

Polylactic Acid Fibre Reinforced Biodegradable Composites

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ABSTRACT

Polylactic acid (PLA) is a well-known biodegradable and sustainable polymer, derived from renewable agricultural sources. Its high price in the past limited its applications to mainly biomedical materials such as bone fixation devices. As the growth of awareness in global environment protection and sustainable development, PLA has attracted increased attention and development. Nowadays, the applications of PLA have been broadened into plastics, textiles and composites etc. Composites have been widely used in industrial applications for several decades, due to their high strength-to-weight ratio and good structural properties. However, most traditional composite materials are composed of two distinct fossil fuel based components. They are not eco-friendly and are difficult to recycle. This study aims at the development of PLA biodegradable composites and the optimisation of the processing parameters to achieve the best mechanical properties of PLA self-reinforced composites (PLA-SRC) for various enduses.

A variety of polymer analytical techniques were used to evaluate crystallinity, thermal properties, and chemical structures of the PLA reinforcement and matrix. Further study was carried out to assess the effects on mechanical properties of PLA-SRC caused by the processing temperature, pressure and holding time. The composites produced at high temperature and/or high pressure have significantly better matrix penetration (fibre wetting), which enhances mechanical properties. However, holding time was found to have no significant effect on the properties of PLA-SRC.

DECLARATION

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LIST OF PUBLICATIONS

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- Jia W.; Gong R.H. Soutis C., Hogg P.J. Biodegradable fibre reinforced composites composed of polylactic acid and polybutylene succinate. Plastics, Rubber and Composites, 2014. 43 (3): p.82-88
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CHAPTER 1. INTRODUCTION

1.1. Research Background

Fibre reinforced composites have high strength-to-weight ratio, good corrosion resistance as well as structure and manufacturing flexibilities compared to metal-based materials. Composite materials have been used in a wide range of industrial applications for several decades. Large-scale applications include various land and sea transportation, such as aircrafts and vehicles; small-scale applications cover sport equipment and biomedical materials, such as tennis rackets and bond fixation devices.

However, most commercial composites are fossil fuel based synthetic materials which have adverse impacts on the environment, due to the limited amount of fossil fuel and the problems of disposal at the end of the product life cycle. Furthermore, with the growth of the environmental awareness and consequent upon a series of new regulations, the industries are being forced to search for eco-friendly materials to replace the existing fossil fuel based polymeric materials, in order to help preserve and protect the environment. Hence, the introduction of eco-friendly composites made from biodegradable or sustainable material, such as natural fibres or man-made cellulose fibres reinforced biodegradable polymer composites have started to attract growing interest in recent years.

Thermoplastic biodegradable polymers are widely used in various applications today such as disposable products and biomedical materials. Biodegradable polymers can be classified into renewable resources-based and petro-based synthetic polymers. Polylactic acid (PLA) is one of the most popular renewable resource-based biodegradable polymers, due to its excellent biodegradability and compostability, as well as attractive cost structure. Nowadays, the applications of PLA have been broadened into food packaging, disposable plastic products, textiles, etc.

However, the poor mechanical properties of the PLA polymer in bulk form restrict its use as high performance materials. The mechanical properties can be improved by introducing foreign fillers (fibres) into the biodegradable polymer to produce a composite. Thus, research in optimising biodegradable composites and seeking new "green" composites is becoming more important. In particular, the applications of PLA polymer as matrix in a natural fibre reinforced composites have drawn intensive research interest.

Since PLA is derived from agriculture products, the growth of using PLA could contribute to the great pressure in food supply. PLA as thermoplastic polymer has repeatable heating-cooling cycle. The recycling of PLA can relief the pressure from the shortage of food supply. In the natural fibres reinforced PLA composite, the recycling of PLA matrix becomes a big challenge, due to the costly and complicated separation method of fibre and matrix. Moreover, the poor interface between natural fibres and PLA matrix leads to problems on achieve strong mechanical properties. However, these problems can be addressed through the use of self-reinforcing composite in which the matrix and the fibre are made from identical or similar polymers.

The current study combines the principle of self-reinforcing composite with the biodegradable polymer, PLA, to produce a PLA self-reinforced biodegradable composite. This can be achieved by using highly orientated PLA fibre as reinforcement and PLA film as matrix. Therefore, a composite that has advantages of disposal through composting, recycling and incineration after service can be developed for a wide range of potential applications.

1.2. Research Objectives

The research in this study can be divided into two parts, which are shown as follows.

I. Design and manufacture of poly(lactic acid) fibre reinforced biodegradable composites

Before the composite manufacturing, the mechanical properties, chemical structures, and thermal properties of PLA reinforcement and matrix were investigated using a range of analytical techniques, including Raman and Infrared spectroscopy and differential scanning calorimetry. Furthermore, a filament winding machine and a hot-pressing mould with temperature monitoring device were designed to achieve good unidirectional and bi-directional fibre alignment and composite performance.

II. Optimise the processing parameters to achieve the best mechanical properties of PLA self-reinforced composite

In order to optimise the processing parameters, the PLA-SRCs were produced under various processing temperatures, pressures and holding times. Given the biodegradable characteristics of PLA polymers, there will be a broad range of potential applications for such a composite, for example, in medical/pharmaceutical, agricultural, and packaging areas. According to the properties required for such applications, a series of relevant tests were carried out, including tensile and flexural tests, as well as soil burial test.

1.3. Brief Contents of the Remaining Chapters

Chapter 2 covers an introduction of textile composites, a literature review of self-reinforcing composites, biodegradable polymers and PLA based composites.

Chapter 3 describes the characteristics of the PLA filament fibre and film. The processing temperature window, fibre shrinkage, the chemical similarity and thermal stabilities of the PLA fibre and matrix are also defined.

Chapter 4 describes the modified composite manufacturing process by using the newly designed manual filament winding machine and hot-pressing mould which allows the monitoring of the actual temperature reached in the composite.

Chapter 5 contains the comparison of the properties between the unidirectional fivestack and four-stack PLA-SRCs.

Chapters 6-9 cover the composite cross-section morphologies, tensile and flexural properties, as well as biodegradability in the soil of the PLA-SRCs that are produced at various processing parameters.

Chapter 10 concludes the current study and suggests future work.

CHAPTER 2. LITERATURE REVIEW

2.1. Introduction

The main aim of this project is to develop a fully biodegradable self-reinforced composite. This chapter reviews related literature on textile composites, self-reinforced composites, biodegradable polymers and their applications in composites.

2.2. Composite Materials

Composite materials have been widely used in a variety of applications including transport, construction, military and biomedicine. Composite materials can be defined as natural or engineered materials usually made up of two or more constituents with different physical or chemical properties that maintain distinct appearances on a macroscopic or microscopic scale in the final product [1]. Unlike a single material, which has all the properties on its own, a composite is designed to have the correct balance of properties that are contributed by each component, based on particular applications [2].

In a modern reinforced composite, a stiff and strong component, known as the reinforcement (mostly in fibre form), is usually embedded in a softer continuous component called the matrix [1]. The function of the reinforcement in a composite is to carry the applied load and provide structural properties such as stiffness, strength, and thermal stability. The matrix has a number of functions: it keeps fibres in place and at proper orientation; it transfers the load to the fibres; it protects the fibres from mechanical damages; it provides rigidity and shape to the structure; and it manages the transverse properties of composites.

In general, the performances of composites are determined by the properties of the matrix and the fibre, the fibre volume fraction, the fibre orientation and the packing arrangement [1]. The interfacial bonding between the fibre and the matrix is also a critical factor in determining the composite properties. This is because a composite usually has a large interfacial area and debonding, cracking and sliding may take place at the interface.

Depending on the nature of matrixes, composite materials can be classified into three types: polymer, metal and ceramic matrix composites. Reinforcement can be in the form of long or short fibres, particulates, and monofilaments. Three typical composites with

different matrix and reinforcement types are shown in Figure 2.1 [1]. Most composites used in industry are polymer matrix based; these can be divided into thermosetting and thermoplastic.



Figure 2.1 Schematic diagram of typical polymer, metal and ceramic matrix composite [1]

2.2.1. Thermosetting composites

Thermosetting polymers are usually characterised by irreversible chemical change in the solidification process [3]. The thermosetting resins begin as a liquid, and convert into a hard solid through the addition of a chemical hardener to form the chemical cross-links between the polymer chains. The mechanical properties of thermosetting polymers are determined by the molecular units that consist of the cross-linking polymer network, and the length and density of the cross-links. The thermosetting polymers are usually brittle materials with low strains due to the tightly bound polymer network.

As thermosetting resin normally has a good penetration into the fibre bundle, it has been used for fabrication of a broad range of structural composites [4]. The most common types of thermosetting resins are epoxy, unsaturated polyester and vinyl ester [1]. The epoxy resin has wide applications in advanced materials, because of its high toughness, high resistance to heat distortion and low shrinkage during curing [1]. Over the past two decades, carbon fibre reinforced epoxy resin composite has played an important role in high performance applications, including construction, aerospace, and automotive, due to its higher strength-to-weight ratio compared to those traditional heavy metal materials.

As the demands for high-performance composites increase, the recycling or biodegradation at the end of the lift cycle of these materials has become a serious issue. This has resulted in a series of new laws to control disposal and recycling of composites. Due to strong cross-links, thermosetting polymer is almost impossible to be remoulded and this leads to a long period for biodegradation. In addition, the separation of resin and fillers during the recycling process of thermosetting composites has become a great challenge.

2.2.2. Thermoplastic composites

Unlike thermosetting polymers, thermoplastic polymers are solid-liquid reversible. Thermoplastic polymers can be melted to liquid at a high temperature, and solidified into a desired shape simply by cooling. Thus, the repeatable heating-cooling cycle can offer a nearly infinite shelf life of product. A semi-crystalline or crystalline thermoplastic polymer has a high degree of molecular order and alignment, which can result in good structural properties. An amorphous thermoplastic polymer has a large amount of molecular entanglements, which could act as cross-links. Thus, the inherent properties of the monomer units and the high molecular weight can provide stiffness and strength for thermoplastic polymers [1].

Thermoplastic polymers are commonly used as polymer matrixes in the composite industry because of their characteristics of failure at higher strain, deformation and melting at higher temperatures, excellent resistance to chemicals and good absorption of water (except nylons). Thermoplastic resins, such as polypropylene, polyethylene, polyethylene terephthalate and aliphatic polyester, are widely reinforced with glass, carbon, aramid fibres or metal.

In comparison to thermosetting composites, thermoplastic composites have several advantages, such as faster processing cycle without curing stages and ease to demould, unlimited shelf life, equivalent or better performance, lower material and manufacturing costs and easier to recycle [4-6]. Many thermoplastic polymers also have good biodegradability, for instance, aliphatic polyesters and polyesters containing aromatic moieties [7]; thus, a wide range of biodegradable composites are based on thermoplastic polymers as matrix.

In recent years, thermoplastic composites are becoming more popular. They are used in many applications, especially in the automotive application as alternatives to the traditional thermosetting composites. For example, glass mat thermoplastic composite has been widely used in the automotive industry such as seat frames, battery trays, under engine covers, etc., as a result of its light weight and high toughness. The advanced thermoplastic composite, carbon fibre reinforced with a polyether ether ketone (PEEK) matrix, also has broad use in aerospace, including wing ribs and panels, fuselage wall linings, etc.

The main manufacturing processes for thermoplastic composites include compression moulding, injection moulding and prepreg layup. Compression moulding (hot pressing), is one of the most popular method, because it has short cycle time and low labour cost and can produce composites with various shapes. Especially in automobile industry, compression moulding is used to produce battery trays, front ends and noise shields etc. [8]. However, this method usually requires costly equipment (hot press) and a suitable compression mould.

Nevertheless, thermoplastic composite has a problem of unsatisfactory interfacial bonding that is usually caused by the high viscosity of the molten matrix. This is because the high melt viscosity of the thermoplastic polymer can lead to difficulty in matrix penetration into fine fibres (poor fibre wetting) during processing. Thus, the composite manufacturing process by compression moulding has high requirements on the processing temperature, pressure and time. In order to provide sufficient matrix penetration, the processing temperature is required to reach to the melting point of the matrix. Proper processing pressure and holding time can also help to improve the matrix penetration.

2.2.3. Textile composites

Nowadays, the applications of composite have widened into high performance fields such as aerospace, military and biomedical. To meet the requirements of these applications, the reinforcement orientation, arrangement and volume fraction are very significant. Textiles, which are structured materials, can satisfy the requirements of fibre orientation and arrangement in composite. By varying the structure of textile preforms, the fibre orientation and arrangement, and fibre volume fraction, which highly determine the properties of composite, will be changed to meet different applications. This section will mainly describe the textile yarns and four basic textile preforms used in composites.

2.2.3.1. Textile yarns

Yarn, the basic component in a textile, can be defined as a continuous strand of textile fibres, and divided into two types which are spun yarn and continuous filament yarn [9]. The spun yarn is known as an assemblage of relatively short fibres (natural fibres) by different yarn spinning process such as ring spinning and open end spinning The continuous filament yarn is made of a grouping of nearly endless parallel continuous filaments (usually synthetic fibres) by processes such as melt spinning, wet spinning, and gel spinning.

In the composites industry, both twisted and untwisted yarns can be used as reinforcement. The twisted yarn is suitable for making knitted, woven or braided fabrics, while the untwisted yarn can be chopped into short strands to either form a short fibre mat or mix with polymer resin to create injection moulding compound. Untwisted yarn is also used as reinforcement of unidirectional composites and filament wound products. Unidirectional (UD) composites are produced by arranging a parallel set of yarns, usually supplied from a yarn creel, and impregnated with resin [10]. As all the fibres in a UD composite are orientated in the same direction, it is a typically anisotropic material. However, the anisotropy of UD composite can be reduced by assembling several layers of unidirectional sheets in desired orientation to form laminates, as shown in Figure 2.2. Due to its high strength and stiffness, UD laminates have great application potential in areas such as aerospace and automobile.



Figure 2.2 Unidirectional laminates

Hybrid yarn, a new reinforcement used in composite manufacturing, is known as the yarn that consists of more than one type of fibre component and can be produced by many spinning processes such as wrap spinning, air-jet spinning and commingling spinning. By using hybrid yarn as the reinforcement of a composite, the uniform matrix and fibre distribution and the protection of reinforcing fibres during further processing can be obtained [11]. Thus, using hybrid yarn is an alternative method of processing thermoplastic composite, in which the thermoplastic polymer in the form of fibre mixes

with reinforcing fibre, to improve the interfacial property between matrix and fibre [11, 12]. Hybrid yarn can also be used to create self-reinforced composites by hot consolidation, where the matrix and fibre are made from the same polymer while have different melting temperatures [13].

2.2.3.2. Woven performs

Weaving is the process of interlacing two sets of yarns (weft and warp) to form a fabric in a specific manner [9]. There are three basic weaves: plain, twill and stain or sateen, shown in Figure 2.3. By means of various combinations or modifications of the basic weaves, a large variety of woven fabric patterns can be created. Since weaving technique can produce the vast variety of single layer fabrics used as reinforcements under high production speed, this process has been used widely in the composite industry.



Figure 2.3 Three basic 2D woven structures

The limited mechanical performance of single layer woven composite restricts its applications for some high-performance materials. Stacking several single layer woven fabrics into multi-layer woven composite is difficult to avoid the possibility of delamination. Hence, a stitching technique is usually used as the through-thickness reinforcement in the multi-layer composite. The stitching process is usually used to reinforce prepreg laminates, but it could break or distort the in-plane fibres, so that the mechanical properties of composite could be degraded [14].

Furthermore, due to the development of textile technology and the requirement of advanced woven fabric, 3D woven fabrics (multi-layered woven) have become the focus of attention. Figure 2.4 shows two common 3D woven fabric structures: orthogonal and angle interlock structure. The impact damage resistance of the 3D woven structure is higher than the 2D woven structure; in addition, the delamination of multilayer woven composites composed of several layers of 2D woven fabrics is overcome by the insertion of through-thickness yarn without any in-plane fibre

breakage. Hence, 3D woven fabrics have been used as reinforcement in many highperformance composite materials.



Figure 2.4 Orthogonal (a) and angle interlock(b) 3D woven fabric

2.2.3.3. Braided performs

Braided fabrics can be made into flat, tubular or solid structures by interlacing three or more yarns diagonally with one or more of the others [15]. By changing the relative position of yarn carriers on the track ring of the braiding machine, various 2D or 3D braided structured can be obtained.

The braiding technique also is widely employed to produce fibre reinforcement in the composite industry. In the braided fabric, at least one axial yarn is non-crimped, thus, the load distribution of the yarns is highly efficient [11]. Depending on the different applications, the braiding process is capable of creating a wide range of complex reinforcing performs by using high-performance fibres, including glass, carbon, aramid, and metallic fibres. Owing to the high drapability, torsional stability, structural integrity, and great impact resistance, there is a wide range of applications of composite materials that use braided fabric as the reinforcement, such as windsurfer masts, aircraft ail shafts, propeller and shafts on marine craft [11, 14].

In recent years, braiding process has also become a novel technique to produce thermoplastic composites. In Khondker et al.'s study [16], a tubular braiding technique was used to create an intermediate micro-braided yarn, where the jute yarns as the reinforcement were braided around by the PLA yarn as the matrix. Then, the microbraided jute/PLA yarns were wound parallel onto a metal frame to fabricate a biodegradable unidirectional composite laminate by melting the PLA yarn at specific moulding temperature and pressure. However, similarly with most composites, it is difficult to obtain good interfacial properties in Khonder's study, because the high molten viscosity of the thermoplastic polymer resulted in poor PLA matrix impregnation into the jute yarn bundles.

2.2.3.4. Nonwoven preforms

Nonwoven fabrics are textile fibre assemblies created either by mechanical interlocking fibres in a random fibre mat, by chemical bonding fibres with cementing medium, or by fusing of thermoplastic fibres [9]. The fibres in a nonwoven fabric can be oriented in one direction or placed in a random manner, depending on the various applications. Due to the great permeability, porosity and softness, and considerable strength, nonwoven fabrics have a wide range of applications, such as hygiene and medical products, filters, and geotextiles etc.

In the composites industry, the nonwoven technique is capable of producing short or long fibre mats as the reinforcement of a composite laminate. Much literature about nonwoven preform composite have been published. Sugino *et al.* [17] invented a carbon self-reinforcing composite, which was generated by coating carbon nonwoven fabrics or a blend of carbon fibre and other organic fibres with a filler-containing liquid. In the study of Vaidya *et al.* [18], a rigid uniform composite made from nonwoven preforms, which are a blend of glass fibre and low melt polyester or bicomponent polyester (sheath)/ polyethylene (core) fibres, was produced by heat pressing in a mould to obtain the desired form. In the last twenty years, composites based on nonwoven fabric have increased applications in many fields, such as construction, filtration, medical protection, automobile, and marine.

2.2.3.5. Knitted preforms

Knitted fabric is constructed by interlocking a series of loops of one or more yarns by either hand or machine [9]. The versatile knitting manufacturing process brings about a huge number of knit structures which have a wide range of applications. There are two main techniques of knitting production: weft knitting and warp knitting. In weft knitting, one continuous yarn at a time is fed into the knitted machine making all of the loops in one row. The rows and columns in a knitted fabric are usually called courses and wales, respectively. On the other hand, in warp knitting, many yarns are simultaneously fed into the machine forming the loops during the same knitting cycle. As highly curved yarn and interlooping of the yarn in knitted fabric result in an elastic and flexible structure, the various knitted fabrics are high volume manufactured for clothing and furnishings, for example, jersey (plain knitted fabric) for T-shirt and socks, and warp knitted fabric for car upholstery.

Unlike woven and braided fabrics, which are very popular textile reinforcement for composite materials, the knitted fabric has not been used widely as reinforcement for composite, because its loose structure can cause low load carrying ability and the fibre content in knitted fabric cannot be sufficiently utilised [19].

Nevertheless, the good formability and drapability of knitted fabric contribute to a relatively easier process for making the knitted fabric into a complex 3-directional shape using existing CAD/CAM techniques. This is one reason why knitted fabric has become more popular in the composites industry in recent years. A sandwich composite material known as a 3D knitted composite, based on a double layer knitted fabric, produced by Philips and the co-workers showed considerable flexural stiffness and compression strength [20]. Also, knitted fabric composites can provide good impact damage resistance [20, 21], which leads to some potential applications such as in automobiles and bicycle helmets, etc. The other advantages of knitted fabric used for composite materials are its low set-up cost and high production speed [19].

To compare the properties of knitted fabric composite with other main reinforcements, Gommers*et al.*[19]presented a graphs in their paper, shown in Figure 2.5, which states that knitted fabrics have better stiffness and strength than short fibre and continuous fibre mats, and higher interlaminar fracture toughness and processability of complex shapes than woven & braided fabrics and unidirectional laminates.



Figure 2.5 Overview and comparsion of some composite properties of the main existing reinforcements [19]

2.3. Self-reinforced Composites

A strong and stable interfacial bonding between the fibre and the matrix in a fibre reinforced composite is critical factor to its mechanical properties because an imperfect interface will result in debonding, cracking and sliding. The interface bonds can be generated by the following mechanisms: matrix adsorption and fibre wetting, molecular chain entanglement following inter-diffusion, interfacial chemical reaction, electrostatic attraction, mechanical keying (achieved by adequate fibre surface roughness), and the presence of residual stresses [1]. However, high interfacial bonding is usually difficult to achieve in a traditional composite, where the fibre and matrix (mostly thermoset polymer) are made from two different materials. This is because the chemical difference, the corresponding distinct surface energies and the characteristic individual properties will restrict the build of good interfacial bonding between the fibre and the matrix [22].

Furthermore, due to the rapid demand growth of reinforced composite in many fields and the increase of environmental legislation, the disposal and recycling of these composites at their end-of-life have become serious issues [23]. To preserve natural resources, recycling of composites is already a significant part in our lives. However, the recycling process of a traditional composite usually requires high technology and cost, due to the difficult separation of the fibre from the polymer matrix [13]. Therefore, the design of an easy to recycle reinforced composite is turning into a researching focus.

2.3.1. Self-reinforced composite based on various polymers

The concept of self-reinforcement polymer composites (SRCs) was first developed by Capiti and Poter [22] to solve these problems in traditional composites. In their study, the self-reinforcement or all polymer composites is defined as the composites in which the matrix and reinforcement are made from similar or identical polymer but in different morphologies. Nowadays, the concept of SRC is widely used for thermoplastic polymer composites based on polyethylene (PE), polypropylene (PP), and polyethylene terephthalate (PET) polymers, but limited to thermosetting composites. This is due to thermoplastic polymer being reversible and having high toughness and durability

The advantages of SRC are good interfacial bonding and easily recycled compared to traditional composites. Several studies have shown that the mechanical properties of a fibre reinforced composite can be enhanced by the transcrystallisation along the fibre-matrix surface, which occurs when the high nucleation density is on the fibre surface [24-26]. Studies on PP composites [27-29] found, via the observations of composite

morphological features, that the bonding between two phases in a SRC is improved by the growth of transverse crystals from the fibre into the matrix. This is because the high chemical similarity between matrix and fibre can provide not only bonding but also high nucleation density for transcrystallisation from the fibres into the matrix, which can further increase the bonding between two phases [22, 27, 29-31]. The phenomenon of transcrystallisation also can be found in all-PE polymer composite [22, 30-32]. The optical micrographs in Figure 2.6, illustrate the phenomenon of transcrystallisation in an all-PP (a) and an all-PE (b) composite.



Figure 2.6 Optical micrographs of all-PP (a) [29] and all-PE (b) [30] composites

Though the thermoplastic composite can be remelted into a new grade, the recyclability is limited by the usages of additives, blends and fibres [23]. However, SRC made from matrix and fibre with the same or similar chemical structure, has simplified the recycling process, due to the removal of the matrix-fibre separation. Hence, the development of SRC reduces the native environmental effect and enhances the recyclability of thermoplastic composite.

Owing to these advantages of self-reinforced composite, there is a large volume of published literature describing the SRC using various polymers. Capiti and Poter[22] first indicated that a relatively good interfacial bonding of one polymer composites in which the low and high molecular weight polyethylene (PE) acted as the matrix and fibre, respectively, was achieved by partially melting the outer sheath of the fibres into the completely melted matrix. Most of the earlier SRC studies [30, 31, 33-36] chose PE due to the high modulus of ultra-high molecular weight PE fibre, about 250 GPa. The high modulus of the all-PE composite leads to a wide range of applications, although the low melting temperature (about 110°C) of PE restricts the utilizations under high temperature conditions.

In the last decade, polypropylene (PP) has gradually been known as a very important polymer for SRC due to its relatively high thermal stability. There are a number of studies published on the production and properties of all-PP composites [27-29, 37-47]. Although PP has higher melting temperatures (about 165°C) than PE, it is still not enough to be used for high temperature applications. Consequently, some researchers were seeking a polymer that has a higher melting temperature for SRC. Poly (ethylene terephthalate), owing to its melting temperature of approximate 260° C, is becoming more attractive for SRC in high temperature applications. Several studies [13, 48-50] have reported good mechanical properties of self-reinforced PET composites. Some researchers have also carried out studies on polyamide (PA) single polymer composites, due to the good properties of high-performance polyamide based fibres, like Kevlar[®] and Twaron[®] fibre [51-53]. In recent years, Polylactic acid, as a novel thermoplastic polymer, has also attracted considerable research interest for SRC production, especially for biomedical applications. The studies of the PLA-SRC composites in biomedical application will be described in section 2.5.2. Moreover, the SRC is not limited by using thermoplastic polymer. Several studies have proved the feasibility of producing cellulose fibre self-reinforced composites [54, 55].

