot-press and autoclave processes. For autoclave process, thermoplastic prepregs are laid up on a mould in a desired sequence. An entire laminate is then bagged under vacuum and placed inside an autoclave. The laminate is then heated up following a preset heat-pressure cycle and a resultant composite is formed after curing [52]. However, for the hot-press processing, a close mould may or may not be necessary [53]. With the use of close-moulds, the pre-cut and weighed amount of fibres (in the forms of chopped, mat or stitched) are stacked together and placed inside a pre-heated mould cavity.

For natural fibre, the fracture of some fibres may occur before resin films are molten if excessive pressure is applied. Sheet moulding compounds (SMCs) and bulk moulding compounds (BMCs) are traditional initial charges for compression moulding process. The charges usually cover 30–70% of the female mould cavity surface [52]. The mould is closed and then pressurised before temperature is applied. The compounds are molten to form the shape of the cavity. Afterward, the mould is opened and the part is ejected. As the fibre can be gently placed inside the mould and no shear stress and vigorous motion are applied, the damage of the fibre can be kept as minimal. In this case, long fibre can be used to produce a biocomposites with higher volume fraction. For the natural fibre composites, short fibres or fibre mats could be pre-mixed with the compounds for compression moulding, it would act as reinforcement to reduce the shrinkage of final products.

4.3. Hot pressing

As mentioned in the previous section, hot press is favourable for simple flat samples as only two hot plates are needed to compress all fibre and matrix together and then heat was applied

subsequently. However, the viscosity of the matrix during the pressing and heating processes is a concern as it is not easy to be controlled, in particular for thick samples. The viscosity of the molten matrix should be low enough to impregnate into the space between fibres and high enough to avoid spurting out. As natural fibres are made by many small filaments, it also takes time for wetting them. Therefore, the controls of viscosity, pressure, holding time, temperature in relation to the types of fibres and matrix, thickness and size of samples are critical to produce quality composites. Several minor defects such as residual stresses, voids, warpage, fibre breakage, sink marks and scorching would cause the reduction of the mechanical properties of the composites. Therefore, process, material and geometric parameters should be optimised to minimise possible defects appear. One more critical issue is, for biodegradable polymers, their processing temperature is normally below 200 °C to avoid the degradation of the polymers. If the products are thick, the heat is required to be transferred from the surfaces of the products toward the core. Carefully studying the temperature gradient is essential to avoid overheating on the surface or sub-temperature in the core to melt the polymers.

Based on the past experience, it was found that the tensile properties of natural fibre composites decrease when the set mould temperature and flow velocity decrease. Most of natural fibres are normally distributed randomly at the beginning and finally aligned toward the matrix flow direction for flat plate moulding [54,55]. The required temperature and pressure for the moulding process may be varied depending upon the thermal and rheological properties of the matrix. Flow of the material is required to expel air entrapped in the mould as well as in the charge. Void morphology in the sample has a negative effect on the flexural modulus and strength, but a clear positive effect on the beam stiffness [56]. During the moulding process, a complex heat transfer and a viscous flow phenomenon take place in the cavity [57]. For a good moulded part, a rapid mould-closing speed is desirable since it avoids the possibility of premature gelation and produces most uniform flow patterns regardless of the charge thickness [52].

Material parameters, for example, increasing the filler content also acts as a heat sink within inside the material as it would decrease the total amount of heat liberated [52]. The initial charge shape, size and its placement location in the mould are crucial parameters as they influence the final properties of a product. The amount of flow in compression moulding is small but critical to the properties and the quality of final parts because the flow controls the orientation of short fibres which is the main factor to determine the physical and mechanical properties of a resultant composite. To help control the moulding process smoothly and effectively, an optimised fibre which possesses high-surface energy, a low expansion, and low swelling should be used so as to lead to a better wetting and impregnation [58].

A slight excess of material is usually placed inside the mould to ensure it is completely filled. It is possible to have varying degrees of flow of fibres and/or of melt in compression moulding, the fibres are initially randomly oriented. However, as the mixture becomes fluid in the mould it deforms and the deformation changes the orientation of the fibres. Orientation distributions can be extremely complicated. Some locations the fibre can retain at randomly oriented, whereas others may have high degree of alignment toward the flow direction. Increasing the fibre content also leads to enhance the anisotropy of final moulding products [59]. A low-viscosity paste may flow too rapidly and cause air entrapment [58]. Different temperatures inside moulded parts would generate different degrees of residual stresses, particular at thick sections. Thus, the temperature distribution and rate of cooling are important in determining how these stresses relax during cooling status [54].