2.3.2. Processing temperature window

Identical or similar chemical structures of matrix and fibre can contribute to excellent interfacial bonding and recyclability of composites. However, the production of SRC usually prefers a large difference in melting temperature of matrix and fibre to allow melting the matrix sufficiently and remaining mechanical properties of oriented fibre. Therefore, the narrow processing temperature window of the SRC is the major challenge. The lower limit of the processing temperature window is usually the minimum temperature required for melting or softening the matrix to provide sufficient wetting and interfacial bonding for SRC; and the upper limit refers to the onset of the melting peak of the fibre [48].

Karger-Kocsis and Bárány [56] summarised several methods which were employed to enlarge the processing temperature window in a variety of SRCs. The most common method is using highly oriented fibres with high or ultra-high density as the reinforcement, and amorphous or low crystalline films with relatively low density as the matrix. Many studies on PE self-reinforced composites [22, 30, 31, 33-35] used this method and had fairly large processing temperature windows. Furthermore, copolymer or blended polymer is also widely used as the matrix to lower the melting temperature of matrix for PP [29, 37, 38, 40-42], PET [13, 48] and polyamide 6 (PA6) SRCs [52]. By using this method the processing temperature can be enlarged up to 50°C for PP and 100°C for PET.

The concept of constrained fibres is another method to enlarge the processing temperature window by increase the melting temperature of reinforcements. The melting temperature of a polymer can be increase either by the increase of the difference of enthalpy or the decease of difference of entropy between crystal and liquid [49]. However, the enthalpies of melting unconstrained and constrained fibres are the same. During overheating, the chains in the constrained fibres cannot move and relax, the gain in entropy per monomer unit is thus reduced [49]. This will result in an increase of melting temperature. The method of using constrained fibres has been successfully used for SRCs made from PE, PP, PET and polyamides [27, 49]. However, the overheating of constrained fibres is very complicated to achieve, because it depends on many parameters such as the crystal size, crystallinity and the kinetics of melting of these crystals [49]. Besides, the degree of overheating is also directly affected by the drawability and extensibility of polymer chains, as well as the effectiveness of constraining.

Nucleation of slowly crystallising polymers (such as PET and PLA) is a method to create SRC at a temperature which is above their glass transition temperature (T_g) but much lower than their melting temperature (T_m), and at high heating and cooling rate. Yao et al. [50, 57] produced the PET and PLA self-reinforced composites by sandwiching the reinforcements between two amorphous PET or PLA sheets. The film-stacked packages were rapidly heated to the temperatures that were higher than the T_g of PET/PLA but lower than their T_m . In order to soften the matrix preceding crystallisation and avoid fibre annealing, the holding time needs to be precisely controlled to a very short time (approximate 10s); in addition, the composites were rapidly quenched by cold water. The optimised processing temperatures were about 180°C and 135°C for PET and PLA SRCs, respectively.

The SRC manufacturing design of Yao et al. is based on the following concept. When the amorphous polymers are heated above glass-transition temperature (T_g), two competing processes of the polymer, which are glass-transition and crystallisation, occur simultaneously. The glass-transition (fusion) process will make the amorphous material soft and rubbery; whereas the crystallisation process will turn it into a hardened phase. Thus, a short holding time is required to soften the matrix but minimise the crystallisation. As shown in Figure 2.7, T_{min} is the minimum processing temperature, where the fusion time is significantly shorter than the crystallisation time; the hatched area denotes the feasible processing window for obtaining good fusion bonding. Thus, the fusion process starts to dominate the crystallisation process from T_{min} [50, 57]. By using the method of slowly crystallising polymer nucleation, a large processing temperature range (50 - 100°C) can be obtained [50, 57]. However, sufficient matrix wetting may not be achievable at a low processing temperature.



Figure 2.7 Feasible process window for SRC by nucleation method [50]

Another method, called undercooling of polymer melt, based on the same principle of nucleation of slowly crystallising polymer, can be used for fast crystallising polymer, such as PE and PP. Dai et al. [44]produced the PP-SRC by the undercooling polymer method at the processing temperature range of 125 to 150°C. However, the highest tensile properties were achieved by the PP-SRC made at 150°C, which is only 2°C lower than the onset melting temperature of the PP fibre. Thus, this method did not show great advantages.

The melting behaviour of a polymer vary according to the crystalline modifications (α , β , γ , δ). Because not all these crystalline forms are stable, the less stable crystal starts to melt prior to the more stable crystal. The processing temperature window of a SRC can be broadened by using the same polymer with different crystalline modifications. Bárány and co-workers [28, 39, 43] have found that the β -PP has a significantly lower melting temperature than α -PP. Hence, this method has been successfully used for producing PP-SRC with a fairly large processing temperature window [28, 39, 43, 45,

47]. Bhattacharyya *et al.*[51, 52]also stated the potential application of this method for polyamide (PA) single polymer composite, because γ -PA has lower melting temperature than α -PA. However, the optimised processing temperature is only 5-10°C lower than the T_m of reinforcements.

2.3.3. Manufacturing methods for self-reinforced composite

The self-reinforced composites can be mainly manufactured by four methods, which are co-extrusion, selective surface dissolution, hot compaction and film stacking. Co-extruded tape is composed of highly oriented homopolymer core and random copolymer skin, which has a lower melting temperature than the core. During consolidation, the copolymer skin is melted to form the matrix around the reinforcement to provide high interfacial bonding. A large processing temperature window for PP SRC, about 20-40°C, can be obtained using this method [40, 42]. Co-extruded tape is also suitable for producing high fibre volume fraction (up to 90%) composites, which are widely used for automotive and constructive products. The material made by this method has a commercial name Pure[®].

The second method to produce the SRC is selective surface dissolution, where the surfaces of fibres are dissolved to form the matrix by chemicals, such as concentrated acid or alkali. This method has been successfully used for all-aramid and all-cellulose fibre SRC [53-55]. However, the properties of these SRCs highly depend on the concentration of the chemicals and immersion time. Too high concentrations of chemicals and too long immersion times will result in remarkable decrease in the mechanical properties of SRCs [53].

The hot compaction technique for producing SRC was first developed by Ward and Hine at the University of Leeds [58, 59]. The composite consolidation is achieved by partial melting of the fibres via careful processing temperature control. Thus, the outer surface of the fibres is melted as the matrix and flows through the residual fibre cores as the reinforcement. After cooling and pressing, the fibre outer binds the fibre cores together and leads to outstanding fibre wetting and interfacial adhesion. However, a precise processing temperature control is critical during composite consolidation, because overheating will reduce the properties of the fibres significantly and insufficient heating cannot offer high bonding strength between fibre and matrix. Zhang and Peijs [13] combined the hot compaction method with bi-component yarn to produce an all-PET composite, in which the melting temperature difference between fibre sheath and core was 40°C. The other disadvantage of the hot compaction was indicated in the study of Hine et al. [35]. If a woven fabric is used as reinforcement, the hot compaction method is difficult to use to provide enough matrix to fill in the gaps between the rough layers of the woven fabric by melting only the outer surface of the fibres that are in the centre of a yarn bundle.

Film stacking is the most frequently used technique for manufacturing SRC. There are numerous studies [27, 29-31, 33, 38, 39, 48, 49] on the feasibility of this method to produce SRCs from PP, PE and PET. In this method, the film that has lower melting temperature than reinforcement is selected as the matrix; and the reinforcement can be in various forms, including highly oriented filament and fabric. Before consolidation, the fibres are sandwiched in between the films in a desired manner to form a film stacked package; then this package is consolidated to produce the composite by hot pressing.

Compared with the hot compaction method, where the fibres are partially melted to build excellent interfacial bonding between the two phases, film stacking method only melts the films; thus, the wetting property of fibres in film stacking composite maybe poorer than that in hot compaction composite. However, Hine and the co-workers [35] combined hot compaction and film stacking to produce woven tape PP and PE SRCs. In their work, the interfaces of the composites made by film stacking, hot compaction and combination of both were compared; the composites made by the combination process showed the highest interfacial bonding.

2.4. Biodegradable and Sustainable Materials

Biodegradable materials can be defined as materials that are able to be broken down into simple elements and compounds such as carbon dioxide and water by microorganisms under natural environment without generating any harmful substances [7, 60]. The biodegradation process, in other words chemical decomposition, usually occur through enzymatic action of microorganisms (bacteria, fungi, etc.), and abiotic reactions including mineralisation, photodegradation, oxidation and hydrolysis [61, 62]. Biodegradable polymers can be divided into three main categories: natural polysaccharides and other biopolymers (e.g. cellulose, wool, silk and chitin); synthetic polymer, particularly aliphatic polyester (e.g. polylactic acid and polybutylene succinate); and polyester produced by microorganisms (e.g. poly (hydroxyl alkanoate) [7, 60]. Recently, due to the rapid growth in the consumption of composite material, biodegradable composite is being developed for more extensive applications. Biodegradable composites (biocomposites) are commonly known as the composites materials consist of biodegradable natural or synthetic fibres as reinforcement and biodegradable or non-biodegradable polymers as matrix [63].

Sustainable materials are usually produced from completely renewable resource, and there is no fossil fuel derived energy in their production processes [60]. Moreover, the definition of sustainability from Cargill Dow LLC, which built the commercialisation of PLA polymers under the trade mark NatureWorksTM, is based on three aspects: economic sustainability, social sustainability and environmental sustainability [64]. Cargill Dow set that the ideal environmentally sustainable material should offer an equivalent function as the product it replaces and available at a competitive price, and has a minimum negative environmental effect. Sustainable materials are also known as "green" materials. An idealised life cycle of green materials is presented in Figure 2.8 [65]. The requirements of innovative green materials include the improvement of material from biodegradable or renewable polymers, the minimisation of using fossil-based materials, the diminution of fossil fuels used during material production, the reduction of carbon dioxide released, the reduction of the quantity of wastes, and the minimisation of hazards from non-ecofriendly chemistry at every stage of the green material life cycle [60].



Figure 2.8 Life cycle of green materials
Figure 2.9 indicates a pyramid diagram of the whole-life energy of plastics after service. Waste reduction is most desirable and can be achieved by re-designing the products to improve their durability. Reuse requires less energy than recycling of the plastic after service; but it normally needs inspection, cleaning and repair for the plastic used for other purposes. Despite many commercial thermoplastic polymers such as PET and PE having good recyclability, most of their raw materials are generated from fossil-fuel and natural gas. Besides, the recycling rates of these recyclable materials are not as high as they could be. Biodegradable plastics, such as PLA, can slowly decompose to harmless components in soil. Composting can reduce the amount of plastic waste going to incineration and landfill, which are the most undesirable methods for waste management. In a study by Themelis et al. in 2011, only about 6.5% of the used plastics were recycled and 7.7% were burned for energy in the U.S.; the remaining 85.8% went to landfill [66]. These plastics will bring environmental pollution at their end-of-life cycle. Moreover, the fast growth of the demand of composites and the limited amount of these natural resources are leading to the increasing in the polymers' price. Therefore, biodegradable and/or sustainable polymers may replace traditional polymers gradually for plastics, textiles and composites.



Figure 2.9 Whole-life energy of plastics after service

Polylactic acid (PLA) is very popular biodegradable polymer and has been commercially manufactured in many countries. It belongs to aliphatic polyester and has outstanding biodegradability and sustainability. Hence, research of novel "green" materials made up of the biodegradable polymer has become a new trend. The following section will focus on the chemical structure and the physical properties.

2.4.1. Polylactic acid (PLA)

Polylactic acid is not a new material. It was developed in 1932 by Wallace Carothers [67]. PLA is one of the family of aliphatic polyesters usually made from α-hydroxy acids. Since PLA is a thermoplastic polymer derived from 100% renewable agricultural sources, mainly corn and sugar cane, it has excellent biodegradability and compostability. Moreover, the strength and modulus of PLA are fairly high. However, owing to the high cost, its initial applications were biomedical, including medical suture implants and controlled drug release [67]. For example, the PLA fibres can be made into a 2D or 3D textile scaffold as an implant, where different human organs can be cultured [68]. In recent years it has been widely developed and manufactured on a large-scale by NatureWorks LLC, USA, who markets the fibre form of the PLA polymer under the "INGEOTM" brand. PLA is now routinely found in a broad range of applications including apparel, food packaging, nappies and wipes, and biodegradable composites.

2.4.1.1. Chemical structure and synthesis of PLA polymer

Compared to commercial synthetic polymers based on limited fossil-fuel or gas resource, polylactic acid $(C_3H_4O_2)_n$ is derived from 100% biodegradable and sustainable polymer lactic acid $(C_3H_6O_3)$ [67, 69]. PLA is a linear aliphatic thermoplastic polyester, commonly made from fully renewable resources, such as wheat, corn and sugar cane and the other products which contain rich carbohydrates [60].

The process of synthesis of PLA polymer is shown in Figure 2.10. In the production of PLA the carbohydrates (starch or sugar) are extracted from plants cells and converted to fermentable sugars by enzyme hydrolysis with water [68]. After the enzyme hydrolysis, the fermentation of dextrose occurs to make the lactic acid. Then, PLA can be formed by either polycondensation or ring-opening polymerisation of lactic acid [68, 70]. The direct polycondensation of lactic acid is based on esterification of monomers. In order to eliminate the water, this process needs to be operated under high temperature and progressive vacuum [71]. The ring-opening polymerisation occurs via lactide as a cyclic intermediate dimer [68, 69]. The ring-opening polymerisation usually gives longer molecules (higher molecular weight) than the direct polycondensation, because it is difficult to remove the water and impurities in the polycondensation [68, 70, 72].



Figure 2.10 The synthesis of PLA polymer

Due to the chirality of lactic acid, the fermentation of sugar produces the lactic acid which exists as two stereoisomers (L- or D-lactic acid). Before ring-opening polymerisation occurs, lactic acid produces the cyclic lactide dimer under milder condition by eliminating water. Three potential forms of lactide can be created. These are L-lactide, D-lactide, and Meso-lactide. The crystalline PLA polymer usually contains high proportion of poly L-lactic acid (PLLA), while the amorphous PLA polymer is produced by a higher proportion of poly D-lactic acid (PDLA) (more than 15%) in the polymer chain [68]. The characteristics of PLA, such as molecular weight, crystallinity, thermal properties, can be changed by varying the amount and sequence of L- and D-lactic acid units [68]. For example, PLA has a melting point in the range from 130 to 230°C, depending on the different ratio and distribution of L- and D-lactic acid units [68, 73].

2.4.1.2. Mechanical properties of PLA

PLA is similar to most thermoplastic polymers, in which the mechanical properties highly depend on the molecular weight, crystallinity and orientation. Semi-crystalline PLA is characterised by good mechanical properties, with tensile strength of 50-70 MPa, tensile elastic modulus of 3 - 4 GPa, elongation at break of 2-10%, flexural strength of 50-120 MPa, and flexural modulus of 3.5-5 GPa [74, 75]. The mechanical properties of PLA are also related to the ratio and distribution of L- and D- lactic acid units. For example, amorphous PLA usually has tensile strength between 50 and 70 MPa, while that of poly DL-lactic acid (PDLLA) is from 40 to 53 MPa [74, 75].

The mechanical properties of PLA can be improved efficiently by drawing the PLA into highly oriented fibre. The mechanical properties of the PLA fibre are determined by a variety of spinning parameters such as draw ratio, roll speed, etc. The tensile strength, elastic modulus and elongation at break of PLA fibre can be developed up to 450 MPa (about 36 cN/tex, based on bulk density of 1.25 g/cm³), 5.7 GPa (draw ratio of 4) and 160% (spinning speed of 1000 m/min) [68, 76, 77]. Figure 2.11 shows a comparison of tensile properties between natural fibres, common synthetic fibres and PLA fibre [68]. It is clear from this figure that the initial modulus of the PLA fibre is similar to the other textile fibres, while the yield after elastic tensile is very obvious and similar to wool. PLA fibre is also very extendable, even its strain at break is higher than wool, which is the most extendable natural fibre. However, the tensile strength of PLA fibre is lower than common synthetic fibres such as Lyocell and high density polyester, but it is higher than viscose and close to cotton fibre.



Figure 2.11 Tensile stress-strain curves for PLA and other common textile fibres [68]

2.4.1.3. Thermal properties of PLA

The glass transition temperature of PLA is between 50°C and 70°C, thus, the PLA polymer is stiff and brittle at room temperature [68]. As has been mentioned, the melting point of PLA polymer is variable in the range from 130°C to 230°C by changing the ratio and distribution of L- and D- isomers in the polymer backbone. For pure PLLA or PDLA, the melting point is between 170°C and 190°C [68, 73]. Ikada *et al.* [78] found that the highest melting point of 230°C of PLA polymer can be achieved by blending PLLA and PDLA to create a stereocomplex polymer. In addition, the crystallisation temperature of amorphous PLA polymer is typically between 110°C - 130°C, based on the molecular weight [73].

As a large amount of biodegradable products based on the PLA polymer have been produced every year and the processing conditions and final properties are highly related to the crystallisation of amorphous and melting behaviour, a lot of studies [79-83] concentrated on the crystallisation and melting behaviour of PLA polymer. A double melting behaviour has been found in the PLA material and reported by a number of authors [79, 80, 82, 83].

In general, the phenomenon of multiple melting endothermal peaks commonly appear in the DSC plots of synthetic macromolecules, and been observed for many semicrystalline polyesters containing flexible or semi-stiff polymers, such as PE, PP, PET and poly(butylene terephthalate) etc. [79, 84]. This phenomenon in principle can be attributed to many factors, such as the presence of two or more crystal forms, molecular weight segregation, varying crystal orientation, and different crystal size and morphologies [79, 85]. The appearance of multiple melting peaks also can be brought about by the original crystals with different stability [85]. The double melting behaviour of PLA is attribute to a low-temperature melting that refers to the fusion of the original crystals with a low thermal stability, followed by melt-recrystallisation, and a high-temperature melting that refers to the more prefect crystals, formed through a melt-crystallisation process during DSC heating scan [79, 80].

2.4.1.4. Biodegradability and compostability of PLA

Despite PLA being a synthetic polymer, it is fully biodegradable and compostable polymer, as it is derived from renewable resource. PLA can be degraded by hydrolysis of the ester bond without any enzyme to catalyse this hydrolysis or by various microorganisms under controlled conditions [69, 86]. The degradation rate is influenced

by ordered molecular structure (crystallinity), molecular weight, surface area, hydrophilic and hydrophobic properties [86]. Because the crystalline structure is more resistant to degradation then the amorphous, the higher the crystallinity, the lower the degradation rate. In addition, the degradation of PLA depends on the degrading environment, such as temperature and humidity. Under the natural environment, PLA has a degradation time from six months to two years, which is much shorter than that of polyethylene, 500-1000 years [69]. However, the degradation time of PLA can be shortened to 3-4 weeks when PLA is composted with microorganisms in an appropriate environment [87].

2.5. Biocomposites

Biocomposites have a broad classification and can be partially or completely biodegradable [62, 88]. The classification of biocomposites is shown in Figure 2.12. Partial biodegradable composites are based on biofibres as reinforcement and non-biodegradable thermoplastic (polypropylene/polyethylene) or thermoset (epoxy/unsaturated polyester) polymers as matrix. If the matrixes are biodegradable polymers, which can be derived from renewable or petro-based resource, the biocomposites are completely biodegradable. The renewable polymers include starch plastics, soy plastics, cellulosic acetate and PLA; the petro-based synthetic polymers include aliphatic polyester, aliphatic-aromatic polyester, polyesteramides, and polyvinyl alcohols [61, 62, 88].



Figure 2.12 Classification of biocomposites [62, 88]

In the biocomposites, biofibres are mainly natural fibres, which can be grouped into wood fibres, strew fibres, bast, leaf and seed/fruit fibres [61, 62, 88]. Due to their low cost, low density, and comparable mechanical properties to glass fibre, natural fibres

have been considered as feasible alternatives to the expensive glass, aramid carbon fibres in a composite, especially in automobile and construction industries [61, 62, 88, 89]. An all-composite made automobile is more than 50% lighter than a similar sized steel automobile; and it could be even lighter by using natural fibre reinforced composites, since natural fibres normally have lower density than the synthetic fibres [89]. The comparison of mechanical properties between natural fibres and highperformance synthetic fibres are shown in Table 2.1. In general, the mechanical properties of natural fibres are lower than those of synthetic fibres. However, the stiffness of hemp and ramie are similar to or even higher than that of the glass fibre; in addition, the specific modulus (modulus/specific gravity) of natural fibres is comparable to that of glass fibre [61, 89, 90].

Furthermore, it has been reported in several studies that 10-11 million vehicles in the United States need to be disposed annually after their end-use, and approximately 25% by weight of the vehicles are discarded as wastes, including plastics, composites, rubber and foams [61, 88]. Thus, the other advantage of using biocomposites to replace glass fibre composite is that the biocomposites have good biodegradability; they can be simply consumed by landfill. In the last decades, natural fibre reinforced composites have been used widely as interior and exterior material with multiple functions. They have been used as door panels, door trim panels, floor mats and spare tyre covers for automobiles to reduce the weight for higher fuel efficiency and to enhance sustainability [88, 89].

Fibre	Density (g/cm ³)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
Jute	1.3-1.49	393-800	13-26.5	1.16-1.5
Flax	1.5	345-1500	27-39	2.7-3.2
Hemp	1.47	550-900	38-70	1.6-4
Kenaf	1.5-1.6	350-930	40-53	1.6
Ramie	1.5-1.6	400-938	6.4-128	1.2-3.8
Sisal	1.45	468-700	9.4-22	3-7
Coir	1.15-1.46	131-220	4-6	15-40
E-glass	2.5	2000-3500	70-73	2.5
S-glass	2.5	4570	86	2.8
Aramid	1.4	3000-3150	60-67	2.5-3.7
Carbon	1.78	4000-4800	230-425	1.4-1.8

Table 2.1 Properties of natural fibres and high-performance fibres [61, 89, 90]

2.5.1. PLA based biocomposites

2.5.1.1. Bast fibres reinforced PLA composites

Compared to synthetic fibres, bast fibres have lower density and higher biodegradability. Since they also have relatively high Young's modulus and tensile strength, bast fibre reinforced PLA composites have attracted significant attention. The bast fibres that are usually used for biodegradable composites are hemp [91-93], jute [16, 94], flax [95-98] and kenaf [99-103].

Various manufacturing techniques are used to produce these composites. The most common manufacturing processes are injection moulding and compression moulding (using film-stacking). The injection moulding method can provide good degree of fibre wetting because the fibre and PLA matrix can be mixed properly in an extruder [93, 97, 102-104]. The disadvantage of this method is that the reinforcement structure of the composite is limited to chopped short fibres. However, compression moulding can use a variety of reinforced structures, including short fibre mat [91, 94, 95, 98], chopped short fibre [92, 100], unidirectional filaments and textile fabric [99, 101]. The degree of fibre wetting is highly depended on the processing temperature, pressure and time. To improve matrix fusion and wettability of fibres, Khonder and the co-workers [16] used a tubular braiding technique to produce a micro-braid yarn. The micro-brad yarn was constituted by a jute yarn as the straight inserted axial reinforcement fibre and the PLA matrix fibre was braided around the reinforcing jute yarn. Then, the micro-braiding yarns were compression moulded to create a unidirectional composite.

The mechanical properties of bast fibre reinforced composites are found to be comparable to glass fibre reinforced PLA composites. They have a tensile strength of 80 MPa and an elastic modulus of 6.7 GPa[105]. Oksman et al. have found that the flax fibre (30-40 wt %) reinforced PLA composite has 44-53 MPa tensile strength and 7.3-8.3 GPa E-modulus, which are higher than or equivalent to those of PP composites [104]. The mechanical properties of flax-PLA composites with higher fibre content (40-60 wt %) have been reported in Alimuzzaman et al.'s study [98]. By changing the moulding temperature and time during heat compression, the highest tensile properties (tensile strength= 80.3 MPa, tensile modulus = 9.9 GPa) flexural (flexural strength = 138.5 MPa, flexural modulus= 9.9 GPa) are achieved by the 50 wt% flax composite at 180°C moulding temperature and 5 min moulding time.

Ochi developed the unidirectional kenaf-PLA composite with 70% fibre content. The tensile and flexural strengths can reach 223 MPa and 254 MPa respectively [99]. The tensile modulus and strength of a short kenaf fibre –PLA with 30% fibre content can reach about 5.5 GPa and 52 MPa, and the flexure modulus and strength are 6 GPa and 85 MPa, respectively [103]. Kenaf-PLA composites also have high heat resistance and strength; thus, they can be used in the housing of electronic products [102].

The mechanical properties of PLA can be significantly improved by inserting jute fibre. Khonder et al. [16] developed unidirectional jute-PLA composites with different fibre volume fractions by using different moulding pressures and temperatures. The tensile strength and modulus increase with increasing fibre volume fraction; while the bending strength and modulus tend to decrease. The maximum tensile strength and modulus are approximately 78 MPa and 8.5 GPa; the maximum bending strength and modulus are 85 MPa and 7 GPa, respectively. Plackett et al. [94] also showed that the mechanical properties of jute-PLA composites are highly determined by the processing temperature. Due to the high melt viscosity of the PLA matrix, the degree of fibre wetting is very poor at relatively low temperature. The tensile strength and modulus of jute-PLA composite are enhanced apparently to 100 MPa and 9.5 GPa by increasing the processing temperature to 210-220°C.

Hu and Lim found [92] the mechanical properties of hemp-PLA composites peak at the fibre volume fraction about 50%. As fibre content increase, the tensile strength, elastic modulus and flexural strength decrease. A possible explanation for this is that the poor fibre wetting at high fibre content, which is due to the insufficient resin fraction to wet all the fibre surfaces. Sawpan et al. [106] successfully evaluated the fracture toughness of hemp-PLA composite by single-edge-notched-bending test. The fracture toughness of the composite is lower than the neat PLA and decreases with the increase of fibre content. This could be caused by the increased stress concentration and PLA matrix crystallinity [106].