The geometry of the moulding part is important which affects the flowing behaviour and fibre orientation. Fibre content inside the rib and around the sharp turning sections is normally much lower than that of other flat sections. It was also found that the larger the rib thickness, the easier the flow (with the fibres) into the ribs. However, a small lead-in radius would reduce the flow or increase the flow resistance into the ribs [60]. High pressure loss at the entrance of the rib is due to viscous friction. This pressure loss will result in fibre–matrix separation in these areas which in turn would weaken the structural integrity of resultant parts and lead to increased sink-mark depth. For the curing process concerned, the material at the centre of the rib sub-structure cures relatively slower than other flat-plate sections. The fibres are dense near to the top surface and around the rib corners, whilst a resin-rich area appeared just below the top surface at the centre [57]. High pressures are required for moulding parts that contain deep ribs and bosses [52]. Thick structures are not easily produced by this technique because of heat conduction. The charge surface temperature quickly attains to the mould temperature and remains relatively uniform compared with the centreline temperature. The centreline temperature increases slowly until the curing reaction is initiated at the mid-thickness of the part. For thin parts, the temperature rise is nearly uniform across the thickness and the maximum temperature in the material seldom exceeds the mould temperature. When the SMCs are placed at the room temperature on the hot mould, the surface of the SMCs soften and make them forming a resin-rich lubricating layer. Thus, for the purposes of modelling, the flow field can be divided into two regions: the core, which occupies most of the flow domain; and a thin lubricating layer. This is shown schematically in Fig. 10 [61]. For a thin part, the extensional deformation becomes more uniform and approaches the same flow pattern observed at fast mould-closing speeds [52]. For a thick part, high moulding temperatures should be avoided. Since the surface temperature first attains to the resin gel temperature, curing begins first at the surface and progresses inward. Curing occurs more rapidly at higher mould temperature but the peak exotherm temperature also increases [100]. Residual curing stresses in the moulded part are reduced as the thermal gradient remains nearly constant across the thickness through preheating [52].

4.4. Resin transfer moulding (RTM)

Liquid composite moulding processes encompass resin transfer moulding (RTM), vacuum assisted resin transfer moulding (VARTM), structural reaction injection moulding (S-RIM), co-injection resin transfer moulding (CIRTM) and other subsets where the basic approach is to separately inject the liquid resin into a bed of stationary preforms. The RTM process has become a popular composite manufacturing process due to its capability for high volume

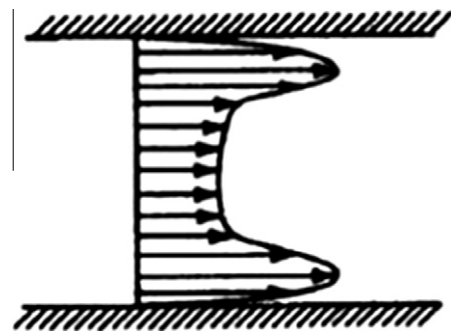


Fig. 10. Transverse velocity profile for "Preferential flow" [61].

Table 3
Common applications of natural fibre reinforced composites.

Potential application	Examples
Automotive	Door panels, seat backs, headliners, dash boards, car door, Transport pallets, trunk liners, Decking, rear parcel shelves, spare tyre covers, other interior trim, spare-wheel pan, trim bin
Aircraft	Interior panelling
Construction	Railing, bridge, siding profiles
Household products and furniture	Table, chair, fencing elements, Door panels, interior panelling, Window frames, door-frame profiles, food tray, partition
Electrical and electronics	Mobile cases, laptops cases
Sports and leisure items	Sports and leisure items: Tennis Racket, bicycle, Frames, Snowboards

production and cost effectiveness. Many studies have been made on the potential of natural fibres as reinforcement with renewable polymers as matrix through RTM [62–67]. In the RTM process, dry fibre preform (impregnating) or porous fibrous preform is placed into the mould cavity. Two matching mould halves are clamped tightly to avoid leakage of resin during injection process. Then, using dispensing equipment, a pressurised molten plastic is injected into the heated mould using single or multiple inlet ports in the mould depending on the complexity of the shape of a final product until the mould is filled with resin. After cooling, the part is then removed from the mould [62]. Post-curing normally is needed to ensure the resin is fully cured (chemically reacted between the resin and its catalyst).

In the RTM process, the resin injection pressure, temperature of the mould, permeability of the fibre mat, preform architecture and permeability, resin viscosity, gate location and configuration, vent control and preform placement techniques are the major processing variables. In general, higher injection pressure and mould temperature would shorten the manufacturing cycle time due to the viscosity of resin is low. However, an excessive injection pressure may cause deformation of the mould and wash-out of the fibre preform. An excessively high mould temperature may induce pre-mature resin gelation and cause short shot. All of the process variables are interrelated and have effects on the mechanical properties of final products. These processing variables have significant effects on different aspects, such as fibre wetting out and impregnation, injection gate design, “dry patch” and void formation [68].

For natural fibre composites, small clearances may exist between the fibre preform and mould edges because of loose edge fibre bundles, poor fitting size, or deformation of the fibre preform in the RTM process. The clearance results in a preferential resin flow path during the mould filling stage. This edge flow can disrupt the uniformity of the flow pattern and cause incomplete wetting of the preform. This phenomenon intensifies with the decrease of preform permeability. At an early stage of the injection process, the velocity differences are very high and then gradually reduce. This is due to the gradual increase in flow resistance which leads to smaller differences in velocity. Edge flow is introduced due to the clearance between the preform and the mould edge. The presence of edge flow leads to the interruption of flow uniformity and the resin near the edge has a tendency to flow much faster than in the main area due to lower resistance. Edge flow is less sensitive to injection pressure variations but fibre concentrations have a dramatic influence. The deployment of preforms larger than the mould eliminates the problem. “Quasi-one-dimensional steady” flow is preferred in order to achieve successful mould filling with complete impregnation and proper ventilation [69].

For fast resin flow without increasing injection pressure, resin can be injected using multiple injection gates. However, with improper injection schemes, the resin front becomes complicated

and numerous air bubbles may form where the flow fronts merge [68]. Because of the high flow resistance and slow flow and impregnation, the resin has a tendency to flow along the channel of least resistance under injection pressure and therefore the effect is intensified. Consequently both the values of mould filling distance differences between the centre and edge and the arrival time of edge flow at the bottom are substantially increased. The edge flow has an adverse effect on the mould filling process which leads to the formation of dry spots and spillage [70]. Due to aforementioned problems, it would induce a difficulty to assure full wetting inside the preform because of the inconsistency of the geometry of natural fibre and inhomogeneous fibre architecture. Such inhomogeneity leads to non-uniform permeability of the fibre preform, which in turn causes the resin velocity to vary from point to point at a micro scale. The capillary pressure, which also prevails at this length scale, exacerbates the spatial variation of the resin velocity. The resulting microscopic perturbations in the resin flow front allow voids to form [71].

While the average velocity field of the resin may appear smooth, the local velocity can vary considerably from point to point at the micro scale. The reason is that the fibre preform has a non-uniform microstructure, and hence its local permeability and the local capillary pressure may differ between inside and outside fibre tows [71]. It has been shown that there is a marked increase in voidage in the areas where flows meet and this is correlated to a deterioration of mechanical properties. The void content within a composite material produced by RTM will depend on the void content of the resin prior to injection and the extent of void formation and growth during mould filling and cure. In general, vacuuming of the mould and injection pot are required prior to the injection process starts.

5. Potential applications

5.1. Ecological applications

Recent increase of the prices of petroleum-based products, strict governmental regulations and taxation systems on carbon footprints and well-educated young generation on the acceptance of adopting green products have driven the growth of developing materials with the use of natural resource to another peak. It therefore creates a new business model for all engineering enterprises to re-invent their capital including human resource to adopt this new change. The application of natural fibre reinforced polymer composites and natural-based resins for replacing existing synthetic polymer or glass fibre reinforced materials is huge. Automotive and aircraft industries have been actively developing different kinds of natural fibres, mainly on hemp, flax and sisal and bioresins systems for their interior components. High specific properties with lower prices of natural fibre composites are making it attractive for various applications. According to Lucintel, a leading global management consulting and market research firm, the global natural fibre composites market reached to US \$2.1 billion in 2010. This market is expected to grow with a CAGR (compound annual growth rate) of 10% over the next 5 years (2011–2016) [72]. Nowadays, new construction materials using natural fibre are well suited for anisotropic and specially tailored lightweight structural components parts such as interior panels inside cars, partitions (or called “dividers”) inside airplanes and coats and other secondary structures with low temperature servicing condition. Table 3 summarizes the potential applications of natural fibre composites in automotive, electrical and electronics, sports and leisure items, construction, aircraft and household products & furniture industries [73–75]. Besides, as natural fibre is formed by several thousands of fibrils together which is an idea structure for energy absorption including sound wave energy, so it is good for best