The poor interfacial bonding is a well-known problem in natural fibre reinforced synthetic composites. Many studies have worked on the improvement of interfacial bonding by fibre surface treatment, the addition of plasticiser and coupling agent. Three types of fibre treatments were used in Huda el al's study, including aqueous alkaline solution, silane coupling agent, and a combination of both [100]. All these three treatments improve the flexural properties of kenaf-PLA composite compared to the

untreated composite. This is because the coupling agent can enhance the interfacial bonding by increasing the cross linking degree in the interface and the fibre surface area [100]. The positive effect of the fibre treatment also includes the removal of fibre surface wax and pectin [107]. The alkali and silane fibre treatments also show significant improvement on the mechanical properties of hemp-PLA composites in several studies [91, 93]. However, Oksman et al. reported that the triacetin plasticiser cannot improve the impact properties of the flax-PLA composite and the fibre mechanical properties are significantly decreased [104].

2.5.1.2. Leaf fibres reinforced PLA composites

Sisal fibre is extracted from the leaves of the Agave sisalana plant with high cellulose content and low microfibril angle [107]. Since it has high tensile strength (700 MPa) and modulus (22 GPa), it has become one of the most commonly used leaf fibres in the composite industry. Several studies have worked on the manufacturing of sisal fibre reinforced PLA composites and the improvement in their mechanical properties. Short sisal fibre reinforced PLA composites with various fibre content (10 - 40 %) were produced by melt blending followed by compression in Wu's study [108]. The tensile stress at break of the sisal-PLA composite decreases with the increase of fibre content. It was also found that the sisal-modified PLA (acrylic acid-grafted PLA) composites have significantly higher tensile stress at break than the unmodified PLA at the full range of fibre contents. This could be due to the improvement in the interfacial bonding through covalent linkages between fibre and matrix or hydophobisation of the cellulose surface [107]. The mechanical properties of a long sisal fibre reinforced PLA composite were investigated in Prajer and Ansell's study [107]. Caustic soda fibre treatment was used to enhance the interfacial bonding between sisal and PLA, in order to improve the tensile and flexural strength and modulus. The highest flexural strength (286 MPa) and modulus (22GPa) are achieved by the treated sisal fibre (60 vol%) - PLA composite; the 50 vol% treated sisal-PLA has tensile strength of 205 MPa and modulus of 12 GPa.

Bajpai et al. [109] evaluated the friction and wear characteristics of the sisal, Grewiaoptiva and nettle fibre reinforced PLA composites by a pin-on-disc rotating type friction and wear tribometer. The wear performance of the PLA matrix is enhanced by the addition of the natural fibres. The sisal-PLA composite shows the highest specific wear rate at 1 m/s sliding speed among the three composites [109]. Banana fibre–PLA composites were developed using melt blending followed by compression [110]. The tensile, flexural and impact properties of silane treated and untreated banana fibre-PLA were assessed. Both treated and untreated composites have higher tensile and flexural properties but lower impact strength than the neat PLA matrix. Moreover, the treated banana fibre-PLA shows higher tensile and flexural strength, and elongation at break compared to the untreated composite. In the study of Asaithambi et al., modified and unmodified banana/sisal fibre reinforced PLA hybrid composites were fabricated by a twin-screw extruder and subsequent injection moulding [111]. The fibre modification is done by an alkali treatment followed by benzoyl peroxide treatment to remove hemicellulose and allied impurities. The modified fibre–PLA composite shows significantly higher tensile and flexural strength and modulus as well as impact strength, compared to the virgin PLA and unmodified fibre-PLA composite.

The mechanical properties of three types of treated abaca fibre-PLA composites were investigated by Shibata and co-workers [112]. The flexural modulus of all the treated and untreated abaca fibre- PLA composite are increased as the fibre content increases from 5% to 20%. There is no obvious difference in flexural properties between the untreated and the three treated fibres-PLA composite, although the SEM images show improvement in interfacial bonding in the cases of butyric anhydride and acetic anhydride treated abaca–PLA composites.

2.5.1.3. Wood fibres reinforced PLA composites

Wood fibre has been used as reinforcement in many polymers such as polypropylene and polybutylene succinate to improve mechanical properties and reduce cost, Maple hardwood fibre reinforced PLA composites (fibre content 10-50 wt%) were produced by melt blending and subsequent injection moulding in the study of Way et al. [113]. The addition of wood fibre significantly improved the mechanical properties compared to the neat PLA matrix. In particular, the tensile modulus (2.5 GPa) and flexural modulus (8.22 GPa) of the 50 wt% wood fibre-PLA composite were 98% and 123% higher than those of the neat PLA.

Pine wood flour (20% and 40% fibre content) reinforced PLA composite has been reported in Pilla et al.'s study [114]. The wood flour-PLA composite was fabricated by melt blending followed by injection moulding. The addition of pine wood flour increases the tensile modulus and maintains the tensile strength, but decreases the

toughness and strain at break of the PLA matrix. The silane coupling agent did not offer significant effect on the properties of the pine wood flour–PLA. Hrabalove et al.[115]produced wood flour-PLA composites with various fibre content up to 50% by melt blending followed by compression. They found that the fibre-matrix compatibility and properties of the wood flour-PLA composite can be optimised by suitable crystalline structure, processing parameters and fibre content.

Pulp fibres, due to their attractive mechanical properties, high property reproducibility and abundant supply, have been used successfully in the composite industry [116]. In Du et al.'s study [116], hardwood and softwood pulp fibre sheets were employed as reinforcement in PLA composites. 30-50 wt% pulp fibres-PLA composites were fabricated by combining wet-laid paper-making process with film-stacking process. All the composites show significantly higher tensile modulus and strength than the PLA matrix. The calculated fibre length efficiency factor in the study for composite tensile strength is very close to continuous random fibre-reinforced composites.

2.5.1.4. Straw and grass fibres reinforced PLA composites

Bamboo is an abundant plant in South-eastern countries and is one of the fastest growing plants. As a result, bamboo fibre has high availability and relatively low cost. Moreover, bamboo fibre has high tensile modulus and elongation at break; its stiffness and specific strength are comparable to those of glass fibre. Thus, many studies have been carried out on bamboo fibre reinforced PLA composites [117-121]. Various short bamboo fibre-PLA composites (10-50 wt% fibre content) were produced by extrusion and subsequent injection or compression moulding and film-stacking [117-119]. Due to poor interfacial bonding between bamboo and PLA composites, these studies used a variety of fibre surface treatments and compatibiliser to improve the interfacial bonding [117-119]. All of these treatments show significant improvement on the mechanical properties of bamboo fibre-PLA composites. The mechanical properties of long bamboo fibre-PLA composites were reported in Rawi et al.'s study [120, 121]. Plain woven bamboo fabric reinforced PLA composites were fabricated by film-stacking at various processing conditions. Optimised processing parameters of 160 °C temperature, 1.05 MPa pressure and 3 minute time were defined. The optimised processing parameters provide tensile modulus and strength of 5.9 GPa and 80.64 MPa, flexural modulus and strength of 4.5 GPa and 143 MPa in the stronger, warp direction [120]. Compared to bamboo fabric-PP composite, the PLA composite offer more significant improvement on impact strength [121].

A large amount of rice or wheat straw and husks is incinerated and discarded every year as agriculture waste. Because of the low content of cellulose in the rice straw fibre, it is difficult to achieve good composite properties and there is not much research on it [122]. However, rice straw fibre does have potential as reinforcement in a biodegradable PLA composite because of its low cost and improvable physico-chemical properties by various treatments. Qin et al. [122] found the tensile strength of the rice straw fibre–PLA composite can be enhanced from 24 MPa to 30 MPa by using poly(butyl acrylate) (7.98 wt %) to modify the compatibility between fibre and PLA matrix.

Due to the large fraction of cellulose in the rice/wheat husks, they have potential to be utilised in biocomposite as reinforcement. In the study of García et al. [103], the rice husk-PLA composites did not show significant improvement in mechanical properties, compare to the pure PLA matrix. However, Tran el al. [123] evaluated the properties of the husk-PLA composites that underwent different fibre treatments, They found that the combination of an alkaline and an silane treatments could provide higher mechanical properties and thermal stability of the husk-PLA composite compared to the composite with only silane treatment.

Another abundant waste material from agriculture product is corncob. Similar to straw/grass fibre, corncob has potential as a filler in a biocomposite due to the low price and high availability. Although the addition of corncob in a PLA composite could offer enhancement in tensile modulus, the tensile strength and elongation at break of the corncob-PLA composite are lower than those of the PLA matrix because of the poor interfacial bonding [124]. However, the tensile properties of corncob-PLA composites can be improved by using a coconut oil coupling agent [124].

2.5.1.5. Seed and fruit fibres reinforced PLA composites

Coconut coir fibre is extracted from coconut husk with hemicellulose and lignin [125, 126]. It has potential applications as reinforcement of a biodegradable composite in automobile and construction due to its low thermal conductivity and bulk density, as well as the low cost. The coir fibre also has higher elongation at break, but lower tensile strength and modulus, compared to other natural fibres because it contains low cellulose and hemicellulose [125, 126]. Short coir fibre reinforced PLA biocomposites fabricated by injection moulding show significantly higher tensile modulus than neat PLA matrix, and the tensile modulus increases with the increase of fibre mass content within the range of 10- 40% [126]. Dong et al. [125] found that short coir fibre reinforced PLA

composites made by hot compression had lower tensile and flexural properties than neat PLA. However, alkali treated coir fibre composites had enhanced mechanical properties compared to the untreated fibre composites [125, 126]. This could be due to the alkali treatment improving fibre wetting and interfacial bonding between PLA polymer and coir fibre [125, 126].

A cotton fibre reinforced PLA composite was developed by Graupner et al. [127]. The mechanical properties of neat PLA are slightly improved by the addition of cotton fibre into the PLA matrix. The cotton-PLA composite shows lower tensile strength and modulus, but higher elongation at break and impact strength compared with hemp- and kenaf-PLA composites. Cotton linter, normally a waste material, is a mixture of residual cotton lint and cotton linters left on the cotton seed after ginning [113]. It was also the third largest fibre source after wood and bamboo in 2001 [128]. Way and the co-workers [113] developed a cotton linter-PLA composites by extrusion followed by injection moulding, and evaluated their mechanical properties and biodegradability. The tensile and flexural moduli and impact strength of the cotton linter –PLA composite with 25 wt% fibre content are 50 - 70% higher than those of the PLA matrix.

2.5.1.6. Biodegradability of natural fibre reinforced PLA composites

The biodegradability of PLA is highly dependent on the exposure environment. The conditions of the biodegradation environment include the presence of PLA degrading microorganisms, temperature, humidity and pH value. Many studies have evaluated the biodegradability of PLA based composites and compared it to that of neat PLA. The findings are varied, likely due to the varying test conditions. The PLA composites tend to be degraded faster at higher temperature (58 - 80°C) and in an enzymatic environment, compared to the soil burial test at room temperature [99, 113, 129, 130]. Most of the natural fibre reinforced PLA composites show faster biodegradability by burial test than the neat PLA matrix [91, 95, 108, 112, 113, 125, 129, 130]. Several studies also reported that although the mechanical properties of natural fibre reinforced PLA composite can be enhanced by fibre surface treatment, the biodegradability of the composites is adversely affected by the treatment [108, 112]. The addition of these chemicals may also bring about harmful chemical residues in the compositing environment at the end-lift-cycle.

2.5.2. PLA self-reinforced composites in biomedical applications

Self-reinforced bioabsorbable composite implants have been used in tissue engineering, especially implants for bone tissue fixation applications [131, 132]. The implants are required to retain the tissue supporting properties for a given period and degrade gradually [131]. PLA, due to its high initial modulus as well as excellent biodegradability and biocompatibility, has been successfully used as implants such as screws and scaffolds for bone fracture fixation [132-135].

A patent [136] first described the surgical osteosynthesis composite material which consisted of the absorbable polymer or copolymer as matrix and reinforcement with the same chemical element. The bioabsorbable self-reinforcing composites can be produced by either extrusion [131-134, 137] or hot compaction [135, 137-140]. In the former method, a self-reinforced structure is induced into the PLA matrix by transferring part of the microstructure of the PLA polymer into oriented elements such as macro/micro-fibrils, extended-chain crystals via mechanical deformation processes, such as free drawing, die drawing, shearing or rolling [137]. The PLA self-reinforced composites with good mechanical modulus, strength and toughness have been successfully produced by extrusion followed by die-drawing in some studies for bone fracture fixation application [131-134, 137].

The hot compaction method is based on partial melting or softening the PLA polymer fibres in a pressurised mould, and coalescing the melted fibres surface together during cooling [136, 137]. This method usually requires precise control of the heating temperature and pressure to give a thin melted/softened surface of fibres and avoid destruction of reinforcement by over-heating. Charles et al. [138] found that the flexural modulus is significantly affected by the compaction temperature and time in the preparation of PLLA SRCs at fixed pressure (50 MPa), and increases with the increase of compaction temperature.

In Nazhatet al.'s study [140], PLLA fibre and/or hydroxyapatite particle were reinforced with PDLLA film to create a biodegradable SRC for bone repairing and augmentation by hot compression. The compression moulding temperature of 100°C is lower than the onset melting temperatures of both the PDLLA matrix (122.8°C) and the PLLA fibre (167.2°C). A good interfacial bonding between two phases may not be achieved at this processing temperature, but the use of a high pressure of 57 MPa in the study helped to build up the interfacial bonding.

2.6. Summary

A number of studies of self-reinforced composites (SRCs) have been reviewed. These studies reported various techniques to produce self-reinforced composites based on a variety of thermoplastic polymers and indicated the advantages and processing limitations of the SRCs. However, very few studies worked on the SRCs made from biodegradable polymers. PLA, as a biodegradable thermoplastic polymer, has fairly good mechanical properties and high processability. Many studies found natural fibre reinforced PLA composites have comparable mechanical properties to and higher biodegradability than some synthetic fibre reinforced composites. However, because PLA is derived from agricultural sources, it is still considered as a high-priced material and more production of PLA may result in strains in food supply. Therefore, improvements in recyclability and utilisation of PLA are becoming more important.

This study aims to utilise the principles of self-reinforced composite with PLA polymer to produce a PLA self-reinforced composite which has good mechanical performance, recyclability and biodegradability.

CHAPTER 3. CHARACTERISATION OF MATERIALS

3.1. Introduction

In this study, PLA filament yarn is employed as reinforcement and PLA film is employed as the matrix material. This chapter evaluates the tensile properties of the PLA yarn and the chemical similarity between the PLA film and the fibre. A processing temperature window is defined based on the thermal properties of the PLA fibre and film. Moreover, the fibre relaxation in terms of fibre shrinkage at processing temperatures, as well as the PLA film and fibre thermal degradability are assessed.

3.2. PLA Filament Yarn

The PLA filament yarn was supplied in the form of a cylindrical bobbin by Haining Xian Gao Fibres Ltd. The yarn contains 216 filaments. The basic information was provided by the supplier and shown as follows:

Linear density: 450 Denier / 50 tex Bulk density: 1.24 g/cm³ Diameter of single filament: 15-16 µm

3.2.1. Tensile Properties of Untreated and Treated PLA Filament Yarn

3.2.1.1. Yarn treatment method

In order to assess the effect of the temperature on the tensile properties of the PLA yarns, the PLA yarns were treated by heating them up from room temperature to the desired temperatures. The PLA yarns were wound onto a specially designed winding plate (described in Chapter 5). The treatment procedure is the same as that used for composite manufacturing. The PLA yarns were treated under three different temperatures from 134°C to 156°C (measured by the thermocouple inserted in the composite mould); and the holding time is set to 10 min, which is the longest holding time used for composite manufacturing.

3.2.1.2. Fibre bundle test method

The tensile tests of PLA yarns were carried out by an Instron 5564 test frame equipped with a 1 kN load cell at a constant crosshead speed of 250 mm/min (BS EN ISO 2062-2009) [141]. The gauge length was set to 150 mm, which is limited by the length of the composite winding plate. 20 specimens were tested for each type of untreated and treated yarns. The specimens were preconditioned in a conditioned testing room

(humidity 65% and temperature 20°C) for 24 hours. The tensile modulus for each sample was measured and calculated automatically by the Instron testing software.

3.2.1.3. Fibre bundle test results

A typical tensile stress-strain curve of the untreated PLA yarn is shown in Figure 3.1, and the tensile properties of untreated and treated yarns are summarised in **Error!** eference source not found. After an initial elastic region with tensile modulus of around 4.85 GPa, the untreated PLA yarn yields at a strain of 3.4% and stress of 140 MPa. The yarn breaking strength is about 329 MPa. The strain at break is approximate 49%.



Figure 3.1 A typical tensile stress-strain curve of untreated PLA yarn bundle

The treated PLA yarns have similar tensile behaviour to the untreated yarn, but they show different tensile properties. The comparison of the tensile properties between treated and untreated yarns are shown in Figures 3.2 - 3.4. It can be seen from Figure 3.2 that the moduli of treated PLA yarns are significantly higher than that of the untreated yarn; there is no significant difference in modulus between the yarns that were treated under different temperatures. This is probably due to the annealing of the semi-crystalline polymer which could result in an increase in the crystallinity, crystallite size and perfection [142]. With the increase of treatment temperature, the tensile stress and strain at yield, as well as the tensile strength of the PLA yarn decrease, but the tensile strain at break increases. A possible explanation for this might be that the PLA polymer chain orientation and strain–induced crystallinity are decreased after the heat treatment.



Figure 3.2 Comparison of tensile modulus between untreated and treated yarns



Figure 3.3 Comparisons of tensile stress and strain at yield between untreated and treated yarns



Figure 3.4 Comparisons of tensile strength and strain at break between untreated and treated yarns

		Tensile modulus (GPa)	Stress at yield (MPa)	Strain at yield (%)	Tensile strength (MPa)	Strain at break (%)
Untreate	Mean	4.85 ±0.05	139.79 ±0.95	3.41 ±0.05	329.33 ±5.15	49.35 ±0.56
d fibre bundle	CV%	2.16	1.46	3.27	3.34	2.44
<140	Mean	5.14 ±0.05	138.41 ±1.10	3.10 ±0.03	284.38 ±3.90	54.74 ±0.71
	CV%	2.05	1.70	1.87	2.93	2.78
140-150	Mean	5.18 ±0.05	136.01 ±1.09	3.01 ±0.03	272.76 ±4.20	55.92 ±0.67
	CV%	1.85	1.71	2.06	3.29	2.54
>150	Mean	5.17 ±0.06	131.95 ±1.19	2.91 ±0.04	264.41 ±3.75	64.71 ±0.76
	CV%	2.53	1.93	2.73	3.03	2.50

Table 3.1 Tensile properties of untreated and treated PLA fibre bundle and single PLA fibre

3.3. PLA Film

A transparent moulded pure PLA film (Figure 3.5) was supplied by Esun Shenzhen Brightchina Industrial Co;Ltd and chosen as the polymer matrix for the composite. The melt flow rates of the films were measured by extrusion of a molten resin from the cylinder of a plastometer through a standard die of specified length and diameter under prescribed temperature and load (BS EN ISO 1133-1:2011) [143]. The basic information of the PLA and PBS films is shown in Table 3.2.



Figure 3.5 PLA film

Table 3.2 Basic information of PLA and PBS films

	Bulk density	Area density	Thickness	Melt flow index
	(g/cm ³)	(g/m ²)	(μm)	(g/10 min, 2.16 kg)
PLA film	1.28±0.02	42.1±2.4	40.3±4.6	9.2±1.5 (190°C); 1.5±0.6 (150°C)

3.3.1. Tensile properties of PLA film

In order to reduce the breakage at the grip edges that usually occurs in thin stripe sample testing due to stress concentration, dumb-bell shape specimens were used. The shape and dimensions of specimen are shown in Figure 3.6. For each type of unheated and

heated film, five specimens were tested at 2 mm/min for PLA film and 5 mm/min for PBS film by Instron 4411, equipped with a 0.5 kN load cell. The grip distance was 60 mm. Since the Instron software cannot detect the initial elastic region of the films, the tensile modulus for each sample is measured by linear fitting the section with the highest slope in the entire initial elastic region. The strain range of the section is selecting by dividing the initial elastic region into 6 equal regions [144].



Figure 3.6 Shape and dimensions of dumb-bell specimen

The tensile properties of heated and un-heated PLA films in transverse (TD) and longitudinal (LD) directions are summarised in Table 3.3. There is no significant difference in the tensile properties between the two directions of both un-heated and heated PLA films. It indicates that the PLA film is an isotropic material. By comparing the tensile properties of PLA film before and after a 150°C heating-cooling treatment, no obvious change can be found in tensile modulus, as well as yielding stress and strain. However, the stains at break in both directions are dramatically reduced after the treatment.

(95% confidence) Tensile modulus (GPa)		Tensile strength (MPa)	Strain at max. stress (%)	Stress at break (MPa)	Strain at break (%)				
			Un-heated	PLA film					
LD	Mean	1.39±0.24	41.62±7.77	3.55±0.47	36.62±3.46	15.12±6.37			
	C.V. %	13.80	15.04	10.64	7.62	33.81			
TD	Mean	1.39±0.20	41.83±3.80	3.42±0.45	35.06±4.70	21.19±13.59			
	C.V. %	11.51	7.31	10.53	10.80	51.67			
	Heated PLA film								
LD	Mean	1.44±0.19	44.03±5.64	3.66±0.18	38.17±6.30	6.26±3.10			
	C.V. %	10.60	10.32	3.98	13.29	39.9			
TD	Mean	1.44±0.16	43.82±6.55	3.47±0.48	42.27±6.77	4.35±1.13			
	C.V. %	8.89	12.03	11.20	12.9	20.87			

Table 3.3 Tensile property of PLA film

3.4. Chemical Similarity of PLA Filament Yarn

The vibrational spectroscopy, such as Infrared (IR) and Raman, are widely used to identify an unknown material and assess the structure features of the material, which can be either organic or inorganic. The information about the state of order of a macromolecular system can be provided by vibrational spectroscopy, via the analysis of different bands, which are resulted from different conformational regularity of the polymer chain and crystallinity of the polymer [145].

Several studies investigating IR and Raman spectrum of PLA based polymer have been published. The study of Goncalves *et al.* [145] presented the differences in IR/Raman spectrum of semi-crystalline and amorphous poly(lactic acid). In the study of Kister *et al.* [146], a series of PLA based polymer with different morphologies, conformations and configurations were examined using vibrational spectroscopes. The differences in the band positions, the shape and splitting of these PLA spectra indicated that IR and Raman are powerful techniques for analysing structural features of PLA based polymers. Besides, certain vibrations of molecule may be inactive in Infrared spectroscopy but active in Raman spectroscopy and vice versa; hence, to obtain the complete spectra to assess the chemical similarity of PBS and PLA materials, both Infrared spectroscopy and Raman spectroscopy were used to obtain the spectra in this study.

3.4.1. Principles of vibrational spectroscopy

3.4.1.1. Infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy is one of the most useful techniques to analyse either organic or inorganic material in the form of solid, liquid or gas. Because FTIR is sensitive to conformation and local molecular environment, it is widely used to clarify the structure of the semi- or crystalline polymers [145]. The broadband infra-red radiation emitted by infra-red source goes through an interferometer to modulate the wavelength. Then, the modulated IR radiation passes through the sample, where IR radiation is absorbed at different wavelengths by the different molecules. The signal of the intensity of the transmitted or absorbed IR radiation is detected by a detector. Finally, a characteristic infrared spectrum, which is plotted by the transmittance or absorbance intensity against the wavelength of IR absorbed, can be generated by specific IR spectrum analysis software.

3.4.1.2. Raman spectroscopy

Electromagnetic radiation can be absorbed, transmitted or scattered by a molecule. In IR spectroscopy, molecule absorbs IR radiation to achieve a higher vibration energy level. As shown in Figure 2.1, the principle of Raman spectroscopy is different from that of FTIR. In Raman, the molecule of sample is excited by a high energy monochromatic laser light ($E_{inc.}$), the frequency of which is usually higher than the vibrational frequencies of the molecules, from its original vibrational state (V_0) to an unstable energy level (virtual state, V_n). The molecule losses part of its energy (E_{loss}) by emission of a photon and then return to the original vibrational state. It is known as Rayleigh scatter. On the other hand, the excited molecule may return to its first vibrational energy level (V_1) rather than its original energy level. Thus, the difference in energy between original and first energy level (ΔE) is equal to the energy difference between incident photon and emitted photon, which is the characteristic of the molecule of the sample. This is known as Stokes scatter. The frequency of Stokes scattering is measured by Raman spectroscopy, in which a plot of scattering intensity as a function of the wavenumber of the vibrational frequency can be obtained.



Figure 3.7 Schematic of Infrared absorption, Rayleigh scatter and Stokes scatter

Although the information of a molecule from Raman and IR spectrum are similar, Raman spectroscopy is particularly employed to analyse non-polar groupings and homonuclear diatomic molecules such as C-C, S-S, which symmetrically vibrate about the centre symmetry. However, the vibrations, which are asymmetric, are infrared active but Raman inactive. Hence, by combing IR and Raman spectroscopes, the complete structural and optical information of materials can be received.

3.4.2. Test method

FTIR spectrum of PLA yarn and fabric, PLA film and PBS film were measured by calibrated Nicolet 5700 FTIR. To enhance the reliability of the FTIR results, three randomly selected test areas on each sample were examined. Raman spectra of these materials were recorded with Master Renishaw CCD detector at room temperature. The samples were excited by inferred laser with a wavelength of 785nm. A 100% laser power of approximate 76 μ W was achieved at the surface of the samples. Two Olympus lens with ×10 and ×50 magnifications were used. For each sample, the testes were repeated three times at different test areas. The spectra of absorbance (counts) as a function of wavenumber (Raman shift) obtained from IR and Raman spectroscopy are presented in the following.

As the PLA fibre and film are commercial products and supplied by two companies, the chemical structures of these two materials were examined by FTIR and Raman spectroscopes. The IR and Raman spectra of the PLA filament and film are shown in Figures 3.7 and 3.8. According to the wavenumbers and vibrational assignments of the semi-crystalline PLA in Kister *et al* 's study [146], the band positions of the PLA yarn and film are summarised in Table 3.4. It is obvious that the PLA film and the filament have almost the same Raman and IR spectra. It indicates that the high chemical similarity between the PLA fibre and matrix can result in good bonding properties in the PLA-SRC. On the other hand, since the PLA film and filament have different crystallinity, the intensity of some bands is different between filament and film. Surprisingly, there are two Raman bands (in Table 3.4) in this study that are not specified in the previous studies on PLA spectra [146, 147].



Figure 3.8 IR spectra of the PLA film and filament



Figure 3.9 Raman spectra of the PLA film and filament

	Raman (cm ⁻¹)				
Assignment	PLA Yarn	PLA Film	Assignment	PLA Yarn	PLA Film
C=0	686	704	COC+C-CH₃	296	299
C=0	755	754	C-CH₃+COC	349	
C-COO	870	866	ССО	397, 408	406
CH₃+CC	922, 955	955	C-CH₃+CCO	512, 585	515
C-CH ₃	1041	1041	C=0	709	705
COC	1087	1078	C=0	736	739
CH₃	1123	1128	C-COO	873	873
COC	1183, 1206	1180, 1208	CH₃+CC	924	
CH+COC	1267	1266	C-CH₂	1044	1045
СН	1303	1303	COC	1100	
CH-CH₃	1357	1359	CH₃	1129	1128
CH ₃	1384, 1453	1382, 1452	C- CH₃		1140
C=0	1746	1747	COC+ CH₃	1182	1185
CH₃	2947	2947	Unknown	1227	1235
CH₃	2995	2995	СН	1295	1299
			CH+CH₃	1342	1342
			CH₃	1387	1384
			CH₃	1454	1455
			C=0	1771	1771
			Unknown	1872	1876
			CH₃	2947	2947

3.5. Processing Temperature Selection

The successful production of a thermoplastic composite by the hot pressing method is dependent on the capacity of the film matrix to flow around and satisfactorily bond to the fibres without notable effect on the fibre physical properties. Thus, an appropriate processing temperature should be based on the thermal properties of fibre and matrix. The processing temperature for composite manufacturing is usually equal to or higher than the melting point of the matrix, but below that of the fibre. Differential Scanning Calorimeter (DSC) was employed to obtain a suitable processing temperature.

3.5.1. DSC principle and explanation of DSC plot

The Differential Scanning Calorimeter, one of the equipment used in thermal analysis, detects the physical and chemical changes that are induced into a polymer by the gain or loss of heat. DSC normally employs an inert material as the reference material to compare with the sample, so that the difference between sample and reference in the relative heat flow (unit of heat supplied per unit of time), which is required to keep the sample and reference at the same temperature, can be detected as the linear increase or decrease of temperature with time.

By measuring the amount of heat that is involved as a material suffers either an exotherm or endotherm, the heat capacity (C_p), the glass transition temperature (T_g), crystallisation temperature (T_c), melting temperature (T_m), the crystallisation enthalpy (ΔH_c), and the melting enthalpy (ΔH_f) can be obtained. Figure 3.10 shows a typical DSC plot with exothermal and endothermal peaks. In this graph, the "x" axis presents temperature, in degree Centigrade (°C), and the "y" axis shows the supplied heat flow, in the unit of Watts per gram (W/g).



Figure 3.10 Typical DSC plot

The difference in enthalpy (Δ H) of the system before and after transition is given by the area under the transition peak. Δ H is positive when endotherm occurs and negative when exotherm occurs. In DSC, the area of the crystallisation exothermic peak represents the crystallisation enthalpy (Δ H_c), and the area of the melting endothermal peak represents the melting enthalpy (Δ H_f) of the sample. Enthalpies of melting and crystallisation are related to the degree of crystallinity of the sample. If the melting enthalpy of the fully crystalline sample (Δ H_f 100%) is known, the crystallinity of sample can be calculated by the ratio of (Δ H_f - Δ H_c) to Δ H_f for 100% crystalline PLA is 93.6J/g [73, 148] and for 100% PBS is 110.5J/g [149].

Namely,

Degree of crystallinity =
$$\frac{\text{melting enthapy-crystalliaation enthalpy of sample}}{\text{melting enthapy of the fully cystalline sample}}$$

$$=\frac{(\Delta H_{\rm f} - \Delta H_{\rm c})}{\Delta H_{\rm f100\%}} \times 100\%$$
(3.1)

3.5.2. DSC test method

DSC tests were carried out by using a calibrated TA Instruments DSC Q100 for the fibre and matrix materials. Three samples from each material, including the PLA yarn and fabric, PLA and PBS films were cut to small pieces (about 1-2 mg) and sealed in hermetic pans and lids. All the samples experienced a heat-cool cycle with a heating and cooling rate of 10°C/min.

3.5.3. Thermal properties of PLA filament and film

The thermal properties of samples have been presented with the exothermic readings on the y-axis on the DSC plot of heat flow as a function of temperature. The glass transition (T_g), crystallisation (T_c) and melting (T_m) temperatures, and enthalpies of crystallisation (ΔH_c) and fusion (ΔH_f) were measured by a thermal property analysis software and are shown in Table 3.5. It can be seen from Table 3.5 that the T_g of PLA filament and film vary from 60°C to 63°C. No crystallisation temperature is found in PLA filament due to their high crystallinity; while T_c can be found in the PLA film at 104°C.

The original crystallinity of materials can be worked out by calculating the difference between enthalpies of fusion and crystallisation divided by the fusion enthalpy of 100% crystallinity, say $(\Delta H_f - \Delta H_c) / \Delta H_{f100\%}$. Since the enthalpies of 100% crystallinity is 93.6 J/g for PLA [73, 148], the degrees of crystallinity of PLA filament is about 56%. However, there is no big difference between the enthalpies of fusion and crystallisation in the PLA film; the PLA film is identified as an amorphous material.

	Т _g (°С)	T₅ (°C)	T _{eim} (°C)	T _{m1} (°C)	T _{m2} (°C)	ΔH_c (J/g)	ΔH _f (J/g)	Degree of crystallinity (%)
PLA	63.0	n/a	159.8	161.1	169.0	n/a	52.0	55.6 ±16.0
filament	±0.2		±0.3	±0.2	±0.5		±15.0	
PLA film	60.0	103.9	138.8	145.1	149.7±	19.3	22.0	Amorphous
	±0.8	±1.8	±1.1	±0.3	0.2	±5.2	±5.4	

Table 3.5 Thermal properties of the PLA filament and film

3.5.4. Processing temperature window

According to the different melting behaviours of the PLA film and filament, a processing temperature window for PLA-SRC manufacturing is defined as from 139°C to 160°C, which is the difference in onset melting temperature of these two materials. The processing temperature window is illustrated in Figure 3.11. This temperature range of 21°C will be further divided into three regions, which are low, mid and high temperature regions. The properties of the composites that were made in these three temperature regions will be compared in the following chapters.



Figure 3.11 DSC melting curves of PLA film and filament

The low temperature (low-temperature) region is defined as $140 \pm 2^{\circ}$ C, at which the PLA matrix start to melt. At 140°C, the PLA matrix has higher viscosity which may result in inadequate matrix penetration. However, 140°C is 19.80°C lower than T_{eim} of PLA fibre and, at this temperature, the fibre molecular relaxation of the PLA fibre can be minimised.

The high temperature (high-temperature) region is over 150 °C, but less than 155°C. At temperatures over 150°C, most of the crystal of the PLA matrix polymers are melted. The lowest viscosity of PLA matrix is achieved. This may result in the best matrix penetration compared to the other two temperature regions. Nevertheless, more fibre molecular relaxation of PLA fibre will occur as this temperature range is very close to T_{eim} of the PLA fibre.

The middle temperature (mid-temperature) region is specified as the temperatures between the high and low-temperature ranges, namely 143-149°C. The crystals of PLA matrix with the higher melting point may not be fully melted, because the temperature range is lower than the 2^{nd} melting point of the matrix (150°C). This provides a compromise between matrix viscosity and thermal degradation.

3.6. Fibre Shrinkage at Processing Temperature Range

The mechanical properties of fibre are highly dependeent on its crystallinity and molecular orientation. A high degree of molecular orientation is usually achieved by drawing at a temperature above the glass transition temperature (T_g) and cooling under tension [150]. The phenomenon of molecular relaxation is common for highly oriented semi-crystalline synthetic fibres, since the crystalline structures and molecular orientation change while the fibres are heated to temperatures above T_g without constraint force. Thus, PLA polymer molecular relaxation during processing may result in fibre shrinkage and affect the fibre mechanical properties.

The PLA fibre bundle experienced a heating-cooling treatment from room temperature to the desired processing temperature. One end of the PLA fibre bundle was fixed on a PTFE film. The original length and the after treatment length were measured by a travelling optical microscope. The fibre length was read from a vernier scale with 0.01 mm precision. Four groups of fibres were heated to 150°C and 140°C with 4 min and 8 min holding time. Five specimens were in each group. The fibre shrinkage in percentage is expressed as the difference between the original and the after-treatment length divided by the original fibre length.

The results of fibre shrinkage after heat treatments are shown in Table 3.6 and Figure 3.12. It can be seen that the PLA fibre shrinkage at 150°C treatment is significantly higher than at 140°C treatment. However, the holding time did not significantly affect the fibre shrinkage at either 150°C or 140°C treatment. It indicates that the temperature is the main factor that affects the PLA fibre molecular relaxation. Therefore, the high processing temperature of 150°C would have greater influence on the mechanical properties of PLA fibre than the holding time.

Fibre shrinkage after treatment	150°C-4min	150°C-8min	140°C-4min	140°C-8min
Average (95% confidence)	6.22 ±0.59	6.35 ±1.08	5.17 ±0.39	4.41 ±0.61
CV%	7.61	13.71	6.12	11.09

Table 3.6 Fibre shrinkage in percentage after heat treatments



Figure 3.12 Fibre shrinkages at various treatment temperatures and holding times

3.7. Thermogravimetry (TG) Analysis

PLA, as a biodegradable polymer, is usually sensitive to external environmental conditions. In particular, when PLA is heated to a temperature over or close to the melting temperature, polymer thermal degradation may occur. Thermogravimetry (TG) was used to evaluate the thermal stability and decomposition of the PLA fibre and matrix.

3.7.1. Principle

Thermogravimetry (TG) is a powerful technique that is used to evaluate the mass change of a sample as a function of temperature or time in a controlled atmosphere. TG can be operated in two modes: temperature-scanning mode and isothermal mode for monitoring mass change by changing temperature and time, respectively [151]. When a polymer sample experiences a thermal treatment (heating or cooling), the sample mass will be changed by desorption, absorption, sublimation, vaporisation, oxidation and decomposition [151]. Thus, TG can be employed to analysis decomposition, thermal and oxidative stabilities of a sample in an inert atmosphereat a simple temperature program, as well as to estimate the lifetime of a product at a complex temperature program, the effect of reactive atmospheres on materials, and moisture and volatiles content of materials [151, 152].



Figure 3.13 Typical TG curve showing a single-stage decrease in mass [153]

A TG is composed of a precise electronic microbalance that supports a sample pan, a furnace, temperature and atmosphere control systems, and a mass recording device [152]. A typical single-stage decrease in mass TG curve is shown in Figure 3.13. Points A and B refer to the points of intersection of the starting-mass line/final-mass line and the tangent to the TG curve at the point of maximum gradient [153]. T_A and T_B are the onset and the end temperatures of decomposition, respectively. T_C corresponds to the mid-point, C. The mass loss can be expressed as the difference between the before-heating mass and the final mass (m_{s} - m_{f}) divided by the before-heating mass (m_s).

3.7.2. Test method

In order to eliminate the possibility of mass loss by moisture vaporisation, all the PLA samples were dried at 50°C for 16 hours in a vacuum oven before the TG test. A PerkinElmer TGA 4000 thermogravimetric analyser was used in this study. To clean the TG sample pan before the test, the pan was heated up to 600°C, at which temperature most of the organic residue can be removed. PLA fibre and film were heated from 30 °C to 600°C in the air at a heating rate of 10°C/min. According to the British standard 2782-1 [153], the PLA film and fibre were cut into small pieces, and the mass for each sample is more than 10mg.

3.7.3. Results

The TG curves of PLA fibre and matrix are shown in Figures 4.10 and 4.11. The thermal stability of the PLA fibre and matrix are presented by means of weight percentage as a function of temperature. It can be seen from the TG curves that with the increase of temperature, from 30 to 600°C, the weight% of PLA fibre and matrix starts to decrease at approximately 350°C and the weight% drops to 0% at 381°C. Therefore, the onset decomposition temperatures for PLA fibre and matrix is 350°C and the end decomposition temperatures is 381°C. Figures 4.10 and 4.11 also demonstrate the weight% of PLA fibre and matrix is still around 100% in the PLA-SRC processing temperature window, namely 140-160°C. It indicates that there is no significant weight loss in this temperature range.



Figure 3.14 PLA fibre TG curve showing a decrease in mass by heating up to 600°C



Figure 3.15 PLA matrix TG curve showing a decrease in mass by heating up to 600°C

3.8. Summary

This chapter describes the basic information and tensile properties of the PLA filament yarn. The 50 tex linear density of the PLA yarn would result in high fibre content at certain number of wraps during filament winding. Moreover, compared to the untreated yarn the treated yarns show significant increases in tensile modulus and strain at break, but decreases in tensile strength and yielding stress and strain. FTIR and Raman spectra of the PLA filament are identical to those of the PLA film. Thus, the high chemical similarity between the fibre and matrix will bring about good bonding properties in PLA-SRC.

The processing temperature window from 139-160°C is selected from the DSC melting curves of the PLA fibre and matrix. Three temperature regions have been defined for further investigations. The fibre shrinkage after heat treatment indicates that the PLA molecular relaxation at high-temperature (150°C) is significantly higher than that at low-temperature (140°C) due to the changes in fibre crystallinity and molecular orientation. There is no obvious difference in fibre shrinkage by changing the heating holding time. Although the PLA fibre shrinkage can be restricted by applying processing pressure, the effect of molecular relaxation on fibre mechanical properties cannot be neglected. From the TG analysis, no significant weight loss resulting from thermal degradation was found in the selected processing temperature window.

CHAPTER 4. COMPOSITE MANUFACTURE

4.1. Introduction

As has been mentioned in the feasibility study (Chapter 3), the PLA fibre reinforced composite can be produced by filament winding following the hot-pressing process. The hand-winding method in the feasibility study resulted in poor fibre alignment and uneven winding tension; the imprecise temperature and pressure controls of the hot press also contributed to large defects on the samples. Therefore, a modified composite manufacturing process for the PLA fibre reinforced composites is required and described in this chapter.

There are two main stages of composite manufacture in this study. In the filament winding stage, unidirectional and bidirectional textile composite preforms and film matrix were stacked together to form a film stacked package by using a manually winding device. In the hot-pressing stage, composite consolidation can be completed by placing the film-stacked package in-between of the male and the female mould of a designed compression mould, then by locating the mould between the two plates of a computer controlled hot press. Furthermore, in order to minimise the hydrolytic reaction of PLA polymer during the composite manufacturing process, the film-stacked package is dried before moving to the second stage. A suitable drying condition is also defined in this chapter.

4.2. Manual Filament Winding

In order to obtain a uni/bi-directional structured film stacked package with parallel and even fibre distribution, a tailored manual winding machine was designed. By using this winding machine either unidirectional (UD) or bi-directional (BD) film-stacked package can be produced in a simple and fast way. Moreover, the design of the winding plate is a crucial part, because it links the entire composites manufacturing process, from the filament winding stage to the hot pressing stage.

4.2.1. Winding machine for unidirectional composites

The schematic diagram of the designed winding machine is shown in Figure 4.1. The winding machine is assembled mainly from 16 different components. The description and function of these components are shown in Table 4.1. As the handle (9) is turned,

the yarn is wound on the plate (6). The displacement of the winding plate in one turn is determined by the thread pitch on the support rod (3). When a finer thread is employed, the unidirectional preform with higher fibre content can be achieved. For this winding machine, the 0.7 mm thread pitch, the smallest available, is used to obtain the highest fibre density for each layer. Moreover, the winding plate is designed to have a two-way movement so that a number of fibre layers can be wound on the plate to vary the fibre content as required. To minimise the variation of yarn tension on the unidirectional preform, a pair of tension discs (15) are used to add constant tension on the yarn before the yarn passes through the yarn guide (13) and is wound on the plate (6). Furthermore, the key point to ensure the filament winding progressing smoothly is to align the centre line of the winding plate (6) with the threaded support rods (3).



Figure 4.1 Schematic diagram of the winding machine for unidirectional filament winding
Table 4.1 Des	cription of the	individual co	omponent of th	he unidirectional	winding machine
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No.	Description (number of component)	Function
1	Base support (2)	Rise the support to avoid winding plate touch the machine base
2	Support (2)	Support winding plate
3	Threaded support rod (2)	Determine the displacement of the winding plate in one turn and provide support force
4	Threaded bush bearings (2)	Allow the thread support rod to spin and translate freely in their axial direction
5	Short plate clamp (1)	Link the winding plate and the threaded rod
6	Winding plates(consist of two plates)	The yarn is winded around the plate to create unidirectional structure preform
7	Long plate clamp(1)	Fix the winding plates in position and prevent matrix flushing during hot pressing
8	Winding ruler (1)	Link the winding plate and the threaded rod and lead winding plate rotating
9	Lever handle (1)	N/A
10	Lever (1)	N/A
11	Coupler (1)	Link handle and threaded support rod
12	Handle support(1)	N/A
14	Tension columns (2)	Guide the yarn from yarn coin to the yarn guide via tension discs
15	Tension discs (2)	Provide constant tension on the yarn
13	Eyelet yarn guide (1)	Guide the yarn to be winded on the plate
16	Machine base (1)	Position winding device, yarn guide, tension dices and tension column

4.2.2. Winding plates for unidirectional composites

Since the processing temperature affects the properties of the composite, especially, for the self-reinforced PLA composite which has a narrow processing temperature window, accurate processing temperature control is required. Thus, it is essential to detect the actual temperature that the composite reaches. This is done by inserting thermocouples in the winding plate. The winding plate is located between a male and female composite mould, described in section 4.3.1. The winding plates and hot press mould are made of aluminium because of its good heat conductivity.

Figure 4.2 shows the schematic diagram of the pilot winding plate. The description and function of the pilot winding plate are shown in Table 4.2. The winding plate consists of a thick middle plate (6) and two thin plates (1) which cover the top and bottom surfaces of the thick plate. There is one groove on each side of the middle plate (6) to accommodate the thermocouples (2). A PTFE coated glass fibre sticker is used to fix the thermocouple tip and

keep it in contact with the plate. A big (4) and a small (3) clamp are used to hold the winding plates in position during winding and hot pressing.



Figure 4.2 Schematic diagram of the pilot winding plate

Table 4.2 Description of th	e individual component of the	unidirectional winding plate
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No.	Description	Function
	(number of component)	
1	Cover plates (2)	Provide a smooth surface for holding the UD preform and
		cover the pair of thermocouples mounted on the middle plate
2	Thermocouples (2)	Test the actual temperature reached by the composite
3	Short plate clamp (1)	See Table 4.1 (component 5)
4	Long plate clamp (1)	See Table 4.1 (component 7)
5	Socket set screws (5)	Hold the plate in position of the clamp
6	Middle plate (1)	See Table 4.1(component 6)

However, when the composite was produced under pressure, the thin aluminium cover plates (0.5 mm thickness) were too thin to carry the compression load. As a result, the thin plates were deformed near the thermocouple grooves by the pressure. The deformation led to two marks on both sides of the composite, shown in Figure 4.3. By using two thermocouples, the actual temperatures that are reached on both sides of the samples can be detected. During the composite producing process of the trial sample, the temperatures detected by the two thermocouples were the same. Therefore, the design of the winding plate was simplified to two thick plates instead of one thick and two thin plates, and only one thermocouple was used in between the two thick plates.

Moreover, the thermocouple grooves on both of the plates were wider than the first design to make it easier to insert and withdraw the thermocouple. The schematic of the final winding plate is shown in Figure 4.4.



Figure 4.3 The composites defect from thermocouple groove on the winding plate



Figure 4.4 Schematic diagram of the final winding plate

Figure 4.5 shows the actual winding process for a five-stack structure composite. In order to release the composite from the metal plates easily after consolidation, polytetrafluoroethylene (PTFE) coated glass fibre releasing films are laid between the metal plates and matrix film. Before winding starts, two pieces of releasing film are stuck on both sides of the winding plate; then two pieces of transparent PLA film matrix are layered. Another two pieces of PLA film will be layer on the top and bottom of the film package before hot pressing. The schematic diagrams of UD film-stacked packages are shown in Figure 4.6. For sandwiched structures an intermediary PLA film is stacked

in between the first and second PLA filament layer to enhance the contact between matrix and fibres so that good wetting of the fibres by the molten matrix film can be obtained during the hot consolidation process. Further comparison between the five-stack and four-stack structured composites is discussed in Chapter 5.

Releasing film (brown) and PLA film matrix (transparent)

First PLA fibre layer and PLA film matrix





Second PLA



Figure 4.5 Five-stack structure film-stacked package preparation: First PLA fibre layer winding (a); Second PLA fibre layer winding (b); Final film stacked package standby for hot pressing (c)



Figure 4.6 Schematic diagrams of four-stack unidirectional (a), 5-stack unidirectional (b) film-stacked packages

4.2.3. Filament winding for bi-directional composites

Unidirectional (UD) structures, can only carry significant load in the fibre direction; bidirectional (BD) structure composites, in which the fibres are orientated in two vertical directions, can provide good mechanical properties in both fibre directions.BD textile composite is usually produced by layering more than two UD composite prepregs. In the case of thermoplastic polymer composite, two hot pressing cycles are required, one for UD prepreg consolidation and one for joining UD prepregs to form BD. Thus, it increases the possibility of fibre molecular relaxation and has a longer processing time. This study integrates the manufacturing process of BD textile preform into one step. There is no need of a second hot pressing cycle.

The bidirectional filament winding, illustrated in Figure 4.7, is accomplished by modification of the unidirectional winding device (Figure 4.1). Two winding rulers are designed for bidirectional winding. A thermocouple is also used for the bi-directional winding plate. When one fibre layer is wound in one direction, the winding plate can be turned 90° for the next fibre layer winding in the perpendicular direction. This BD winding device is flexible for producing any fibre arrangement in 90° and 0° directions, such as 90/90/0/0 or 90/0/90/0, see Figure 4.8. The bidirectional PLA preform and the composite are shown in Figure 4.9.



Figure 4.7 Schematic diagram of modified winding machine for bidirectional filament winding



Figure 4.8 Schematic diagrams of 90/0/90/0 bidirectional (a), 90/90/0/0 bidirectional (b)



Figure 4.9 Bidirectional PLA preform (a) and composite (b)

4.3. Hot Pressing

The hot pressing stage is carried out by a Dr Collin[®] laboratory platen press (plates dimension: 30 cm*30 cm), see Figure 4.10. Although the hot press has a computer controlled system, it lacks temperature accuracy, which is confirmed by comparing the

temperatures that are detected by the thermocouple and the temperature sensors inside the hot press plate. The thermocouple detected temperature is regarded as the real composite processing temperature instead of the temperature showing on the hot press monitor.



Figure 4.10 Computer controlled hot press

4.3.1. Composite moulds

Figure 4.11 illustrates the composite mould for the hot pressing process. The composite mould (30 cm*30 cm) is made up of a male mould, a female mould and a plug. The winding plates, which are wound by the PLA filaments and PLA film, are sandwiched between the male (top) and female (bottom) moulds during processing. The female mould is designed to have three walls to allow the unidirectional winding plate to be located in between the male and female moulds. There is a slot on the wall of the female mould to allow the thermocouple to pass through and connect to the data logger. A plug is used to block the thermocouple slots to prevent the molten matrix from flushing out. For unidirectional composite processing, the large clamp on the winding plate serves as one wall of the mould to prevent the matrix flushing out. However, there is no big clamp for the bidirectional winding plate, thus, a metal bar is required to be assembled on the female mould to be the fourth wall.



Figure 4.11 Designed hot-pressing mould



Figure 4.12 Composite defects on the trial composite sample (T1)

Since the PLA self-reinforced composites in this project are very thin (about 0.02 mm), they are sensitive to any defects either from raw materials or processing. Figure 4.12 shows some defects on the top and bottom side composites of the trial sample (T1). To investigate the cause of defects, a series of trial samples have been produced. The defect in Figure 4.12 may be caused by the uneven surface of the composite mould and/or the

uneven pressure from the hot press. Because the defects on the two sides of the composites appeared in the same location (right centre), to exclude the possibility of uneven pressure caused by the non-alignment of the hot press plate, the second trial sample (T2) was made by turning the mould 90°. From the observation of this sample, the defects appeared at exactly the same place. It indicates that the composite defects are caused by the uneven surface of the composite mould.