using its inherent advantage for developing noise barriers and impact resistance structures. Moreover, eco-friendly measures taken by the electronic industry is another major growth driver for these composites in electrical and electronics applications. Recently, a major research focus on natural fibre composites, mainly on the plane-based fibre is on their fire resistance properties. Many reports have addressed that by using natural fibres as supplement and/or reinforcement of thermoplastics, the amount of Carbon Monoxide provided during fire is less than that of their host materials.

5.2. Bio-medical applications

For biomedical applications, protein based natural fibre such as silkworm silk, feather and spider silk fibres are suggested rather than other type of plant based natural fibre. Silk fibres as sutures for human wound dressing have been used for centuries [76]. Recently, regenerated silk solutions have been used to form a variety of biomaterials, such as gels, sponges and films, for medical applications [77]. Moreover, silk has been exploited as a scaffold biomaterial for cell culture and tissue engineering in vitro and in vivo [78]. Bioengineering is usually defined as a basic research-oriented activity closely related to biotechnology and genetic engineering which are used for the modification of animal or plant cells, or parts of cells, to restore their function or repair their damage regions, or to develop new microorganisms for beneficial ends [1]. Concerning the implementation of technology in bio-engineering, biomaterials are mainly used in the applications of directing, supplementing, or replacing the functions of living tissues in the human body [72].

Natural fibre composites, mainly on the animal-based fibres are being used for bone repairs and implant development recently as a replacement for traditional metallic materials such as stainless steel and titanium. Although stainless steel and titanium provide sufficient strength and rigidity to align the bone and control motion while healing of bone fracture, they are too stiff as compared with the properties of nature bone [Alan Paper]. By using the animal based fibre as reinforcement for biodegradable polymer for tail-making a new class of biocomposites can enhance the strength of recovered bones and also minimise the risk of the second surgery for removing any metallic implants inside the body. In general, several critical issues are guided on choosing the appropriate natural fibre composites for biomedical and bioengineering applications, these include: (1) biodegradability, (2) bioresorbability, (3) biocompatibility, (4) sterilizability (5) functionability (6) manufacturability, and (7) mechanical and thermal properties [79–81]. Although many works have been conducted along the similar line on applying animal fibres into new class of bio-grade polymer composites, the path is still a long way to go for viva and in vivo examinations.

6. Conclusion

The development of natural fibre reinforced polymer composites has been a hot topic recently due to the increasing environmental awareness on reducing the use of fossil fuel and its related products. Natural fibre can be classified for plant-based and animal-based. The selection criteria are highly dependent on their type, application and cost. However, there is still uncertain on which type of manufacturing processes that are suitable for producing these composites as their materials and mechanical characteristics are different as compared with traditional carbon and glass fibre composites in general. Some processes, their original design were not targeted for natural fibres, while their technologies have been well developed for fast and reliable composite production. This paper addresses a comprehensive review on different

types of composites manufacturing process and their effects to the natural fibre and its composites.

Acknowledgement

This project is supported by the Hong Kong Polytechnic University Grant (G-U688) and the University of Southern Queensland.