In order to reduce the composites defect from composite mould unevenness, the third trial sample (T3) was placed in the mould with two pieces of rubber sheet, which are layered on the top and bottom of the film stacked package. The rubber sheets reduced the defects effectively. Because the rubber sheet is soft, the composite surface conforms to the distribution of fibres, leading to peaks and troughs on the composite surface (Figure 4.13). To solve this problem, two thin aluminium plates (0.5 mm thickness) were layered in between the rubber sheets and the film stacked package. The final arrangement of the hot pressing mould (Figure 4.14) improves the appearance of the composite. Nevertheless, the two rubber sheets can only improve the composite appearance when it is produced under a pressure lower than 2 MPa. Obvious defects still can be observed on the composite made under 3 MPa pressure using two rubber sheets, as shown in Figure 4.15.



Peaks and troughs on the composite surface

Figure 4.13 Composite defects on the trail samples (T3)



Figure 4.14 Final arrangement of hot pressing mould



Figure 4.15 Defects on the composite made by applying 3 MPa pressure (a) and the enlarged picture (b)

4.3.2. Composite consolidation

The various PLA self-reinforced composites are produced by a film-stacking method at different processing parameters, including processing temperature, pressure and holding time. The processing pressure and holding time are monitored by the hot press directly.

Figure 4.16 shows the temperature recording system during composite processing. A "K type" thermocouple with 10 cm plug is inserted in between the two winding plates that

are sandwiched by the female and male mould. The thermocouple connects with a thermocouple data logger to record the actual temperature of the sample; a laptop is used to monitor temperature changes and generate an actual time-temperature profile during composite consolidation.



Figure 4.16 Consolidation temperature recording system

The time-temperature and time-pressure profiles of composite consolidation are shown in Figure 4.17. The composite mould was placed between the two plates of the hot press and heated from the stating temperature (T_s) to the desired consolidation temperature (T_c).Heating and cooling processes at a rate of 10°C/min took about 11-13 min. The consolidation pressure (P_c) was applied to the film-stacked package from when the heating started and was held constantly until the sample had been cooled to the releasing temperature (40°C -50°C). The holding time (t₂— t₃), during which the temperature is held at T_c, is set to 6 min and 10 min in the hot press programme. Since the thick composite mould (about 5 cm thickness) and the use of the low heat conductive rubber sheets delayed the heat transfer from the hot plate to the samples, the actual mould temperature and hot press temperature were not synchronous. The actual time-temperature plots in Figure 4.18, illustrate that the actual processing time was 2 min shorter than the set time. The entire duration from the insertion of the film stacked package into the hot press to the removal of the composite laminate was approximately 30-35 min ($t_1 - t_5$).



Figure 4.17 Time-temperature and time-pressure profiles for composite manufacturing



Figure 4.18 Actual time-temperature plots of 6 and 10 min processing time

According to the DSC results in Chapter 4, the processing temperature window is about 21 °C, from 139 °C to 160 °C. As a result the imprecise temperature control and the temperature tolerance (\pm 5 °C) of the hot press, the PLA-SRC samples are classified into three temperature groups based on the processing temperatures that were detected by the thermocouple during composite manufacturing process. The consolidation temperature for each sample is determined by the average temperature during the holding period.

The three temperature groups are low-temperature $(140\pm2^{\circ}C)$, mid-temperature $(143 - 149^{\circ}C)$ and high-temperature (above 150°C). The composites were also produced under four different pressures (0.5 - 2MPa) and two holding times of 4 and 8 min (i.e. 6 and 10min). Hence, twenty-four different PLA-SRCs were produced. The composite processing parameters and coding system are shown in Table 4.3. The chapters of composite consolidation and impregnation (Chapter 6), tensile and flexural properties (Chapters 7 & 8), and biodegradability (Chapter 9) will follow this sample coding system. The schematic diagram of the film-stacked package is shown in Figure 4.19. Two composite laminates were produced during each process, one laminate from each side of the aluminium plate.

Holding time	Consolidation	Consolidation Temperature (°C)					
	Pressure	140 ±2 °C (Low- temperature)	142 - 149 °C (Mid-temperature)	≥ 150 °C (High- temperature)			
6 min	0.5 MPa	Low-0.5-6	Mid-0.5-6	High-0.5-6			
(actual 4	1 MPa	Low-1-6	Mid-1-6	High-1-6			
min)	1.5 MPa	Low-1.5-6	Mid-1.5-6	High-1.5-6			
	2 MPa	Low-2-6	Mid-2-6	High-2-6			
10 min	0.5 MPa	Low-0.5-10	Mid-0.5-10	High-0.5-10			
(actual 8 min)	1 MPa	Low-1-10	Mid-1-10	High-1-10			
	1.5 MPa	Low-1.5-10	Mid-1.5-10	High-1.5-10			
	2 MPa	Low-2-10	Mid-2-10	High-2-10			

Table 4.3 Composite processing parameters and sample coding system



Figure 4.19 Schematic diagram of the film-stacked package

4.4. Drying Condition for Film-Stacked Package before Hot Pressing

Early studies [154-161] have reported that some polyesters (such as PLA) are sensitive to thermal degradation. The molecular weight is decreased during thermal processing or under hydrolytic conditions, due to hydrolysis, depolymerisation, oxidation degradation, as well as intramolecular and intermolecular reactions. PLA is a linear aliphatic polyester. The ester bonds of these polyesters tend to be hydrolysed in the presence of water. Although several studies [154, 157, 158] found that the hydrolysis of the mainchain ester bonds is insignificant as a cause of degradation, they also reported that the polyester hydrolysis during thermal processing cannot be neglected. Thus, the final properties of the PLA self-reinforced composites would be affected by the molecular weight reduction due to the hydrolysis of main chain ester bonds. In order to remove the moisture content in the PLA films and filaments, it is essential to use a vacuum oven to dry the film-stacked packages before composite processing by the hot press.

From the literature, the drying conditions for PLA polymer should be achieved between $40 - 80^{\circ}$ C and between 5-24 hours. To obtain a suitable drying condition for the PLA based film-stacked packages, the PLA films and yarns were dried at 40°C, 50°C and 60°C for 8, 16 and 24 hours by a vacuum oven. In theory, the longer the drying time and/or the higher the drying temperature, the more the moisture content in the polymer can be removed. However, when the PLA film was dried at 60°C, it shrank, because this temperature is close to the glass transition temperature of the PLA film. As a result, the upper limit of the drying temperature is 60°C. Furthermore, due to the limited availability of the vacuum oven, the samples can be dried only for 16 hours. Thus, the drying condition of 50°C and 16 hours was selected.

4.5. Summary

An improved composite manufacturing method has been described in this chapter. The good fibre distribution and alignment, adjustable fibre content and controlled winding tension are achieved by the winding device. The winding device can be used for producing both unidirectional and bi-directional composite preforms. However, the BD composite in this study is only for demonstration, no further analysis was made, due to the time limitation. The following chapters will focus on the properties of UD composites. A tailored composite mould allows the recording of the actual processing temperature. The processing pressure is computer controlled by the state-of art hot press. Furthermore, a suitable drying condition was defined and applied to all the film-stacked packages before hot-pressing.

CHAPTER 5. COMPARISON BETWEEN FIVE-STACK AND FOUR-STACK UNIDIRECTIONAL STRUCTURES

5.1. Introduction

The modified composite manufacturing process is used to produce unidirectional PLA self-reinforced composites (PLA-SRCs) with higher fibre content. As shown in Figure 4.6, the four-stack structure consists of a top film layer, a bottom film layer, and a two fibre layers in the middle; the 5-stack structure is composed of one top film layer, one bottom film layer, and an additional film layer in-between the two layers of PLA fibres. Thus, the fibre content of the four-stack structure is higher than that of the five-stack structure. The fibre weight fractions for the five-stack and four-stack composites are 45% and 55%, respectively. However, the high melt viscosity of PLA matrix is expected to cause difficulty for the matrix to penetrate to the centre of the yarn bundle in the four-stack structure. The objective of this chapter is to compare the properties of these two structures and find a more suitable structure for further research.

5.2. Tensile Properties

5.2.1. Tensile test method

The tensile test method for the unidirectional PLA-SRC is based on the British standard BS EN ISO 527-5:1997 [162]. The scope of the standard is limited to composites that have thickness of 1 ± 0.2 mm, while the thickness of PLA-SRCs in this study is about 0.2 mm. Thus, some modifications of the test method are required. Various materials were tried as end tabs for the rectangular shaped PLA-SRC specimen to prevent grip slippage and specimen crushing close to or in the gripped regions. The trial tabbing materials included glass fibre reinforced composite (1.5 mm thickness), aluminium plate (1.5 mm thickness), rubber and paper card (0.8-1.2 mm thickness). Unfortunately, the results from the trial tests indicated that none of these methods was suitable for the PLA-SRC. Therefore, the standard tabbing method could not be applied in the study.

To reduce the stress concentration on the edge of the grip region, dumbbell shaped specimens were also used for tensile testing. As shown in Figure 5.1, the fibres in narrow parallel-sided section of the dumbbell were pulled out from the wide section. Thus, the dumbbell shape specimen is not suitable for thin unidirectional composite

either. Furthermore, an extensioneter is required in the tensile test standard to determine the gauge length change at any time during the test. However, the available clip extensioneter could not be used for the PLA-SRC specimen, because it would bend the specimen.



Figure 5.1 The fibres of narrow parallel-sided section of the dumbbell shape specimen been pulled out from the wide section

After numerous trial tests, the following tensile test method was employed. The specimens were gripped with unglued sandpaper to prevent grip slippage. In order to calibrate the tensile strain, removal compliance was completed by recording the tensile curve of very much stiffer material (metal plate) than the PLA-SRC; then the curve was applied automatically in the Bullhill[®] analysing software. The tensile tests for unidirectional PLA-SRC was performed at crosshead rate of 5 mm/min using a desktop Instron 3344 testing rig equipped with a 2 kN load cell at room temperature (BS EN ISO 527-5:1997). Five specimens for each composite were tested. The dimension of each specimen is 15 mm (width) \times 150 mm (initial distance between grips) \times approximate 0.2 mm (thickness). In order to get the average thickness and width for each specimen, the thickness and width were measured three times from different places on the specimen.

Tensile modulus in this test is obtained by a computer defined method[144]. The algorithm of this method is searching the first point load and maximum load value as the start and end values, respectively; dividing the region between start and end values into six equal regions; determining the slope of each region by square fit algorithm; searching the pair of consecutive regions which has the highest slope sum and assigning the slope of the region that has the highest slope in the pair as the modulus. The yielding point is taken as the zero-slope point immediately following the elastic region. Tensile strength refers to the stress at the point where maximum load occurs.

5.2.2. Composites tensile behaviour and failure modes

All the PLA-SRCs experience yielding process (elastic-plastic transition) after elastic deformation and undergo stress-whitening during the tensile test. The phenomenon of stress-whitening is due to polymer crazing. It is clear from Figure 5.2 that the colour of the tensile area of PLA-SRC turned white after tensile testing. Crazing is defined as localised plastic deformation, which results in the formation of small and interconnected micro-voids [142]. Crazing is the initial stage of cracking and created at high stress regions and propagates perpendicular to the tensile loading direction. Figure 5.3 illustrates that fibrillar bridges are in-between the micro-voids; in addition, as the strain increases, fibrillar bridges break and micro-voids grow to generate cracks, which can absorb fracture energy and increase the toughness. PLA polymer crazing is also found in the study of Pilla et.al [163] on PLA composites. The tensile failure modes of the PLA-SRCs depend on their processing conditions. Three tensile failure modes can be identified.



Figure 5.2 Comparison of tensile area and grip area of a tested PLA-SRC



Figure 5.3 Schematic pictures of Craze and Crack-craze

In the first mode (Mode A), the PLA matrix breaks before the fibre; the PLA fibres still carry the load until the limit of the fibre tensile strain is reached. A typical stress-strain curve of failure Mode A is illustrated in Figure 5.4. As the tensile strain increases after yielding, a transverse crack propagates to break the matrix, so that the stress drops at

matrix breaking. In addition, debonding between fibre and matrix occurs. As the debonding area increases, the film matrix delaminates from the fibre layer. The area of matrix delamination may finally spread to nearly all the sample length. Thus, tensile strength and strain at break of composites are determined by the PLA fibre, rather than the entire composite. More than one matrix crack could be observed. This could result in a zigzag stress-strain curve. Besides, tensile strength may occur before the complete failure of the composite in cases where the matrix ruptures. In these cases, the fibres keep carrying the load after tensile strength and break when the next peak stress is achieved. In this case, breaking stress is less than tensile strength and the strain at break is bigger than that at tensile strength. Mode A failure is common in composites which have relatively poor interfacial bonding, especially in composites that are produced at low processing temperature and/or low pressure.



Figure 5.4 Typical tensile stress-strain curve for composite failure at Mode A

Figure 5.5 shows a typical stress-strain curve of the composite which had a Mode B failure. Since the PLA matrix has lower breaking strain than the PLA fibre, after the yielding point, the matrix starts to undergo crazing. As the strain increases, the microvoids enlarge and fibrillar bridges break to form matrix transverse cracks. Later on, the large number of transverse cracks propagate and link to each other to create bigger cracks. As the matrix cracking grows, the load is progressively transferred to the fibre

resulting in the final complete failure. In this case, long pulled-out fibres and local matrix debonding can be found. The tensile strength is given at the breaking point, thus, breaking stress is equal to tensile strength. In some cases, the matrix cracks could extend to the entire specimen before ultimate break. Owing to the debonding and micro-crack growth, composites with Mode B failure usually have high strain at break, which can provide high tensile fracture toughness.



Figure 5.5 Typical tensile stress-strain curve for composite failure at Mode II

Composites with Mode B failure commonly have stronger interfacial bonding than those with Mode A failure. In failure Mode A, the poor bonding cannot transfer the load properly to the fibre, stress concentration distributes at matrix cracks, leading to matrix break. On the other hand, in Mode B failure, the load can be gradually transferred across the interface to the fibre after matrix cracking starts.

In Mode C, the matrix and fibre are broken at the same time, while the composites fail in a "step mode", as shown in Figure 5.6. The initial composite partial failure occurs at the weakest point, usually on one of the edges of the specimen. If the resultant stress redistribution is not high enough to break the neighbouring fibres, when the stress increases, a crack grows along the axial direction (axial splitting) to break the matrix combined with the fibre/matrix interface breaking; then, further stress concentration builds up at other weak points, resulting in further breaks. The cross-section image in Figure 2.1 shows that the fibre is absent in some regions of the composites. Fibre absence may provide a channel for axial direction crack growth. Axial splitting may occur more than once during testing, thus, the stress drops more than once before the ultimate failure.

No obvious debonding and matrix delamination are found in the specimen. For the composites that failed in Mode C, the tensile strength is measured at the first partial break. These composites have relatively lower strain at break than composites with other failure modes. The pulled-out fibres in Mode C are shorter than those in Mode B. This also indicates a stronger bonding in Mode C than in Mode B.



Figure 5.6 Typical tensile stress-strain curve for composite failure at Mode C



Figure 5.7 Cross-section image of fibre absent region

5.2.3. Tensile results of four-stack and five-stack composites

The mechanical properties of a thermoplastic based composite are highly dependent on the consolidation degree which is significantly affected by the processing temperature. At high processing temperature, high consolidation degree can be achieved; but the high temperature may affect the properties of the fibre due to molecular relaxation. In this section, both five-stack and four-stack structured PLA-SRCs are produced at the same processing pressure (1 MPa) and time (6 min), but various temperatures from 138° C - 155° C. The summaries of the tensile properties and the ANOVA analysis are presented in Tables 5.1 and 5.2; in addition, the main tensile features of the composites against the consolidation temperatures are shown in Figures 5.8 - 5.15.

	FOUR-STACK									
Proc. temp . (°C)		Tensile Modulus (GPa)	Stress at yield (MPa)	Strain at yield (%)	Tensile strength (MPa)	Tensile stress at break (MPa)	Tensile strain at strength (%)	Tensile Strain at break (%)	Failure mode	
143	mean	7.71 ±0.17	78.99 ±2.30	1.37 ±0.03	102.85 ±9.81	102.76 <u>±9.89</u>	24.18 ±2.16	25.54 ±2.20	A	
145	cv‰ mean	1.81 7.38 ±0.40	2.35 74.96 ±4.21	1.49 1.35 ±0.05	7.68 83.07 ±11.25	7.75 82.29 ±12.34	7.20 14.77 ±10.64	6.94 17.09 ±6.23	В	
	CV%	4.38	4.53	2.95	10.91	10.93	58.00	29.37		
147	mean	8.17 <i>±0.27</i>	80.81 <i>±1.53</i>	1.34 <i>±0.06</i>	109.30 <i>±9.20</i>	109.30 <i>±9.20</i>	24.22 ±3.77	24.22 ±3.77	В	
	CV%	2.70	1.52	3.46	6.78	6.78	3.77	3.77		
152	mean	7.64 ±0.25	76.29 <i>±2.90</i>	1.34 <i>±0.03</i>	103.94 <i>±7.77</i>	103.94 <i>±7.77</i>	25.36 <i>±3.12</i>	25.36 ±3.12	В	
	CV%	1.94	1.58	2.96	6.14	6.14	11.52	11.52		
153	mean	7.81 ±0.24	80.14 <i>±2.97</i>	1.34 <i>±0.03</i>	96.13 <i>±9.02</i>	96.13 <i>±9.02</i>	18.29 <i>±6.51</i>	18.29 ±6.51	B &C	
	CV%	2.67	3.27	1.62	8.28	8.28	6.51	6.51		
					ANOV	Α (α=0.05)				
F _{cr}	it				2.87					
F _{ca}	al	8.84	7.56	0.997	8.41	4.38	8.43	5.53		
P-va	lue	0.000280	0.000754	0.432	0.000378	0.0105	0.000373	0.00365		

Table 5.1 Tensile properties summary of four-stack structure composites

By comparing the calculated F-value (F_{cal}) and critical F-value (F_{crit}) of the tensile features in Tables 5.1 and 5.2, except the F_{cal} for strain at yield, the F_{cal} for all the other features of both five-stack and four-stack composites are greater than the F_{crit} and the Pvalues are less than 0.05. This indicates that the processing temperature has significant effect on the tensile properties of both structures (except strain at yield). Moreover, the calculated F-values of the five-stack structure PLA-SRC (F_{cal} = 17~117) are far greater than the critical F-value (F_{crit} = 2.62), and P-values are far less than 0.05. In contrast, the calculated F-values of four-stack structure are only in the range of 4 to 9, which is not greatly higher than the critical F-value (F_{crit} = 2.87). This reveals the effect by the processing temperature on the tensile properties of five-stack PLA-SRC is more significant than that on the four-stack PLA-SRC.

FIVE-STACK									
Proc. temp . (°C)		Tensile modulus (GPa)	Stress at yield (MPa)	Strain at yield (%)	Tensile strength (MPa)	Tensile stress at break (MPa)	Tensile strain at strength (%)	Tensile Strain at break (%)	Failure mode
138	mean CV%	7.07 <i>±0.17</i> 1.93	69.30± 0.73 0.85	1.30±0 .05 2.85	106.36 <i>±2.51</i> 1.9	104.12 <u>+</u> 5.35 4.14	27.66 <i>±1.58</i> 4.61	28.86±0 .72 2.01	A
143	mean CV%	7.28 ±0.17 1.89	74.38± 3.24 3.51	1.32±0 .06 3.44	99.69 <i>±6.82</i> 5.51	99.67 <i>±6.82</i> 5.51	26.08 <i>±2.95</i> 9.12	26.08 <u>±2.95</u> 9.12	A
145	mean CV%	7.48 <i>±0.11</i> 1.19	75.97 <i>±1.47</i> 1.58	1.34 ±0.07 4.32	104.86 <i>±5.42</i> 4.61	104.56 <i>±4.65</i> 3.58	25.88 <i>±0.82</i> 2.56	26.27 ±1.24 3.79	A & B
148	mean CV%	7.87 <i>±0.15</i> 1.53	76.46 <i>±1.49</i> 1.57	1.24 ±0.03 2.17	99.86 <i>±5.4</i> 4.35	99.86 <u>±5.4</u> 4.35	28.86 <i>±0.70</i> 1.96	28.86 ±0.70 1.96	В
152	mean CV%	7.65± 0.20 2.05	76.88± <i>1.80</i> 1.89	1.34 <i>±0.03</i> 1.40	97.35 <i>±2.93</i> 2.42	97.35 <i>±2.93</i> 2.42	23.94 <i>±3.60</i> 12.12	23.94±3 .60 12.12	С
155	mean CV%	7.60 <i>±0.16</i> 1.73	76.57 <i>±1.85</i> 1.95	1.30 ±0.02 1.4	76.76 ±2.13 2.23	75.77 ±2.26 2.4	2.77 <i>±4.10</i> 119.15	8.00±0. 64 6.47	n/a
ANOVA (α=0.05)									
F _{ca}	ıl				2.62				
Fcr	it	24.17	17.02	4.78	42.58	105.79	38.02	117.01	
P-va	lue	1.21*10 ⁻⁸	3.32*10 ⁻⁷	0.00358	3.65*10 ⁻¹¹	1.52*10 ⁻¹⁵	1.21*10 ⁻¹⁰	4.81*10 ⁻¹⁶	

Table 5.2 Tensile properties summary of five-stack structure composites

It can be seen from the tensile failure mode of the PLA-SRCs with the two structures in Tables 6.1 and 6.2 that all the samples that were made at relatively low temperature had Mode A failure with large area delamination. As the processing temperature increases, the failure mode changed from Mode A to Mode C. This indicates that the interfacial bonding of PLA-SRC is improved by increasing processing temperature within a

suitable range. However, at 155°C, the five-stack composite has a totally different failure mode from the three defined modes. Cracks start at natural flaws and grow gradually until the neighbouring fibres break; the failure crack is continuous and sharp; no obvious micro-cracks and only small area of local debond can be found. Compared to the other three failure modes, the five-stack composite has a relativity planar fracture. This failure mode indicates that the fibres are well bonded with the matrix. However, the processing temperature of 155°C is too close to the onset melting temperature of fibre and the fibre molecular relaxation degrades the fibre and less stress is required to break the neighbouring fibres when the crack grows. Furthermore, the tensile strength of the composites that have other failure modes is significantly higher than their yield stress, while the tensile strength of the 155°C five-stack composite occurs at or near the yielding point.

As shown in Figures 5.8 – 5.11, the tensile properties of four-stack PLA-SRC do not show significant change when the processing temperature increase, although the four-stack PLA-SRC made at 148°C appears to have highest tensile modulus. For the tensile properties of the five-stack PLA-SRC, shown in Figures 5.12 and 5.13, the initial modulus and stress at yield reach peaks at the processing temperature of 148°C. Figures 5.14 and 5.15 show that there has been a decrease in tensile strength, as well as stress and strain at break as the processing temperature increases from 138°C to 155°C. Moreover, it can be seen from Tables 5.1 and 5.2 that the tensile properties of most of the five-stack structure composites have lower variation than those of four-stack composites, because the interleaved film leads to higher property evenness.



Figure 5.8 Tensile modulus of four-stack PLA-SRC as a function of processing temperature



Figure 5.9 Tensile stress and strain at yield of four-stack PLA-SRC as a function of processing temperature



Figure 5.10 Tensile strength of four-stack PLA-SRC as a function of processing temperature

The tensile modulus, stress at yield and strength of four-stack composites are higher than those of the five-stack composites. This is because, although the interleaved films in five-stack composites increase the contact area between fibre and matrix to give better bonding properties, it also increases the composite thickness and decreases fibre content. Despite the maximum load and load at yield of five-stack structure are higher than those of four-stacked structure, the tensile strength and tensile stress at yield of the former are higher than those of the later by dividing the thickness. Nevertheless, the major advantages of five-stack structure are to reduce the delamination, provide stronger bonding between PLA fibre and matrix and improve the composite property reproducibility.



Figure 5.11 Tensile stress and strain at break of four-stack PLA-SRC as a function of processing temperature



Figure 5.12 Tensile modulus of five-stack PLA-SRC as a function of processing temperature



Figure 5.13 Tensile stress and strain at yield of five-stack PLA-SRC as a function of processing temperature



Figure 5.14 Tensile strength of five-stack PLA-SRC as a function of processing temperature



Figure 5.15 Tensile stress and strain at break of five-stack PLA-SRC as a function of processing temperature

To achieve effective reinforcement in a composite, the fibre should be evenly distributed in the matrix. The fibre content (fibre weight/volume fraction, f) in the composite is one of the key factors that affect the composite mechanical properties. The well-known "Rule of Mixtures" (in Equation 5.1) indicates the stiffness of a composite (E_c) and is a weighted average of the stiffness of the fibre (E_f) and matrix (E_m), determined by the fibre volume fraction [1].

$$E_c = (1 - f)E_m + fE_f$$
 5.1

In this study, the fibre weight fraction is 50% - 55% and 40% - 45% for four-stack and five-stack PLA-SRC, respectively. The modulus of PLA yarn is 4.85 GPa, which is lower than the modulus of the PLA-SRCs (about 7 - 8 GPa). Thus, the composite does not conform the "Rule of Mixtures". A similar finding was showed in Li and Yao's study [57], where the Young's modulus of the single PLA composite is higher than the sum of the PLA yarn and sheet. However, the reason for this is not clear. From the

tensile results of treated and untreated PLA fibre in Section 3.3, the tensile modulus of PLA fibre tends to be increased after heat treatment. This could be a possible reason for the increase in PLA modulus, when it becomes a single PLA polymer composite by the hot-pressing method.

5.3. T-peel Test

A T-peel test was carried out to evaluate the interfacial strength between PLA matrix and fibre in the four-stack and five-stack PLA-SRCs. Previous work [35, 41, 48, 50, 57] on other thermoplastic SRCs reported that better interfacial properties could result in higher peeling strength and cohesive failure mode; peeling strength increased as the processing temperature increased. From the tensile test results in Section 5.2.3, the composites that made at medium temperature have higher tensile modulus in both four and five-stack structures. Hence, the T-peel test will focus on mid-temperature composites that made at 1 MPa and 0.5 MPa.

5.3.1. T-peel test method

Because of the poor matrix penetration in the four-stack structure composite and the imperfection of the composite manufacturing process, small unbonded zone can be found at the edges of the composite. Figure 5.16 demonstrates the unbonded zone of the composite, where the composite can be peeled apart from the centre of the fibre layer. In this section, Peel strength of four-stack and five-stack composites were determined by a T-peel test (BS EN ISO 11339:2010) which is used to measure the peeling force of a T-shaped boned assembly of two flexible adherents [164].



__Unbonded zone

Figure 5.16 Unbonded zone of a composite

The T-peel test in this study was performed by an Instron 4300 test rig equipped with a 0.5 kN load cell. The dimension of the T-peel test specimens, as shown in Figure 5.17 (a), was reduced from the standard dimension by a ratio of 0.6. The T-peel specimen has an unbonded region (length: 30 mm) which is employed to clamp the specimen at an angle of 180°. Figure 5.17(b) illuminates a four-stack composite being peeled at a

constant crosshead rate of 100 mm/min. The average, maximum and minimum peeling forces are determined from the recorded force for 60 mm of the peeling length. It is worth noting that the first 15 mm and the last 15 mm peeling length are discarded. Peeling strength is defined as force per unit width in a peeling mode and is calculated from the recorded peeling force.



Figure 5.17 Schematic diagram of a T-peel specimen (a) and picture of a four-stack composite under T-peel testing (b)

The tested PLA-SRCs are the four-stack and the five-stack composites made under the following processing conditions: medium temperature (146 - 148°C), 0.5 MPa and 1 MPa pressures and 6 min holding time (mid-0.5-6-non, mid-0.5-6-san, mid-1-6-non and mid-1-6-san). The peeling strength and peeling failure mode differences caused by the inserting of interleaved film and various processing pressures will be discussed in the following sections.

5.3.2. Results of T-peel test

The average, maximum and minimum peeling strengths of the composites are summarised in Table 5.3. It is clear that there is no significant difference in the mean values of the averages, minimum and maximum peeling strengths of the four-stack and five-stack composites made under the same conditions. Fixed peel-width was used to calculate the peeling strength for each sample, while the peel-width of five-stack composite was decreased due to the incomplete peeling, as shown in Figure 5.18. It indicates that the actual peeling strength of five-stack PLA-SRC is higher than that of the four-stack. However, the CV% of the results show that the four-stack composites

have higher variation than the five-stack ones. This is in agreement with the tensile test results in section 5.2.3.

Peeling strength (N/100 mm)		mid-0.5-6-non mid-1-6-non (4-stack) (4-stack)		mid-0.5-6-san (5-stack)	mid-1-6-san (5-stack)
Average	Mean	49.51 ±11.61	41.29 ±10.56	48.83 ±5.15	45.21 ±5.02
	CV%	22.35	24.37	10.05	10.58
Maximum	Mean	65.70 ±11.10	55.02 ±12.64	66.90 ±8.67	59.60 ±8.29
	CV%	16.09	21.89	12.35	13.25
Minimum Mean		33.56 ±12.37	28.16 ±10.76	29.06 ±7.45	32.18 ±5.08
	CV%	35.13	36.41	24.44	15.05

Table 5.3 Peeling strength of the selected five-stack and four-stack composites

It can be seen from the pictures of the peeled four-stack specimens in Figure 5.19 that a large amount of fibres was peeled out from the matrix in both mid-0.5-6-non and mid-1-6-non specimens. This is because the high viscosity of molten PLA matrix restricts matrix penetration to the centre part of the fibre bundle. Thus, fibres are partly embedded into the matrix. The high peeling strength is mainly caused by the breakage of the partial embedded fibres, rather than the breakage of the bond between fibre and matrix. Moreover, two layers of fibres are intermeshed during the composite manufacturing process under pressure. This also increases the resistance to the separation of the fibre layers during the peeling process. On the other hand, incomplete peeling of five-stack specimens could be the result of good bonding between the interleaved film and the outer layer films with the help of the applied pressure, as shown in Figures 5.20 (b) and 5.21 (b). This bonding could provide high peeling strength. In this case, the matrix failure is changed from peeling to partial tearing.



Figure 5.18 Pictures of peeled mid-0.5-6-san (a) and mid-1-6-san (b) composite



Figure 5.19 Pictures of peeled mid-0.5-6-non (a) and mid-1-6-non (b) composite



Figure 5.20 Cross-sectional images of 0.5 MPa pressure processed four-stack and five-stack structure composites (processing condition: mid-temperature, 6 min): c) and d) are the enlarged a) and b)

The different peeling failure mode also can be explained by observing the composite cross-section images. The cross-sections of the composites were prepared by mounting the composites into epoxy resin and then through grinding and polishing processes. The polished cross-sections were examined by a Leica[®] DM600M optical microscope.

Figure 5.20 shows the cross-sections of the four-stack (a & c) and five-stack (b & d) composites that are made under 0.5 MPa pressure. It can be seen from Figure 5.20 (a) and (c) that only the fibres at the boundary of the fibre bundle contact with the matrix and many voids are present within the fibre bundle, since the high viscosity of the melt PLA matrix causes the poor matrix penetration. The white spots within the fibre bundle may indicates the voids which can provide weak points for peeling failure. In contrast, the interleaved film matrix layer in the five-stack structure, in Figure 5.20 (b) and(d), provides large contact between fibre and matrix in the five-stack structure. This may bring about stronger interface bonding. However, fibre internal cracks can be observed at some parts of the composites, where the fibre bundle is thick, as shown in Figure 5.20 (d). This may be caused by the polishing and grinding process.



Figure 5.21 Cross-sectional images of 1 MPa pressure processed four-stack and five-stack structure composites (processing condition: mid-temperature, 6 min)

Similar results can be found in Figure 5.21, which illustrates the cross-sections of the four-stack (a & c) and five-stack (b & d) composites made under 1 MPa consolidation pressure. The five-stack structure shows better matrix penetration and more fibre and matrix contact than the four-stack structure. No significant difference can be found in the cross-sectional images of the composites which were made under 0.5 MPa and 1 MPa pressures.

5.3.3. SEM images of peeled fracture surface

Figure 5.22 illustrates the gold coated peeled fracture surface of Mid-0.5-6-non composite. The gap, in Figure 5.22 (a), shows that the Mid-0.5-6-non failure is in between of the fibre layers and caused by insufficient matrix penetration in this composite. It can be seen from Figure 5.22 (b) that the peel-out fibres tangle with each other, which reflects one possible reason for the high peeling strength. Relatively clean fibre surface are demonstrated in Figure 5.22 (c); while fibrillated surface can be seen in some regions. In contrast, Figure 5.22 (d) shows that the fibrils are peeled out from the PLA fibres where fibre and matrix are bonded. It indicates that the good bonding can be achieved where fibre and matrix contact. Similar to mid-0.5-6-non, mid-1-6-non

composite failed within the fibre layer, as shown in Figure 5.22 (a) and (b). The peeled– out fibres and fibre entanglement can be observed in Figure 5.23 (a) and (c). Clean fibre surface and some fibrils in mid-1-6-non are also shown in Figure 5.23 (d).



Figure 5.22 SEM images of Mid-0.5-6-non peeled fracture surface: a) gap in between of the fibre layers; b) tangled peel-out fibres; c) clean PLA fibre surface; d) fibrils peeled out from PLA fibre surface



Figure 5.23 SEM images of mid-1-6-non peeled fracture surface: a) gap in between of two fibre layers; b) enlarged a); c) tangled peeled-out fibres; d) clean fibre surface and partial fibrillated surface

From the peeled fracture surface of mid-0.5-6-san, it is apparent that numerous fibres have been peeled out, in Figure 5.24 (a). Figure 5.24 (b) shows some partially broken PLA matrix and the fibres grooves. They indicate that the bonding between fibre and matrix prevents the matrix from peeling and finally results in matrix breakage. Fibrillated PLA fibre fracture surface can be observed in Figure 5.24 (c). Similar fibrillated surface also can be observed in the peeled matrix surface in Figure 5.24 (d). The SEM images of peeling fracture surfaces in Figure 5.25 (a) and (b) also show large numbers of fibrils peeled out from PLA yarn. It can be seen from Figure 5.25 (c) and (d) that parts of outer PLA film is still stuck with the interleaved film. The embedded PLA fibre can be observed in Figure 5.25 (e) and (f). Compared to the four-stack PLA-SRCs that were made under the same condition, all the five-stack PLA-SRCs failures are in a

cohesive peeling fracture mode. This is because the interleaved film enhances the contact between fibre and matrix to offer stronger bonding in the five-stack structure.



Figure 5.24 SEM images of Mid-0.5-6-san peeled fracture surface: a) numerous peel-out fibres and matrix failure; b) enlarged image of a); c) fibrillated fibre surface; d) fibrillated matrix surface



Figure 5.25 SEM images of mid-1-6-san peeled fracture surface: a) fibrillated PLA fibre surface; b) enlarged image of a); c) peeled matrix fracture surface; d) enlarged image of c); e) PLA fibre embedded in PLA matrix; f) enlarged image of e)
5.4. Discussion

A feasible tensile test method for the thin PLA-SRC has been found after a series of trial tests. Three tensile failure modes have been defined by tensile testing observation and analysing stress-strain curves. The processing temperature range, 140° C - 160° C was selected according to the DSC results of PLA fibre and film. It is apparent from the tensile results that there are significant effects on the tensile properties of both five-stack and four-stack PLA-SRCs by the processing temperature ($F_{cal}>F_{crit}$, p<0.05).

With the increase of processing temperature, tensile strength and strain at break of the five-stack composites decrease; in contrast, tensile initial modulus and stress at yield of the five-stack composites reach a peak at 148°C. Moreover, the tensile properties of five-stack PLA-SRC decrease dramatically when the processing temperature reaches 155°C, because fibre molecular relaxation and orientation change may occur at high temperatures. However, no obvious trend on the tensile properties can be detected in the four-stack composites. Comparing the tensile properties of the four-stack and five-stack systems, the addition of an interleaved film reduces delamination and increases the property evenness.

The T-peeling testing results indicate that there is no significant difference in the peeling strength between mid-temperature four-stack and five-stack composites. The outer film of the five-stack PLA-SRC was incompletely peeled out, due to the improved bonding properties. Thus, the actual peeling strength of five-stack PLA-SRC might be higher than the four-stack one. The cohesive and fibril fracture surfaces are also shown in SEM images of the peel fracture surface. The cross-sections of the four-stack PLA-SRC indicate poor matrix penetration in the four-stack structure composite. This is because the high melt viscosity of the PLA film results in greater difficulty for matrix flow into the centre of the PLA fibre bundle. In five-stack structure, the interleaved film in-between the PLA fibre layers provides more contact between fibre and matrix, which results in better interfacial bonding in five-stack PLA-SRC.

Although the four-stack PLA-SRC has higher fibre content, it is difficult for PLA matrix to penetrate into the centre part of the fibre bundle to form strong interface. The results of cross-sectional images, tensile and T-peel tests in this chapter show that inserting an interleaved PLA film to create the five-stack PLA-SRC improves the bonding properties between PLA fibre and matrix. The following chapters will focus on the investigations on the properties of five-stack PLA-SRC.

CHAPTER 6. CONSOLIDATION AND IMPREGNATION

6.1. Introduction

Good interfacial bonding in a composite requires the largest possible contact area between fibre and matrix, which highly determines the consolidation degree (fibre wetting) in a thermoplastic composite. Poor consolidation normally leads to great void content and delamination, especially when the film-stacking method is used. The polymer matrix melt flow index is one of the important factors that affect the consolidation degree during composite manufacturing. Polymers having smaller melt flow index have higher melt viscosity and flows more slowly; polymers having lower melt viscosity flow faster. In addition, the melt flow index of PLA polymer becomes lower at higher temperature. For instance, the PLA matrix used in this study has a melt flow index of approximately 9.2 g/min at 190°C and 1.5 g/min at 150°C. The application of proper processing pressure can also enhance the molten matrix penetration. The change in holding time affects the consolidation degree as well. This is because a shorter time may bring about insufficient impregnation; a longer time may result in over-heating of the fibre [101]. This chapter examines the cross-sectional morphologies of the composites that were produced at different processing conditions. The consolidation degree of various PLA-SRCs will be assessed from these crosssectional images.

6.2. Sample Preparation and Test Method

The cross-sections (CS) of each composite were prepared by mounting the composites vertically in epoxy resin. After grinding and polishing, the cross-sections were examined by using the Zeiss optical microscope. It is worth to note that the sample coding in this chapter follow the Table 4.3 in chapter 4.

6.3. 0.5 MPa Pressure Produced PLA-SRC

Figures 6.1 and 6.2 show the cross-sectional images of 6 min and 10 min holding time PLA-SRCs that were made at low temperature and 0.5 MPa (low-0.5-6 and low-0.6-10). The small circles in the images are the cross-section of the fibres. The large amount of black dots in-between fibres refers to the voids. It is apparent that the matrix is surrounding the fibre bundles and contacting only with the boundary fibres. As the low processing pressure and temperature result in poor matrix penetration, obvious voids within fibre bundles can be seen in Figure 6.1. Similar results can be obtained in low-

0.5-10, Figure 6.2. There is no significant difference in terms of consolidation degree between the composite that were made with different holding times.

The optical microscope CS images of 6 min and 10 min holding times PLA-SRCs made at mid-temperature and 0.5 MPa (mid-0.5-6 and mid-0.5-10) are shown in Figures 6.3 and 6.4. There is no significant difference in consolidation degree between the low-temperature and mid-temperature 0.5 MPa samples. Furthermore, obvious voids and continuous cracks in-between the fibres can be observed in parts of the composite, as shown in Figure 6.3 (b). Although most of the crystals of the PLA matrix are melted at mid-temperature, the high melt viscosity restricts the penetration of the molten polymer into the fibre bundles. The insufficient contact between the fibre and matrix may result in poor mechanical properties in the PLA-SRC.

It can be seen from the CS images in Figures 6.5 and 6.6 that the high-0.5-6/10 composites have greater consolidation degree than the mid/low-0.5-6/10 composites. Since no obvious voids can be found, it can be inferred that the high processing temperature can provide better fibre wetting even at low pressure (0.5 MPa). Moreover, the decreasing sharpness of the fibre contour may indicate an enhanced bonding between fibre and matrix.



Figure 6.1 CS images of low-temperature, 0.5 MPa, 6 min produced PLA-SRC (low-0.5-6)



Figure 6.2 CS images of low-temperature, 0.5 MPa, 10 min produced PLA-SRC (low-0.5-10)



Figure 6.3 CS images of mid-temperature, 0.5 MPa, 6 min produced PLA-SRC (mid-0.5-6)



Figure 6.4 CS images of mid-temperature, 0.5 MPa, 10 min produced PLA-SRC (mid-0.5-10)



Figure 6.5 CS images of high-temperature, 0.5 MPa, 6 min produced PLA-SRC (high-0.5-6)



Figure 6.6 CS images of high-temperature, 0.5 MPa, 10 min produced PLA-SRC (<u>high-0.5-10</u>)

6.4. 1 MPa Pressure Produced PLA-SRC

The CS images of low-temperature, 1 MPa, 6 and 10 min produced PLA-SRCs (low-1-6/10) are shown in Figures 6.7 and 6.8, respectively. Similar to low-0.5-6/10 PLA-SRCs, the low-1-6/10 composites illustrate poor matrix penetration. Besides, due to the insufficient matrix melt and low pressure, the interleaved PLA film does not bond with the outer films at some region of the composites, as shown in Figures 6.7 (c) and 6.8 (a). This unbounded region would result in poor mechanical properties. Thus, there is no significant improvement in consolidation degree of the low-temperature PLA-SRC by increasing the pressure to 1 MPa.

It is clear from the CS images of mid-1-6/10 samples in Figures 6.9 and 6.10 that the PLA fibre bundles are surrounding by the matrix and a large amount of voids can be found within the fibre bundles. Similarly, only the fibres that are at the outer boundary of the fibre bundle contact with the matrix, which leads to lower interfacial contact between fibre and matrix.

On the other hand, the CS images of high-1-6/10 in Figures 6.11 and 6.12 have different morphologies compared to the low and mid-temperature samples. The fibre bundles are more compacted and have fewer voids. The improved consolidation degree in high-temperature samples and the low sharpness of the contour of the fibre indicate good bonding between fibre and matrix. However, the voids between fibres still can be found

in some regions of the composite, Figure 6.12 (c). This may be caused by insufficient processing pressure.



Figure 6.7 CS images of low-temperature, 1 MPa, 6 min produced PLA-SRC (low-1-6)



Figure 6.8 CS images of low-temperature, 1 MPa, 10 min produced PLA-SRC (low-1-10)



Figure 6.9 CS images of mid-temperature, 1 MPa, 6 min produced PLA-SRC (mid-1-6)



Figure 6.10 CS images of mid-temperature, 1 MPa, 10 min produced PLA-SRC (mid-1-10)



Figure 6.11 CS images of high-temperature, 1 MPa, 6 min produced PLA-SRC (high-1-6)



Figure 6.12 CS images of high-temperature, 1 MPa, 10 min produced PLA-SRC (high-1-10)

6.5. 1.5 MPa Pressure Produced PLA-SRC

The CS images of low-1.5-6 PLA-SRC in Figure 6.13 illustrate obvious voids between fibres. There is no significant difference in consolidation degree between this composite and the low-temperature composites that were made under 0.5 and 1 MPa pressures. Surprisingly, the low-1.5-10 sample shows higher consolidation degree than the low-1.5-6 samples. This may be due to the PLA matrix melting more thoroughly with longer holding times.



Figure 6.13 CS images of low-temperature, 1.5 MPa, 6 min produced PLA-SRC (low-1.5-6)



Figure 6.14 CS images of low-temperature, 1.5 MPa, 10 min produced PLA-SRC (low-1.5-10)



Figure 6.15 CS images of mid-temperature, 1.5 MPa, 6 min produced PLA-SRC (mid-1.5-6)

Nevertheless, the CS images of mid-1.5-6, as shown in Figure 6.15, indicate higher consolidation degree than low-1.5-6. There is no obvious difference in terms of consolidation degree between mid-1.5-10 and low-1.5-10. However, the voids (white or black spots) between fibres can still be observed in both mid-1.5-6 and mid-1.5-10 composites. Compared to the mid-temperature 0.5 and 1 MPa samples, the fibre bundles of mid-1.5-6/10 are more compact and have fewer voids. It can be inferred that the consolidation degree of PLA-SRC is enhanced as the processing pressure increases.

The CS images of high-1.5-6/10 PLA-SRCs are shown in Figures 6.17 and 6.18. The contours of the fibres are blurry; voids are almost absent from the composites. These

indicate that better fibre wetting is achieved in the high-temperature composite, compared to the low/mid-temperature composites that were made at the same pressure and holding time. There is no difference in consolidation degree between high-1.5-6 and high-1.5-10.



Figure 6.16 CS images of mid-temperature, 1.5 MPa, 10 min produced PLA-SRC (mid-1.5-10)



Figure 6.17 CS images of high-temperature, 1.5 MPa, 6 min produced PLA-SRC (high-1.5-6)



Figure 6.18 CS images of high-temperature, 1.5 MPa, 10 min produced PLA-SRC (<u>high-1.5-10</u>)

6.6. 2 MPa Pressure Produced PLA-SRC

Figures 6.19 and 6.20 illustrate the CS images of PLA composites made at low-temperature, 2 MPa pressure, 6 and 10 min holding time (low-2-6/10). The fibre bundles between the matrix layers seem to be more compact and the voids between fibres are smaller and less, compared to the low-temperature samples that were made at lower pressures. Furthermore, some parts of the low-2-10 composites are void-free, as shown in Figure 6.20 (c). It indicates that fibre wetting of the low-temperature produced PLA-SRCs is improved by increasing the processing pressure.

Similarly, the consolidation degree of mid-temperature PLA composite is enhanced by increase the pressure to 2 MPa, as shown in Figures 6.21 and 6.22. Fewer and smaller voids can be found in the CS images, while continuous cracks may be detected at the centre of the fibre bundle in some parts of the composite, Figure 6.21 (b).

The CS images of high-2-6/10 composites are shown in Figures 6.23 and 6.24. The CS morphologies of high-2-6/10 are similar to all the high-temperature composites that were produced at various pressures. Sufficient matrix penetration of high-temperature sample provides the largest contact area between fibre and matrix, and strong interfacial bonding can be achieved.



Figure 6.19 CS images of low-temperature, 2 MPa, 6 min produced PLA-SRC (low-2-6)

50 µm 1 b 100 µm

Figure 6.20 CS images of low-temperature, 2 MPa, 10 min produced PLA-SRC (low-2-10)



Figure 6.21 CS images of mid-temperature, 2 MPa, 6 min produced PLA-SRC (mid-2-6)



Figure 6.22 CS images of mid-temperature, 2 MPa, 10 min produced PLA-SRC (mid-2-10)



Figure 6.23 CS images of high-temperature, 2 MPa, 6 min produced PLA-SRC (high-2-6)



Figure 6.24 CS images of high-temperature, 2 MPa, 10 min produced PLA-SRC (high-2-10)

6.7. Summary

By observing the cross-sectional images of the composites that were made under various processing conditions, the following main findings can be made:

- The poor matrix penetration in the low and mid-temperature composites can be improved by increasing the processing pressure. Although PLA matrix has high melt viscosity at low and mid processing temperatures, with the help of higher pressure, the consolidation degree can be enhanced significantly.
- There is no significant difference in consolidation degree of the high-temperature samples that were produced at different pressures. The PLA viscosity at high temperature is low enough for the PLA matrix to penetrate into the fibre bundles. Even at low pressure (0.5 MPa), a good consolidation degree can still be achieved.
- 3. The consolidation degree of the high-temperature composites is significantly higher compared to the low and mid-temperatures PLA-SRCs that were made at the same pressure. The melt flow rate of PLA matrix is increased with the increase of processing temperature to give better matrix penetration. This finding is consistent with the studies of Bárány et *al* [38, 39] who found the consolidation degree of the self-reinforced polypropylene is significantly improved by increasing the processing temperature.
- 4. The effect of changing holding time from 6 min to 10 min on the consolidation degree is not significant for most of the PLA-SRCs.

CHAPTER 7. TENSILE PROPERTIES

7.1. Introduction

According to the comparison between five-stack and four-stack polylactic acid selfreinforced composites (PLA-SRCs) in Chapter 5, the five-stack PLA-SRC shows better fibre wetting and less voids than the four-stack one. Thus, this chapter focuses on the tensile properties of five-stacked PLA-SRC. Mechanical properties of self-reinforced composite are highly influenced by the processing parameters such as temperature, pressure and holding time. The tensile properties and fracture surfaces of PLA-SRCs that were made under various processing conditions will be evaluated in this chapter.

7.2. Test Methods

The specimens were tested using the same method as described in Section 5.2. The tensile properties of twenty-four different PLA-SRCs were tested. For each type of composite, five specimens were tested by Instron 3344 testing rig with a 2 kN load cell at 5 mm/min crosshead rate at room temperature (BS EN ISO 527-5:1997) [162]. The specimen dimension is 15 mm (width) \times 150 mm (initial distance between grips) \times approximate 0.2 mm (thickness). The thickness and width for each specimen was measured and use to calculate the tensile stress individually.

Six tensile properties are analysed. These are tensile modulus, tensile strength, tensile stress and strain at yield, tensile strain at break and toughness. It should be noted that the fibre weight fraction for the five-stack PLA-SRCs is about 45%. The samples are coded in the same way as described in Table 4.3 in Chapter 4.

Toughness, or the strain energy density of a material, is a measure of the energy absorption of the material up to fracture. Toughness can be measured in either dynamic (high strain rate) tests, for example the Charp and Izod impact tests, or in static (low strain rate) tests [142]. In this study, the in-plane toughness of composites is calculated by simply integrating the area of the tensile stress-strain curve up to the fracture point (strain at break).

As described in Chapter 6, the PLA-SRCs failed mainly in three different modes. For most of the specimens that failed in Modes A and B, the tensile stress decreases to zero gradually after the maximum stress. In the case of gradual failure, the breaking point is regarded as the point where the maximum stress occurs. If the maximum stress of the specimen occurs before the composites completely rupture (breaking stress is less than tensile strength), the breaking point is regarded to be where the last peak stress occurred after the maximum stress (rebounded stress). For the specimens that failed in "step" mode (Mode C), the first failure is considered as the breaking point.

7.3. Results

Figures 7.1 - 7.6 illustrate the tensile properties of the different PLA-SRCs. The twenty-four samples are divided into eight groups based on pressure and holding time. The four groups on the left and right are the tensile properties of composites made at 6 min and 10 min holding times, respectively. The processing temperature increases from the low to the high temperature (left to right) in each group. The dash-dot lines in some of the figures refer to the mean of the PLA film. The tensile properties and failure modes for each sample are also summarised in Tables 7.1 and 7.2.

It can be seen from the Figure 7.1 that the average of tensile modulus of the unidirectional PLA-SRCs distributes in the range of 7 GPa up to 8 GPa. Within the high pressure groups (1.5 and 2 MPa), the change of temperature does not affect significantly the tensile modulus. However, in the low pressure groups (0.5 and 1 MPa), the moduli of the mid-temperature and high-temperature composites are higher than those of the low-temperature. This is due to the PLA matrix viscosity is reduced at higher processing temperatures to provide better fibre wetting. Modulus of low-temperature composite in both 6 min and 10 min groups increases with the increase of processing pressure. No significant difference in modulus can be found between 6 min and 10 min processed composites.