References

- [1] Bronzino JD. Biomedical engineering handbook: biomedical engineering fundamentals. CRC Press; 1999.
- [2] Global Biomaterial Market (2009–2014). Markets and Markets; 2009.
- [3] Bledzki AK, Sperber VE, Faruk O. Natural and wood fibre reinforcement in polymers. *Rapra Rev Reports* 2002;13(8):2.
- [4] Baillie C. Green composites: polymer composites and the environment. CRC Press; 2004.
- [5] Mohanty AK, Misra M, Drzal LT. Natural fibres, biopolymers, and biocomposites. Francis Group: CRC Press Taylor; 2005.
- [6] Pickering KL. Properties and performance of natural-fibre composites. Woodhead Publishing Limited; 2008.
- [7] Xie Y, Hill CAS, Xiao Z, Militz H, Mai C. Silane coupling agents used for natural fiber/polymer composites: a review. *Composites Part A* 2010;41:806–19.
- [8] Mohanty AK, Misra M, Hinrichsen G. Biofibres. Biodegradable polymers and biocomposites: an overview. *Macromol Mater Eng* 2001;276–277:1–24.
- [9] Zahn H, Hles JF, Nlenhaus M. Wool as a biological composite structure. *Ind Eng Chem Res* 1980;19:496–501.
- [10] Simpson WS, Crawshaw GH. Wool: science and technology. Cambridge: England Woodhead Publishing; 2002.
- [11] Feughelman M. Mechanical properties and structure of alpha-keratin fibres: wool, human hair and related fibres. University of New South Wales Press; 1997.
- [12] Kock JW. Physical and Mechanical properties of chicken feather materials. Thesis. Georgia Institute of Technology; 2006.
- [13] Barone JR, Schmidt WF. Polyethylene reinforced with keratin fibres obtained from chicken feathers. *Compos Sci Technol* 2005;65:173–81.
- [14] Cheng S, Lau KT, Liu T, Zhao YQ, Lam PM, Yin YS. Mechanical and thermal properties of chicken feather fiber/PLA green composites. *Composites: Part B* 2009;40:650–4.
- [15] Altman GH, Diaz F, Jakuba C, Calabro T, Horan RL. Silk-based biomaterials. *Biomaterials* 2003;24:401–16.
- [16] Saravanan D. Spider silk- structure, properties and spinning. *J Text Apparel, Technol Manage* 2006;5(1):1–20.
- [17] Bonino MJ. Material Properties of Spider Silk. Thesis. NY: University of Rochester Rochester; 2003.
- [18] Atkins E. Silk's secrets. *Nature* 2003;424.
- [19] Shao ZZ, Vollrath F. Surprising strength of silkworm silk. *Nature* 2002;418.
- [20] Hardy1 John G, Scheibel1 Thomas R. Silk-inspired polymers and proteins. *Biochem Soc Trans* 2009;37:677–81.
- [21] Perez-Rigueiro J, Elices M, Llorca J. Effect of Degumming on the Tensile Properties of Silkworm (*Bombyx mori*) Silk Fibre. *J Appl Polym Sci* 2002;84:1431–7.
- [22] Jiang P, Liu H, Wang C. Tensile behavior and morphology of differently degummed silkworm (*Bombyx mori*) cocoon silk fibres. *Mater Lett* 2006;60:919–25.
- [23] Fakirov S, Bhattacharya D. Handbook of engineering biopolymers: homopolymers, blends and composites. Cincinnati (OH): Hanser; 2007.
- [24] Lewin, Menachem. Handbook of fibre chemistry, 3rd ed. Boca Raton (FL), USA: CRC Press; 2006.
- [25] Vroman I, Tighzert L. Review biodegradable polymers. *Materials* 2009;2:307–44.
- [26] Kolybaba M, Tabil LG, Panigrahi S, Crerar WJ, Powell T, Wang B. Biodegradable polymers: past, present, and future. An ASAE Meeting Presentation 2003; RRV03-0007.
- [27] Ikada Y, Tsuji H. Biodegradable polyesters for medical and ecological applications. *Macromol Rapid Commun* 2000;21:117–32.
- [28] Lim LT, Auras R, Rubino M. Processing technologies for poly(lactic acid). *Prog Polym Sci* 2008;33:820–52.
- [29] NatureWorks™ PLA 3051D technical data sheets, NatureWorks LCC.
- [30] Amnat J, Tokiwa Y. Review biodegradation of poly(L-lactide). *Biotechnol Lett* 2004;26:771–7.
- [31] Antoine LD, Davies P, Baley C. Interfacial bonding of flax fibre/Poly(L-lactide) bio-composites. *Compos Sci Technol* 2010;70:231–9.
- [32] Matuana LM, Balatinez JJ. Surface characterization of esterified cellulosic fibers by XPS and FTIR Spectroscopy. *Wood Sci Technol* 2001;35:191–201.
- [33] Saheb DN, Jog JP. Natural fiber polymer composites: a review. *Adv Polym Technol* 1999;18(4):351–63.
- [34] Keener TJ, Stuart RK. Maleated coupling agents for natural fibre composites. *Composites: Part A* 2004;35:357–62.
- [35] Kazayawoko M. Surface modification and adhesion mechanisms in woodfiber-polypropylene composites. *J Mater Sci* 1999;34:6189–99.