After the elastic region, as the strain increases to approximate 1.2%, all the PLA-SRCs yielded at a stress of around 70 MPa. From Figures 8.2 and 8.3, no clear trend of tensile stress and strain at yield can be found. However, tensile stress at yield for the composites made under low pressure and low temperature (low-0.5-6/10 and low-1-6), are significantly lower than those of the mid-temperature and high-temperature samples in the same group.



Figure 7.1 Tensile modulus of PLA-SRCs produced under various conditions



Figure 7.2 Tensile stress at yield of PLA-SRCs produced under various conditions



Figure 7.3 Tensile strain at yield of PLA-SRCs produced under various conditions

After yielding and before the breaking point, the various PLA-SRCs have different tensile behaviours. The matrixes of some samples are broken before the complete failure of the composite. The stress drops considerably when the matrix breaks. However, the PLA fibres still carry the load; and the maximum tensile stress is achieved when the stress reaches the limit of the PLA fibre. This tensile behaviour is typical for samples that failed in Mode A. It can be seen from Tables 7.1 and 7.2, that only the composites made under low pressure and low temperature (low-0.5/1 MPa-6/10) failed in Mode A. This is because the matrix is not sufficiently molten to give good fibre wetting at low processing temperature; in addition, the low pressure cannot assist the matrix penetrate into the fibre bundle. Moreover, from the data in Tables 7.1 and 7.2 (underlined), tensile stresses at break of the low-0.5/1-6 and low-1-10 samples are lower than their tensile strength. This reveals that after the tensile stress reaches the tensile strength, it increases to the second peak stress resulting by the rest of the specimens.

It is apparent from Figure 7.4 that the tensile strength of the low-temperature composite increases with the increase of processing pressure. A possible explanation for this is that the bonding property at low-temperature is improved, because the consolidation degree is enhanced by raising the processing pressure. This finding corroborates the images of composite cross-section in Chapter 6, where the cross-sectional images of low-temperature composites at higher pressures have fewer voids than that at lower

pressures. Although the matrix was not completely molten at the low temperature, the high pressure forced the matrix to contact with more fibres leading to higher bonding strength. The high pressure could also help the outer layer films to bond with the interleaved film. This reduces matrix delamination. However, local delamination is present around the cracks of some specimens. In addition, in the group of high pressure samples (1.5 and 2 MPa), the mid and high-temperature samples failed at lower stress compared to the low-temperature. This result may be explained by the significant fibre relaxation at high temperature.



Figure 7.4 Tensile strength of PLA-SRCs produced under various conditions

Figure 7.5 shows the tensile strain at break of PLA-SRCs. It is clear from this figure that there is no significant difference between the samples made at different temperatures in the 0.5 MPa groups. However, the strains at break of the high-temperature samples are significantly lower than those of the low/mid-temperature in the higher pressure groups. The mean of the strain at break decreases as the temperature increases in the 1.5/2 MPa-6/10 groups. The high breaking strain of low-temperature samples may be caused by the high strain of the PLA fibre since the PLA fibre carries the load after matrix breaking. No clear effect on the tensile strain at break by the holding time can be found.



Figure 7.5 Tensile strain at break of PLA-SRCs produced under various conditions

The toughness obtained by integrating the area of stress-strain curve of PLA-SRCs is presented in Figure 7.6. It is apparent that the toughness of PLA-SRC is significantly enhanced by reducing the processing temperature when the composites were produced at 1.5 and 2 MPa pressures. However, no clear trend of toughness can be found in low pressure groups. With the increase of pressure, the toughness of low-temperature samples increases in both 6 min and 10 min holding time groups. Similar results to the other tensile properties can be found, the change in holding time does not significantly influence the toughness of PLA-SRC.

Comparing the PLA-SRCs and the pure PLA film, all the PLA-SRCs have considerably higher tensile properties. The tensile modulus of PLA-SRC (6.8 - 8.2 GPa) is more than five times higher than that of the PLA matrix (1.4 GPa). The tensile strength and toughness of the PLA-SRCs are approximate 2-3 times higher than those of the matrix. The strain at break of PLA-SRC (21- 32%) is also significantly higher than that of the matrix (15-21%).

The failure modes of PLA-SRCs are shown in Tables 7.1 and 7.2. With the increase of processing temperature while the pressure and holding time remain constant, the failure mode is changed from Mode A to Mode C. However, as the pressure increases to 1.5 and 2 MPa, the failure mode of low-temperature composites turn into Mode B, because

the high pressure improves the consolidation degree. All the high-temperature composites failed in Mode C which has relatively shorter fibre pull out and no delamination. This is because the PLA matrix can melt sufficiently when the processing temperature reaches 150°C which is higher than the upper melting temperature of the PLA film. Thus, even at low pressures, the matrix still has the capability to provide good fibre wetting. No obvious delamination can be found in any of the specimens that failed in either Mode B or Mode C.



Figure 7.6 Toughness of PLA-SRCs produced under various conditions

In Mode C failure, samples were ruptured gradually in a "step" mode. As a result there is a strain difference between the first stress decreases (composite partly rupture) and the final stress decreases to nearly zero (completely rupture). As shown in Tables 7.1 and 7.2, the strain difference between the first and complete rupture of the Mode C failed composites is up to 7%. Besides, after the first tensile stress drop, the remaining part of the composite can still carry up to 80% of the maximum load. Therefore, in practical applications, the PLA-SRCs with this failure behaviour can provide early rupture warning for material replacement or repair. It is not taken into account in the toughness.

Table 7.1 Tensile property features summary of PLA-SRCs produced at holding time of 6 min

Sample code	Tensile Modulus (GPa)	Tensile stress at yield (MPa)	Tensile strain at yield (%)	Tensile strength (MPa)	Tensile stress at break (MPa)	Tensile Strain at break (%)	Toughness (MPa)	Failure mode (strain difference between
								first and complete rupture)
Low-0.5-6	6.78	64.76	1.21	80.31	<u>79.16</u>	25.37	17.58	A
	±0.15	±0.99	±0.02	±8.47	<u>±9.48</u>	±3.86	±3.38	
CV%	1.82	1.23	1.50	8.49	9.64	12.26	15.47	
Mid-0.5-6	8.16	75.41	1.21	107.39	107.39	28.57	24.41	B & C
	±0.26	±2.33	±0.01	±6.38	±6.38	±1.33	±1.66	(≤
CV%	2.57	2.48	0.58	4.79	4.79	3.76	5.43	2.9%)
High-0.5-6	7.29	71.00	1.30	98.77	98.77	28.49	22.41	C
	±0.26	±1.46	±0.07	±6.60	±6.60	±3.64	±3.44	(≤
CV%	2.87	1.66	4.39	5.38	5.38	10.31	12.35	7.1%)
Low-1-6	7.07	69.30	1.30	106.36	<u>104.12</u>	28.86	23.53	А
	±0.17	±0.73	±0.05	±2.51	<u>±5.35</u>	±0.72	±0.66	
CV%	1.93	3.51	2.85	1.90	4.14	2.01	2.26	
Mid-1-6	7.87	76.46	1.24	99.86	99.86	28.86	24.02	В
	±0.15	±1.49	±0.03	±5.40	±5.40	±0.70	±1.24	
CV%	1.53	1.57	2.17	4.35	4.35	1.96	4.17	
High-1-6	7.65	76.88	1.34	97.35	97.35	23.94	19.83	B & C
	±0.20	±1.80	±0.03	±2.93	±2.93	±3.60	±3.28	(≤
CV%	2.05	1.89	1.95	2.42	2.42	12.12	13.32	1.8%)
Low-1.5-6	7.59	74.26	1.30	117.73	117.73	29.41	26.11	A & B
	±0.25	±2.27	±0.04	±8.71	±8.71	±1.70	±2.65	
CV%	2.70	2.47	2.59	5.96	5.96	4.66	8.18	
Mid-1.5-6	7.54	71.73	1.25	87.63	87.63	27.66	22.38	B & C
	±0.11	±1.52	±0.05	±5.11	±5.11	±2.04	±4.22	(≤
CV%	1.17	1.71	3.05	4.69	4.69	5.93	15.20	2.8%)
High-1.5-6	7.56	70.92	1.23	90.95	90.95	26.93	20.38	С
	±0.10	±1.54	±0.05	±4.21	±4.21	±1.36	±1.27	(≤
CV%	1.08	1.74	3.41	3.73	3.73	4.06	5.01	3.6%)
Low-2-6	7.45	74.93	1.32	117.63	117.63	29.56	26.11	В
	±0.31	±2.29	±0.03	±3.42	±3.42	±1.27	±1.02	
CV%	3.16	2.46	1.73	2.34	2.34	3.46	3.16	
Mid-2-6	7.47	72.89	1.28	90.62	90.62	26.01	20.38	В
	±0.22	±2.03	±0.04	±6.42	±6.42	±3.05	±3.04	
CV%	2.38	2.24	2.48	5.71	5.71	9.46	12.00	
High-2-6	7.47	73.82	1.29	84.81	84.81	21.20	15.93	С
	±0.21	±4.46	±0.06	±4.73	±4.73	±2.71	±2.14	(≤
CV%	2.26	4.87	3.63	4.49	4.49	10.28	10.81	4.3%)

Table 7.2 Tensile property features summary of PLA-SRCs produced at holding time of 10 min

Sample	Tensile	Tensile	Tensile	Tensile	Tensile	Tensile	Toughness	Failure
code	Modulus	stress at	strain at	strength	stress at	Strain at	(MPa)	mode
	(GPa)	yield	yield (%)	(MPa)	break	break (%)		(strain difference
		(MPa)			(MPa)			between first
								and complete rupture)
Low-0.5-10	7.00	67.75	1.26	84.49	84.49	28.02	20.36	А
	±0.17	±0.84	±0.04	±3.28	±3.28	±0.75	±1.05	
CV%	1.90	1.00	2.49	3.13	3.13	2.17	4.17	
Mid-0.5-10	7.25	69.52	1.25	82.82	82.82	26.45	19.28	В
	±0.10	±1.63	±0.03	±8.10	±8.10	±4.33	±3.83	
CV%	1.11	1.89	2.12	7.88	7.88	13.19	16.02	
High-0.5-10	7.08	72.48	1.34	92.43	92.43	25.33	19.39	С
	±0.15	±1.05	±0.05	±5.92	±5.92	±2.65	±553	(≤6.6%)
CV%	1.65	1.17	2.76	5.16	5.16	8.43	10.51	
Low-1-10	6.98	70.16	1.28	89.68	<u>89.43</u>	25.91	19.84	А
	±0.18	±1.99	±0.02	±4.44	<u>±4.77</u>	±1.32	±1.21	
CV%	2.1	2.28	1.46	3.98	4.30	4.10	4.90	
Mid-1-10	7.34	70.51	1.25	83.67	83.67	27.74	20.47	В
	±0.12	±1.61	±0.02	±5.17	±5.17	±1.83	±1.96	
CV%	1.33	1.84	1.18	4.97	4.97	5.31	7.71	
High-1-10	7.44	72.08	1.24	83.76	83.76	22.53	16.50	С
	±0.13	±1.26	±0.06	±2.98	±2.98	±3.45	±2.85	(≤ 5.5%)
CV%	1.35	1.41	3.99	2.87	2.87	12.35	13.92	
Low-1.5-10	7.29	71.40	1.26	114.39	114.39	31.29	26.51	A & B
	±0.07	±0.63	±0.03	±1.89	±1.89	±0.70	±0.91	
CV%	0.74	0.71	1.77	1.33	1.33	1.81	2.75	
Mid-1.5-10	7.58	69.17	1.16	88.17	88.17	28.12	21.12	В
	±0.09	±0.4	±0.01	±3.62	±3.62	±1.49	±1.09	
CV%	0.92	0.47	0.98	3.31	3.31	4.26	4.17	
High-1.5-10	7.51	73.53	1.29	90.17	90.17	26.60	20.40	С
	±0.19	±1.49	±0.06	±6.78	±6.78	±2.25	±2.49	(≤4.5%)
CV%	2.00	1.63	3.4	6.06	6.06	6.80	9.82	
Low-2-10	7.27	70.86	1.27	117.02	117.02	31.74	27.26	В
	±0.11	±1.39	±0.04	±4.24	±4.24	±1.13	±1.75	
CV%	1.24	1.58	2.63	2.92	2.92	2.88	5.15	
Mid-2-10	7.45	69.89	1.21	85.34	85.34	27.79	20.33	B & C
	±0.16	±0.49	±0.04	±5.18	±5.18	±1.54	±1.65	(≤ 1.9%)
CV%	1.71	0.57	2.55	4.88	4.88	4.46	6.52	
High-2-10	7.77	72.56	1.20	84.33	84.33	25.74	19.08	С
	±0.24	±1.40	±0.05	±4.91	±4.91	±2.42	±2.43	(≤2.9%)
CV%	2.46	1.55	3.12	4.69	4.69	7.56	10.25	

7.4. Fracture Surfaces of the PLA-SRCs

The PLA-SRCs usually failed in three modes, depending on the various processing parameters. The three failure modes were described in Chapter 5. The SEM images of samples showing the three failure modes are presented in this section. All the samples were gold coated and examined by Quata 200 SEM.

7.4.1. Tensile failure mode A

As shown in Tables 7.1 and 7.2, the tensile failure Mode A is common for the PLA-SRCs that were produced at low-temperature and/or low pressure. A large area of matrix delamination was found in most of the composites. Figures 7.7 (a)–(d) show the inner surface of the delaminated PLA matrix. There are many fibre grooves caused by the pulled-out fibres. However, clear micro-cracks can be found only at a high magnification (×12000), as shown in Figure 7.7 (d). Moreover, Figures 7.7 (e) and (f) demonstrate clear pulled-out fibre surfaces; no fibril and matrix residuals can be seen. It indicates poor bonding properties of these PLA-SRCs.



e fFigure 7.7 SEM fracture surfaces of Mode A failed PLA-SRCs: (a-d) inner surface of the matrix; (d) enlarged view of (c); (e-f) clean surface of pulled-out PLA fibres; (f) enlarged view of (e)

7.4.2. Tensile failure mode B

From Tables 7.1 and 7.2, it can be seen that most of the mid-temperature and some of the low-1.5/2 MPa specimens failed by Mode B. Local matrix delamination can be found at the regions where large cracks are present. The SEM images of the inner and outer surfaces of a delaminated film are shown in Figure 7.8. Large numbers of transverse cracks were found on the film at a low magnifications (×80 and ×120), Figures 8.8 (a) and (b). The enlarged images, Figures 7.8 (c) and (d), also show many micro-cracks and crazes across the pulled-out fibre grooves. The fibrillated inner matrix surface is observed from Figures 7.8 (c) and (d). Similarly, Figure 7.9 illustrates obvious fibrils and matrix residuals on the pulled-out fibre surfaces.



Figure 7.8 Delaminated matrix film of PLA-SRCs failed in Mode B: (a) cracks on inner surfaces of delaminated film; (b) outer surface of delaminated film; (c) & (d) fibrils, micro-cracks and crazes on the inner surface.



Figure 7.9 Pulled-out PLA fibre surfaces of PLA-SRCs failed in Mode B: (a)-(d) fibrils and matrix residuals on fibre surface; (d) enlarged view of (c)

The fracture surfaces of Mode B failed composites are shown in Figure 7.10. Extremely long pulled-out fibres are shown in Figure 7.10 (a). The three layers of film matrix are distinguishable and separated from the fibre layers, Figure 7.10 (b). However, large amounts of fibrils can be seen from the surface of the matrix, as shown in Figures 7.10 (d) and (f). Conversely, Mode A failed composites, in Figure 7.7, display much cleaner fracture surfaces. Therefore, the fibrillated fracture surface and matrix residuals in failure Mode B indicate that the composites have better bonding between fibre and matrix.



e fFigure 7.10 SEM fracture surface in axial direction of PLA-SRCs failed in Mode B: (a) extensive pulled-out fibres; (b)-(d) fracture surface of interleaved film matrix; (d) enlarged view of (c); (e)-(f) fibrillated matrix surface of outer film matrix; (f) enlarged view of (e)

7.4.3. Tensile failure mode C

It is apparent from Tables 7.1 and 7.2 that all the high-temperature PLA-SRCs failed in Mode C. The fracture surfaces of the PLA-SRCs that failed in Mode C are shown in Figures 7.11-7.13. The pulled-out fibres in Figures 7.11 (a) and 7.12 (a) are significantly shorter than those in Figure 7.10 (a), because Mode C failed composites have better interfacial bonding than Mode B failed ones. Figures 7.11 (b) - (d) also show the fibrillated fibre surfaces at the fibre root region. It can be seen from Figures 7.11 (e) and (f) that two fibres are separated on the top and bottom sides, while bonded together in the middle part. This may be due to the fibre surface partial melting in the high-temperature composites.

The fracture surfaces in Figures 7.12 (a) and (b) illustrate that the interleaved film is bonded with the outer film. In addition, the axial direction fracture surfaces in Figures 7.12 (c) and (d) show the interleaved film do not separate from the fibre layers either. A great number of matrix residuals and fibrils can also be found on the fibre surfaces in Figures 7.12 (c) and (d). In contrast, the interleaved film in Mode B failed PLA-SRCs, as shown in Figure 7.10 (b), is separated from the outer films and the fibre layers. This finding indicates that better fibre wetting and stronger interfacial bonding are achieved in the composites with Mode C failure.



e f Figure 7.11 Fracture surfaces of composites failed in Mode C: (a) long pull-out fibres; (b) fibrillated fibre surface; (c) & (d) enlarged the views of (b); (e) bonding between two partial melted fibres; (f) enlarge view of (e)



Figure 7.12 Fracture surfaces of composites failed in Mode C: (a) cross-section of composite fracture surface; (b) enlarged view of (a); (c) composite fracture surface in axial direction; (d) enlarged view of (e)

A more interesting result, as shown in Figure 7.13, is that fan-shaped regions with equal width can be found around the fibre grooves on the matrix fracture surface of the composites that failed in Mode C. A possible explanation of this might be that the fan-shaped regions are the thick interface regions that formed by PLA polymer nucleation on the interface. The matrix fibrils at the fan-shaped regions indicate that strong interfacial bonding could result in matrix plastic deformation surrounding the fibres. Similar to Mode B, a large amount of micro-cracks and crazes are present on the matrix of Mode C failed PLA-SRCs, as shown in Figure 7.14. Unlike in Mode B, no delaminated film matrix can be found in Mode C. In Figures 7.14 (c) and (d), although the matrix is cracked, it is still bonded with the fibres.



Figure 7.13 Fracture surfaces of composites failed in Mode C: (a) fan-shaped interface region; (b)-(d) enlarge views of (a)


Figure 7.14 Matrix fracure surface of composite failed in Mode C: (a) large amount of matrix micro-cracks; (b) enlarged view of (a); (c) matrix crazes and embedde fibres; (d) enlarged view of (c)

7.5. Discussion

The tensile properties of the PLA-SRCs that were produced at different processing temperatures, pressures and holding times are evaluated in this chapter. The tensile properties are highly dependent on the bonding between fibre and matrix. High consolidation degree can result in large fibre/matrix contact area (i.e. fibre wetting). Fibre wetting can be improved by reducing matrix viscosity using higher temperature, higher processing pressure and longer holding time. However, raising the processing temperature to close to the melting point of the fibre and using long holding time will increase the risk of fibre polymer relaxation and thermal degradation. Very high pressure may also damage the composite structure. Several studies reported that optimal properties are determined by two competing processes, the fibre annealing process and the growth of interfacial transcrystalline [31, 34, 38, 39]. Polymer annealing can result in oriented polymer molecular relaxation at high processing temperatures so that the 145

tensile properties decrease. The growth of transcrystalline at the interface can provide strong fibre and matrix bonding. The high chemical similarity between fibre and matrix in a self-reinforced composite is also beneficial to the growth of the transcrystalline [22, 29, 30].

The tensile results of the PLA-SRCs indicate that the processing temperature considerably affects the tensile properties after yielding (strength and strain at break); whereas the tensile properties before yielding (modulus, stress and strain at yield) are only influenced by the temperature when the composites were made at low pressures (0.5 and 1 MPa). The processing pressure has a significant effect on the tensile properties of the low temperature made PLA-SRCs. This is because the fibre wetting of the low-temperature composites can be improved by increasing the pressure. The matrix with high melt viscosity can be forced to penetrate into the fibre bundles. However, the effect on tensile properties by changing pressure is insignificant at high processing temperature, as matrix melt viscosity is low. These results corroborate the findings of the effects on composite morphologies by changing the processing parameters in Chapter 6.

Furthermore, there is no obvious effect on tensile properties by changing the holding time from 6 min to 10 min. This finding corroborates the results of fibre relaxation (Section 3.6), which shows insignificant differences of fibre shrinkage after undergoing the heating treatments at two the different holding times. It is also consistent with Bárányetal's study [39], where they found the processing temperature is a more controlled parameter than the holding time for self-reinforced polypropylene when the processing pressure is constant.

The SEM images of the fracture surfaces of the three tensile failure modes indicate that the composites that were made under different conditions have distinctive bonding properties. Most of the low-temperature and/or low pressure composites failed in Mode A, with obvious matrix delamination and clean pulled-out fibre. Both failure Modes B and C show massive micro-cracks on the matrix. This is because the PLA matrix has lower failure strain than the PLA fibre, with the increasing of the tensile strain, the matrix starts to craze, and the crazes then propagate to form cracks. As the matrix cracking continues, the load is transferred to the fibres progressively through the interface because of the better bonding in the composites produced at high and mid temperatures. In contrast, due to the poor interfacial bonding in Mode A failed composites, the stress tends to break the interface between fibre and matrix first, rather than develop the cracks in the matrix. Thus, no obvious micro-crack can be found on the matrix of these composites. However, the shorter pulled-out fibres and sufficient matrix penetration in the Mode C failure composites (high-temperature composites) indicate stronger bonding compared to composites with Mode B and Mode A failures. Furthermore, since the high processing temperature is close to the onset melting temperature of the PLA, fibre partial melting can be found from SEM images of high-temperature composites. The fibre partial melting at high processing temperature could also bring about strong bonding between PLA fibre and matrix.

Very few studies have been done on self-reinforced PLA composites. In Li and Yao's [57] study, PLA-SRCs that contain 50 wt% fabric and 25 wt% yarns as reinforcements were produced by the nucleation method. Comparing the tensile properties of the PLA-SRCs in this study to those reported by Li and Yao, most of the PLA-SRCs (equivalent fibre wt%) in the current study show higher or similar tensile modulus and tensile strength, while the strain at break is more than five times higher .

In summary, higher tensile modulus can be achieved when the PLA-SRCs are made at high pressure and/or high temperature; the tensile strength and toughness of the composites that were produced at low temperature but high pressures (1.5 and 2 MPa) are much higher than the others. The superior tensile properties of the PLA-SRC compared to the pure PLA film indicate that the tensile properties of PLA plastic can be significantly enhanced by embedding high crystalline PLA fibre into amorphous PLA films to form a single polymer composite.

CHAPTER 8. FLEXURAL PROPERTIES

8.1. Introduction

This chapter describes the principle and testing method for flexural properties of PLA self-reinforced composites (PLA-SRCs). A three-point long beam loading system was employed to estimate the flexural modulus and strength of the composites. The results and discussions will focus on flexural modulus, flexural strength, deflection at flexural strength and flexural failure modes.

8.2. Determination of Flexural Properties

A flexural (bending) test is used to measure the flexural stress-strain behaviour until fracture of a rectangular or circular cross-sectional beam occurs. The beam is subjected to loads applied transverse to the long dimension [165]. The three-point loading method is one of the most common bending tests for fibre-reinforced polymer composite materials. As shown in Figure 8.1, a specimen is freely supported by two spans (rollers or pins) and deflected at a constant speed by a loading nose (mid-span) until rupture occurs at the outer surface [166, 167]. The force applied by the top roller (F) and resulting deflection (s) are measured during the test for flexural stress and strain calculations.

Figure 8.2 shows three typical flexural stress-strain curves. Curve A shows a specimen that breaks before yielding. In this case, the flexural stress (σ_{fB}) and strain at break (ε_{fB}) are equal to the flexural strength (the flexural stress at maximum load, σ_{fM}) and strain at flexural strength (ε_{fM}), respectively. Curve B shows a specimen that breaks after yielding. In this case, $\varepsilon_{fB} < \varepsilon_{fM}$. Curve C shows a specimen that has the flexural strength at ε_{fM} but no fracture is detected [166, 167]. In the British standard (BS EN ISO 14125:1998), flexural modulus (E_f) is defined as the ratio of the stress difference ($\sigma_f'' - \sigma_f'$) divided by the corresponding strain difference ($\varepsilon_f'' - \varepsilon_f'$)in the initial linear portion of the curve. Since the PLA-SRCs in this study are hot-pressed composite sheets (around 0.2 mm thickness), the following description is mainly based on the rectangular cross-sectional long-beam method.