- [36] Gonzaleza AV, Cervantes-Uca JM, Olayob R. Effect of fiber surface treatment on the fiber–matrix bond strength of natural fiber reinforced composites. *Composites: Part B* 1999;30:309–20.
- [37] Mohanty AM, Drzal LT. Novel hybrid coupling agent as an adhesion promoter in natural fiber reinforced powder polypropylene composites. *J Mater Sci Lett* 2002;21:1885–8.
- [38] Zulkifli R, Azhari CH, Ghazali MJ, Ismail AR. Interlaminar fracture toughness of multi-layer woven silk/epoxy composites treated with coupling agent. *Eur J Sci Res* 2009;27:454.
- [39] Chaivan P, Pasaja N, Boonyawan D. Low-temperature plasma treatment for hydrophobicity improvement of silk. *Surf Coat Technol* 2005;193:356–60.
- [40] Serizawa S, Inoue K, Iji M. Kenaf-fiber-reinforced poly(lactic acid) used for electronic products. *J Appl Polym Sci* 2006;100:618–24.
- [41] Huda MS, Huda MS. Green composites from recycled cellulose and poly (lactic acid): physico-mechanical and morphological properties evaluation. *J Mater Sci* 2005;40:4221–9.
- [42] Huda MS, Drzal LT, Misra M. Wood-fiber-reinforced poly(lactic acid) composites: evaluation of the physicochemical and morphological properties. *J Appl Polym Sci* 2006;102:4856–69.
- [43] Huda MS, Lawrence TD. A study on biocomposites from recycled newspaper fiber and poly(lactic acid). *Ind Eng Chem Res* 2005;44:5593–601.
- [44] Huda MS, Drzal LT, Mohanty AK, Misra M. Chopped glass and recycled newspaper as reinforcement fibers in injection molded poly(lactic acid) (PLA) composites: a comparative study. *Compos Sci Technol* 2006;66:1813–24.
- [45] Birgitha N. Natural fiber composites optimization of microstructure and processing parameters. Thesis; 2007.
- [46] Qi Fang, Hanna Milford A. Rheological properties of amorphous and semicrystalline polylactic acid polymers. *Ind Crops Prod* 1999;10(1):47–53.
- [47] Kim SK, Lee SW, Youn JR. Measurement of residual stresses in injection molded short fiber composites considering anisotropy and modulus variation. *Korea-Aust Rheol J* 2002;14(3):107–14.
- [48] Lee KS, Lee SW, Youn JR, Kang TJ, Chung K. Confocal microscopy measurement of the fiber orientation in short fiber reinforced plastics. *Fibers Polym* 2001;2(1):41–50.
- [49] White JR. On the layer removal analysis of residual stress Part 1. Polymer mouldings with depth-varying Young's modulus. *J Mater Sci* 1985;20(7):2377–87.
- [50] Folkesa MJ, Russell DAM. Orientation effects during the flow of short-fibre reinforced thermoplastics. *Polymer* 1980;21(11):1252–8.
- [51] Chen J, Sellers K. Nanotechnology and the environment overview of manufacturing processes. CRC Press; 2009.
- [52] Mallick PK. Fiber-reinforced composites materials, manufacturing, and design. 3rd ed. CRC Press; 2008.
- [53] Ruihua HU, LIM JK. Fabrication and mechanical properties of completely biodegradable hemp fiber reinforced polylactic acid composites. *J Compos Mater* 2007;41 (13).
- [54] Kim KT, Jeong JH. Effect of molding parameters on compression molded sheet molding compounds parts. *J Mater Process Technol* 1997;67(1):105–11.
- [55] Jendlia Z, Meraghni F. Micromechanical analysis of strain rate effect on damage evolution in sheet molding compound composites. *Composites: Part A* 2004;35:779–85.
- [56] Hagstrand PO, Bonjour F. The influence of void content on the structural flexural performance of unidirectional glass fibre reinforced polypropylene composites. *Composites Part A* 2005;36:705–14.
- [57] Kim DK, Choi HY, Kim N. Experimental investigation and numerical simulation of SMC in compression molding. *J Mater Process Technol* 1995;49:333–44.
- [58] Comte E, Merhi D. Void formation and transport during SMC manufacturing: effect of the glass fiber sizing. *Polym Compos* 2006;27(3):289–98.
- [59] Dumont P, Orgéas L, Corre SL. Anisotropic viscous behavior of sheet molding compounds (SMC) during compression molding. *Int J Plast* 2003;19:625–46.
- [60] Christensen SK, Hutchinson B. Fibre-matrix separation in ribbed SMC and BMC parts. In: Annual Technical Conference ANTEC, Conference Proceedings 1997;1:782–5.
- [61] Abrams LM, Castro JM. Predicting molding forces during sheet molding compound (SMC) compression molding. I: model development. *Polym Compos* 2003;24(3):291–303.
- [62] Sreekumar PA, Joseph K, Unnikrishnan G. A comparative study on mechanical properties of sisal-leaf fibre-reinforced polyester composites prepared by resin transfer and compression moulding techniques. *Compos Sci Technol* 2007;67:453–61.
- [63] Williams GI, Wool RP. Composites from natural fibers and soy oil resins. *Appl Compos Mater* 2000;7:421–32.
- [64] Ferland P, Trochu F. Concurrent methods for permeability measurement in resin transfer molding. *Polym Compos* 1996;17(1):149–58.
- [65] Kim SK, Daniel IM. Determination of three-dimensional permeability of fiber performs by the inverse parameter estimation technique. *Composites: Part A* 2003;34:421–9.
- [66] Ikegawa N. Effect of Compression Process on Void Behavior in Structural Resin Transfer Molding. *Polym Eng Sci* 1996;36(7):953–62.
- [67] Warrior NA, Turner TA, Robitaille F, Rudd CD. Effect of resin properties and processing parameters on crash energy absorbing composite structures made by RTM. *Composites: Part A* 2003;34:543–50.
- [68] Kang MK, Jung JJ, Lee WL. Analysis of resin transfer moulding process with controlled multiple gates resin injection. *Composites: Part A* 2000;31:407–22.
- [69] Richardson MOW, Zhang ZY. Experimental investigation and flow visualisation of the resin transfer mould filling process for non-woven hemp reinforced phenolic composites. *Composites: Part A* 2000;31:1303–10.
- [70] Rodriguez E, Giacomelli F, Vazquez A. Permeability–porosity relationship in RTM for different fiberglass and natural reinforcements. *J Compos Mater* 2004;38(3):259–68.
- [71] Kang MK, Lee WL, Hahn HT. Formation of microvoids during resin-transfer molding process. *Compos Sci Technol* 2000;60:2427–34.
- [72] Black J. Biological performance of materials: fundamentals of biocompatibility. CRC Press; 2006.
- [73] Flahiff CM, Blackwell AS, Hollis JM. Analysis of a biodegradable composite for bone healing. *J Biomed Mater Res* 1996;32:419–24.
- [74] Claes L. The mechanical and morphological properties of bone beneath internal fixation plates of differing rigidity. *J Orthop Res* 1989;7(2):170–7.
- [75] Burns AE, Varin J. Poly-L-lactic acid rod fixation results in foot surgery. *J Foot Ankle Surg* 1998;37(1):37–41.
- [76] Wang YZ. In vivo degradation of three-dimensional silk fibroin scaffolds. *Biomaterials* 2008;29:3415–28.
- [77] Vepari C, Kaplan DL. Silk as a biomaterial. *Prog Polym Sci* 2007;32(8-9):991–1007.
- [78] Wang YZ. Stem cell-based tissue engineering with silk biomaterials. *Biomaterials* 2006;27:6064–82.
- [79] Teoh SH. Engineering materials for biomedical application. World scientific; 2004.
- [80] DiGregorio BE. Biobased performance bioplastic: mirel. *Chem Biol* 2009;16(1):1–2.
- [81] Ambrose CG, Clanton TO. Bioabsorbable implants: review of clinical experience in orthopedic surgery. *Ann Biomed Eng* 2004;32(1):171–7.