Figure 8.1 Three-point loading scheme



Figure 8.2 Typical flexural stress-strain curves[166]

When a bending load is applied to a beam, the top surface of beam is in a compression state, while the bottom surface is in a tension state [142]. Figure 8.3 shows a segment of the beam of Figure 8.1. It is assumed that there is a neutral plane (x) at distance c above the bottom surface of the beam that has no change in length [165]. All elements above the neutral plane are compressed, while those below it are extended. As shown in Figure 8.3, all the curvatures have the same angle θ but different radius. Assuming plane x' is at distance y below the neutral plane x, the strain ε for plane x can be expressed as:

$$\varepsilon_f = \frac{x'-x}{x} = \frac{\theta(r+y)-\theta r}{\theta r} = \frac{y}{r}.$$
 (8.1)

To obtain the strain of the outer surface of the beam, y is half of the thickness, say h/2; thus

$$\varepsilon_f = \frac{h}{2r} \tag{8.2}$$

It can be seen from Figure 8.1 that, the flexural moment of the beam, M, is equal to

$$M = \frac{FL}{4},\tag{8.3}$$

and flexural stress of the outer surface of the beam, σ_f , is equal to

$$\sigma_f = \frac{Mc}{I} = E_f * \varepsilon_f \quad , \tag{8.4}$$

where *c* is the distance from the neutral plan to the outer surface, here c=h/2, E_f is the flexural modulus of the beam, *I* is moment of inertia of a rectangular cross section, can be expressed as

$$I = \frac{bh^3}{12} \quad (b \text{ is the width of the beam}) [142]. \tag{8.5}$$

By substituting Equation (8.3) and (8.5) into (8.4), the flexural stress of a beam with rectangular cross section is

$$\sigma_f = \frac{3FL}{2bh^2} \tag{8.6}$$

The displacement of the beam (s) is given as

$$s = \frac{FL^3}{48 E_f I} [165]. \tag{8.7}$$

Substituting Equation (8.3) into (8.4),

$$E_f = \frac{FLh}{8I\varepsilon_f}.$$
(8.8)

Combing Equation (8.7) and (8.8), the strain of the outer surface of the beam can be expressed as:

$$\varepsilon_f = \frac{6sh}{L^2}.$$
(8.9)

Therefore, the flexural stress (σ_f) and strain (ε_f) can be calculated by using Equation (8.6) and (8.9), based on the recorded load (*F*) and deflection (*s*) as well as the known parameters, including specimen thickness (*h*), width (*b*) and distance between two spans (*L*).



Figure 8.3 A segment of the beam

8.3. Three Point Flexural Test Method

There are two commonly used standards for testing flexural properties of polymer matrix composites, which are British standard (BS EN ISO 14125:2011) and ASTM international standard (ASTM D7264). Six basic failure modes are described in BS EN ISO 14125:2011, as shown in Figure 8.4 [166]; the interlaminar shear fracture is not acceptable. ASTM D7264 defines the failure mode of local buckling on the compression surface, which is not described in ISO 14125:2011. The local buckling can be fibre micro-buckling or ply-level buckling, which may lead to or occur prior to delamination of the outer ply [168].

A short-beam method is recommended for specimens that fail by interlaminar shear stress and reported in British standard (BS EN ISO 14130:1998) [169]. The long- or short- beam flexural test is classified by the ratio of span distance to the specimen thickness (L/h). The British standard 14130:1998 specifies L/h is 5:1, while the thickness of PLA-SRC is only about 0.2 mm, which is too short for the short-beam method in this study.

The three-point long-beam flexural tests were performed by a Zwick / Roell Z2.5 test frame at a constant crosshead speed of 2 mm/min and using a 25 N load cell. Since the specimens have the thicknesses (h) of about 0.2 mm, the outer span (L) of 8 mm is used to provide a support span-to-thickness ratio (L/h) of 40:1. Figure 8.5 illustrates that the PLA-SRC is supported by two spans. Twenty-four PLA-SRC samples which were made at different processing parameters were tested. The samples are coded in the same way as described in Table 4.3. Five specimens (dimension: 20 mm × 15 mm × thickness) were tested for each type of composite. The length direction of specimens coincides with fibre orientation. For composites with high variations, the number of test specimens was increased to 10.



Tensile fracture of fibre



Compressive fracture





Tensile fracture (including interlaminar shear)

Compressive fracture (including interlaminar shear)



Interlaminar shear fracture

Figure 8.4 Examples of possible three-point bending failure modes [166]



Figure 8.5 Composite specimen undergoing long-beam flexural test

In this study, flexural test results focus on the flexural modulus, strength and deflection at flexural strength. Since a large bending deflection (s > 0.1 L) is obtained, the following equations for flexural stress and strain are applied to correct the calculation results [166].

$$\sigma = \frac{3FL}{2bh^2} \left\{ 1 + 6\left(\frac{s}{L}\right)^2 - 3\left(\frac{sh}{L^2}\right) \right\}$$
(8.10)

$$\varepsilon = \frac{h}{L} \left\{ 6\frac{s}{L} - 24.37 \left(\frac{s}{L}\right)^3 + 62.17 \left(\frac{s}{L}\right)^5 - \mu (2\frac{s}{L} - \frac{h}{L}) \right\}$$
(8.11)

where μ is an effective coefficient of friction between specimen and span.

The coefficient of static friction, μ , is equal to the tangent of the angle of friction, $tan(\theta)$. The angle θ is determined by the height (l_1) and the side length (l_2) of a right triangle, in 152 which the object starts sliding, see Figure 8.6. The coefficient of friction between the span and the PLA-SRC was measured using the following method. The span metal bar (object) was placed on the top of a PLA-SRC covered metal plate. l_1 is gradually increased until the span metal bar started sliding. Tan (θ) is calculated by the measured l_1 and l_2 . Five tests were carried out to obtain the average of μ , which is about 0.48.



Figure 8.6 Angle of friction θ



Figure 8.7 Typical force-deflection flexural curve with toe region[168]

Furthermore, in ASTM D7264 and BS EN ISO 14125 standards the flexural modules can be given by Chord modulus with strain ranges of 0.001 - 0.003 and 0.0005 - 0.0025, respectively. A toe region, see AC in Figure 8.7, which is usually a result of take-up slack and alignment or seating of the specimen, can be found in a typical force-deflection curve; thus it does not represent the property of the material [168]. However, the suggested strain ranges in both of the ASTM and British standard locate in the toe region of the force-deflection curve of the PLA reinforced composite specimens in this study. Hence, flexural modulus in this chapter is obtained by applying linear regression to the initial linear part of the curve. The strain range for linear regression is selected by dividing the region from the start point to the highest stress point or yielding point into

6 equal regions [144]. The modulus is determined by the region which has the steepest slope [144].

8.4. Flexural Failure Modes

Because the processing conditions of the PLA-SRCs affect the fibre wetting and bonding property, these PLA-SRCs failed in different flexural modes. From the direct observations of the tested specimens and the load-deflection and stress-strain curves of the PLA-SRCs, the failures can be classified into three modes. The typical stress-strain and load-deflection curves of the three failure modes are shown in Figure 8.8. The failure modes for all the composite samples will be taken into account in the results and discussion section.



Figure 8.8 Typical load-deflection (a) and stress-strain (b) curves of three flexural failure modes

a) Mode A: centre local plastic deformation

It can be seen from Figure 8.8 that the Mode A curve (black) has an apparent plastic deformation region after the elastic region. The local plastic deformation of the specimen occurs at mid-span position. No delamination or crack can be found on the specimen. As shown in Figure 8.9, an obvious "white mark" can be observed in the centre of the specimen. The "white mark" may be caused by polymer crazing, which is very localised plastic deformation and common fracture behaviour for some thermoplastic polymers.



Figure 8.9 The specimen before testing (a) and flexural tested specimen that failure in Mode A(b)

b) Mode B: Top layer buckling near support span with centre plastic deformation

From the Mode B curve (red) in Figure 8.8, the plastic deformation starts after elastic deformation; and as the strain increases, the flexural stress drops suddenly, where a crack occurs. In Mode B, one or more buckling cracks can be found on the top layer of the composite and near the support span position. The crack may propagate throughout the entire width of the specimen or stop propagating in the middle; it may also locate on one or both sides of the midspan, see Figure 8.10. The SEM images of the buckling cracks on the top surface of the specimens are shown in Figure 8.11. These SEM images indicate that the buckling cracks consist of many micro-cracks and local plastic deformation. No obvious matrix break can be found.



Figure 8.10 Flexural tested specimens that fail in Mode B, a) crack throughout the specimen width; b) crack stop propagating on the half-way; c) & d) two cracks appear on both side of the mid-span



Figure 8.11 SEM images of buckling cracks:(a & c)top matrix plastic deformation; (b & d) enlarged views of the plastic deformation and the micro-cracks

a) Mode C: delamination near support span

In mode C, obvious delamination occurs near the support span region, as shown in Figure 8.12; the centre plastic deformation can also be found in some specimens. This failure mode can also be considered as pre-mature failure due to the poor bonding between fibre and matrix. It can be seen from the Mode C curve (blue) in Figure 8.8 that the flexural stress dropped at small flexural strain while delamination occur.



Figure 8.12 Flexural tested specimens failed in Mode C

Figure 8.13 shows the cross-section of the buckling region of the specimen that failed in Mode B. It indicates that buckling occurs at the top layer of the matrix. The top film matrix only debonds with the interleaved film matrix, while the bottom matrix and interleaved matrix are still bonded. On the other hand, Figure 8.14 shows the cross-section of the delimitation region of the spacemen that failed in Mode C. In Figure 8.14 the interleaved film is delaminated from both the top and bottom film matrixes. Comparing Figure 8.13 and Figure 8.14, much more fibres are debonded with the PLA matrix in the latter. It reveals that better fibre and matrix bonding is achieved in the PLA-SRC with flexural failure Mode B.



Figure 8.13 Cross-section SEM image of buckling failure specimen (Mode B)



Figure 8.14 Cross-section SEM image of specimen delamination (Mode C)

8.5. Results

Figures 8.15 - 8.17 show flexural modulus, strength and deflection at the flexural strength of the 24 PLA-SRCs. The 24 samples are divided into eight groups of three samples each. Each group was made at the same processing pressure and time, but different temperatures. In the figures, the four groups on the left half and right half are the samples made at holding times of 6 min and 10 min, respectively. For the four groups in each half of the figure, the pressure is increased from 0.5 to 2 MPa from the left to the. The flexural properties of the PLA-SRCs are summarised in Tables 8.1 and 8.2.



Figure 8.15 Flexural modulus of PLA-SRCs produced at various processing parameters

As shown in Figure 8.15, the flexural modulus of PLA-SRCs distributes in the range from 5 GPa to 7.5 GPa. It is apparent that the means of flexural modulus of the PLA-SRCs is increasing with the increase of the processing temperature (low, mid and hightemperature) in the group of composites that were made under same processing pressure and time. However, the moduli of the mid-temperature composites show no significant difference from those of low-temperature and high-temperature; only flexural modulus of the high-temperature composites is significantly higher than that of the lowtemperature. This indicates that the temperature differences between mid-temperature and low/high-temperature are too small to have significant effect on flexural modulus, while the big temperature difference between low-temperature and high-temperature composites gives notable effects on the flexural modulus. It can also be seen from Figure 8.15 that there is no obvious effect on flexural modulus by processing pressure and time.



Figure 8.16 Flexural strength of PLA-SRCs produced at various processing parameters

Figure 8.16 compares the flexural strengths of the PLA-SRCs. It is clear from this figure that when the composites were made under 0.5 and 1 MPa pressures, the flexural strengths of high-temperature composites are significantly higher than those of the low-and mid-temperature composites. However, in the sample groups made at higher pressures (1.5 and 2 MPa), the differences in flexural strength between high-temperature composites and low/mid-temperature are insignificant. In addition, the variations of low- and mid-temperature composites are considerably higher than those of the high-temperature. The high variation maybe caused by the imperfections of the composites manufacturing process and voids that are a result of the improper matrix penetration at low pressure and/or low temperature. Furthermore, the average flexural

strengths of low and mid-temperature are enhanced as the pressure increases from 0.5 to 1.5 MPa. No significant difference in flexural strength can be found between the samples that were made at different holding times.



Figure 8.17 Deflections at flexural strength of PLA-SRCs produced at various processing parameters

The deflections at flexural strength of the various PLA-SRCs are shown in Figure 8.17. For composites produced at 0.5 and 1 MPa pressures, the deflections of the high-temperature composites are markedly higher than those of the low- and mid-temperature composites. On the other hand, the effect on deflection by the processing temperature is insignificant when the composites were made at 1.5 and 2 MPa pressures. Furthermore, there is no significant difference in the deflections of the high-temperature composites that were made under various pressures and holding times.

Time		6 min							
Pre	Temp	Flexural	Flexural	Deflection at	Failure mode				
(MPa)		Modulus	strength (MPa)	flexural	A 0/	D 0/	<u>C</u> 9/		
		(GPa)		strength (mm)	A 70	D 70	C 70		
0.5	Low	5.70±0.51	97.64±36.41	1.32 ± 0.45	0	30	70		
	CV%	12.51	52.13	48.26					
	Mid	6.16 ±0.58	91.55 ±25.41	1.14 ±0.3	0	50	50		
	CV%	13.06	38.81	36.43					
	High	6.63 ±0.26	151.95 ± 5.8	1.94 ±0.06	100	0	0		
	CV%	3.14	3.07	2.49					
1	Low	5.88 ±0.30	120.96 ± 19.98	1.48 ±0.33	10	40	50		
	CV%	7.13	23.08	31.48					
	Mid	6.22 ±0.36	106.82 ± 32.00	1.28 ±0.41	10	30	60		
	CV%	8.12	41.87	44.47					
	High	6.42 ±0.335	151.99 ± 2.42	1.98 ±0.04	100	0	0		
	CV%	4.21	2.42	1.77					
1.5	Low	6.16 ±0.23	143.48 ± 21.63	1.71 ±0.41	20	80	0		
	CV%	33.05	12.14	19.43					
	Mid	6.25 ±0.27	154.06 ± 6.33	1.93 ±0.05	40	60	0		
	CV%	3.53	3.31	2.20					
	High	7.17 ±0.46	159.56 ± 8.08	2.02 ±0.09	100	0	0		
	CV%	5.14	4.08	3.77					
2	Low	5.85 ±0.29	148.49 ± 16.33	1.83 ±0.29	40	60	0		
	CV%	4.00	8.85	12.55					
	Mid	5.91 ±0.32	143.72 ± 14.02	1.86 ± 0.30	60	40	0		
	CV%	4.40	7.85	12.87					
	High	6.16 ±0.38	149.58 ± 7.50	1.95 ±0.05	100	0	0		
	CV%	4.90	4.04	2.07					

 Table 8.1 Flexural properties of PLA-SRCs produced at 6 min processing time

It can be seen from the summary of failure modes of the twenty-four PLA-SRCs in Tables 8.1 and 8.2 that Mode A failures increases as the processing temperature increases. All the high-temperature composites failed in Mode A (A% = 100%) while the low- and mid-temperature composites failed in more than one mode. Moreover, in the sample groups that were produced with the same pressure and holding time, the total number of Mode C failures declines as the pressure increases from 0.5 to 2 MPa. It indicates that an increase in processing temperature and pressure can reduce the chance of PLA-SRC buckling and delamination during bending. This is because the matrix penetration is improved, leading to an increase in the bonding area between fibre and matrix as well as a decrease in void content.

Time		10 min							
Pre (MPa)	Temp	Flexural	Flexural	Deflection at	Failure mode		de		
(1 111 a)		(GPa)	strength (MPa)	strength (mm)	A %	<i>B%</i>	С%		
0.5	Low	5.73 ±0.32	85.00 ± 21.78	0.94 ±0.29	0	20	80		
	CV%	7.90	35.81	43.23					
	Mid	6.48 ±0.25	128.65 ± 19.92	1.72 ±0.16	0	100	0		
	CV%	3.27	12.47	7.46					
	High	6.27 ± 0.27	148.12 ± 2.28	2.00 ± 0.06	100	0	0		
	CV%	3.47	1.24	2.46					
1	Low	5.95 ±0.37	107.39 ± 9.22	1.07 ±0.13	0	50	50		
	CV%	8.76	12.00	17.01					
	Mid	6.27 ±0.15	127.81 ±22.39	1.53 ±0.31	10	60	30		
	CV%	3.29	24.49	28.21					
	High	6.66 ± 0.27	158.44 ± 6.15	1.98 ±0.12	100	0	0		
	CV%	3.24	3.13	4.67					
1.5	Low	6.02 ± 0.28	147.37 ± 10.51	1.91 ±0.19	60	40	0		
	CV%	3.78	5.74	7.85					
	Mid	6.44 ± 0.37	151.43 ± 11.46	1.76 ±0.23	20	80	0		
	CV%	4.58	6.09	10.48					
	High	6.90 ± 0.50	157.92 ± 10.72	1.97 ±0.13	100	0	0		
	CV%	5.84	5.47	5.12					
2	Low	6.12 ±0.23	133.64 ±9.10	1.57 ±0.20	0	100	0		
	CV%	2.99	5.48	10.01					
	Mid	6.55 ±0.34	150.18 ±13.88	1.84 ±0.28	40	60	0		
	CV%	4.14	7.44	12.4					
	High	6.93 ±0.40	157.54 ±8.89	1.98 ±0.12	100	0	0		
	CV%	4.68	4.54	4.73					

Table 8.2 Flexural properties of PLA-SRC that were produced under 10 min processing time

8.6. Discussion

The flexural properties of the PLA-SRCs have been reported in this chapter. Three flexural failure modes have been defined: centre plastic deformation (Mode A), top layer matrix buckling with centre plastic deformation (Mode B) and near support span delamination (Mode C).

The results of flexural feature properties in terms of modulus, strength and deflection at strength reveals that the flexural properties of the PLA-SRCs are highly determined by the processing temperature and pressure. At the same pressure, flexural modulus and strength are enhanced by increasing the processing temperature. This finding is in

agreement with Wu *et al.*'s study [170] which showed flexural modulus and strength of a braided single PLA composite increased with the increase of consolidation temperature.

Moreover, in the current study, when PLA-SRC is made at low and middle temperatures, the flexural strength is considerably improved by increasing the pressure. This finding is consistent with Wu *et al.*[170] who also found that the flexural strength improved with the increase of consolidation pressure when the braided PLA-SRC is made at 140 °C.

When the composites were made at low pressure (0.5 and 1 MPa), the flexural strength and deflection of high-temperature composites are significantly higher than those of the low and mid-temperature composites. However, once the pressure increases to 1.5 and 2 MPa, the differences in flexural strength and deflection among the three groups of composites made at various temperatures become insignificant. This finding indicates that the processing temperature is the dominate factor affecting flexural properties of PLA-SRC when the composites are made at low pressure. The holding times does not significantly affect the flexural properties of PLA-SRC.

The results from the flexural stress-strain curves and the flexural failure modes show that the flexural properties of PLA-SRC are depended on the consolidation degree (fibre wetting). The difference in flexural failure mode of the PLA-SRCs indicates that the composite that is made at high temperature has enhanced fibre wetting, which is due to the relatively low matrix melt viscosity. Thus, all the high-temperature composites failed in Mode A. No significant difference in flexural properties can be found between the high-temperature composites made at different pressures. This finding is in agreement with the finding from the cross-sectional images in Chapter 6 which showed no significant effect on consolidation degree of high-temperature composites by processing pressure. The findings for tensile properties of PLA-SRCs are similar. The tensile properties of low temperature made PLA-SRCS are significantly influenced by the processing pressure, while the effect on the tensile properties of the high temperature made composites is insignificant.

High processing pressure could also help the matrix penetration for low-temperature composites, leading to better bonding. Although top layer buckling can still be seen at some of the low-temperature high pressure specimens, their flexural strength is improved with the increase of pressure. However, most of the low-temperature and low

pressure composites failed in Mode C with obvious delamination because the matrix is difficult to penetrate into the core of the fibre layer and bond with the other matrix layer.

CHAPTER 9. BIODEGRADABILITY

9.1. Introduction

PLA is an aliphatic polyester and derived from renewable resources such as starch and sugar. Although PLA cannot be degraded easily in natural environment, it has better biodegradability compared to petro-based polymers and can be degraded in soil by a wide variety microorganisms [86, 171]. The biodegradability of PLA changes depending on the environment. Hydrolysis plays an important role in the degradation of PLA in the natural environment; while PLA tends to have higher degradation rate in the environment where enzymes are present [86, 129, 171]. This chapter focuses on the biodegradability of the PLA self-reinforced composites (PLA-SRCs) in compost soil compared to those of the PLA film and fibre. The biodegradability of these materials will be evaluated by means of measuring weight loss and observing surface morphological changes.

9.2. Method

Soil burial test has been widely employed to evaluate the biodegradability of plastics, because the test condition is similar to the actual environment of use and disposal [86]. In this study, the soil burial test was carried out by burying the PLA film, fibre and composites in flower pots which contain a mixture of compost soil (Miracle-Gro[®] moisture control enriched compost) and vermiculite (Verve[®]) with a maxing ratio 5:1. Vermiculite is a clay mineral that has good capacity for water capacity, and also known to be a microbial carrier, allowing survival and full activity of microbes [172].

The sketch of the burial test is shown in Figure 9.1. The pots were covered by a porous film to keep good ventilation and control moisture loss. A saucer is placed under the pot that has several holes in its bottom. This is used to maintain the moisture content of the compost by keeping certain level of water in the saucer. The samples were buried at a depth of about 10 cm. The moisture content and temperature of the soil were measured regularly. The moisture content was kept to about 80% by regular watering [112, 129]. The pH value of the compost soil was maintained at 7. During the time of the burial test which was 44 weeks, the room temperature varied from 16 - 29 °C.



Figure 9.1 Sketch of the burial test pot

There are 8 sets of specimens for each composite, PLA film and fibre. Each set contains 5 specimens. The dimensions of the PLA film and composite are 1 cm * 1 cm [173]. Figure 9.2 illustrates the labelled PLA samples in the compost soil. The biodegradability of the samples was assessed by measuring the weight loss after burying in the soil.

Weight loss % =
$$\frac{W_o - W_b}{W_o} \times 100$$
 (9.1)

where W_o is the initial mass and W_b is the mass after a certain time of burial.

The buried samples were dug out every 4 or 8 weeks, and washed in distilled water. An ultrasonic bath was used to clean the samples. All the samples were dried in a vacuum oven at 50 °C for 16 hours before measuring the weight.



Figure 9.2 Burial test

9.3. Results

9.3.1. Weight loss

The weight losses of the PLA film, fibre and SRCs that were buried in the compost soil are shown in Figure 9.3. It can be seen that there is no significant change in the weight of the PLA fibre and the PLA-SRCs; while the weight of the PLA film was reduced with time. A possible explanation for this is the biodegradation takes places more easily in the PLA that has low molecular weight and low crystallinity. As has been mentioned in section 3.5.3, the PLA film is amorphous while the PLA yarn is a high crystalline material.



Figure 9.3 Weight loss of samples after burial test

9.3.2. Surface morphologies

Although the weight losses of the samples after buried in the soil are very small, the SEM images of the PLA samples illustrate changes of morphology after burial. The reference SEM images of the PLA film and fibre surface before the burial are shown in Figure 9.4. Since the surface of the PLA composite is covered by PLA film, the SEM images of the PLA film before burial test is also considered as the reference for the composites.

Figure 9.4 shows the smooth surface of the PLA film and fibre before burial. Figures 9.5 - 9.8 indicate that biodegradation occurs randomly on the surface of the PLA film and composite. Erosions are clearly present on the surface of the PLA film after burying in the soil for several weeks, see Figures 9.5 and 9.6. It can be seen from these images that the rough surface and holes produced by biodegradation have random shapes and distribution. This finding is consistent with results from other researchers [108, 112, 174].



c d Figure 9.4 SEM images of PLA film (a) & (b) and fibre (c) & (d) before burial test



e f Figure 9.5 SEM images of PLA film after burial tests for 20 weeks (a) & (b) and 44 weeks (c) - (f) showing the holes and rough surfaces by biodegradation



c figure 9.6 SEM images of PLA film after burial tests for 36 weeks showing the surface erosion by biodegradation

Similar results can be found in the SEM images of the PLA-SRCs after burying in soil for weeks. Figure 9.7 shows that rough areas and the holes appear randomly on the surface of the PLA-SRCs by biodegradation. Figure 9.8 illustrates filamentous microorganisms, which could be fungi and actinomycetes, distributing randomly on the surfaces of the samples.

The morphologies of the PLA fibre after burying in soil are shown in Figure 9.9. Comparing the SEM images of PLA fibre before and after burial, there is no significant change. This may indicate that microbial attacks occur less on the PLA fibre that has high crystallinity.



e fFigure 9.7 SEM images of PLA-SRC after burial tests for 8 weeks (a) & (b) ,16 weeks (c) & (d) and 20 weeks (e) & (f) showing the holes and the rough surface by biodegradation



c Figure 9.8 SEM images of PLA film after burial tests for 28 weeks (a) and (b) and PLA-SRCs after burial tests for 20 weeks (c) and (d)



e f Figure 9.9 SEM images of PLA fibres after burial tests for 20 weeks (a) & (b), 36 weeks (c) & (d) and 44 weeks (e) & (f)

9.4. Discussion

The weight losses of the PLA samples after burying in the compost soil for up to 44 weeks are insignificant. However, by comparing the SEM images of these samples before and after burial, changes in morphologies show that biodegradations do occur on the surfaces of PLA film and composites, but not on the surface of the PLA fibre. This may indicate that the biodegradation rate of PLA is highly depended on the physical and chemical structures [86]. The amorphous material, PLA film, is easier to be degradent by the microorganisms compared to the PLA fibre. In the initial stage of degradation, the hydrolysis usually starts at the amorphous region of PLA, and the crystalline PLA is less susceptible to hydrolysis [134]. This result corroborates the findings in previous research which showed that the crystalline PLA is more resistant to degradation than the amorphous PLA [175-178].

Different biodegradation rates for PLA have been reported. Several studies [95, 112, 129] showed that there is no obvious degradation of PLA films after 6 to 24 weeks in soil. However, the neat PLA was degraded about 10% by weight after 14 weeks in Wu's study [108] and 18% by weight after 18 days in Dong et.al 's study [125]. An explanation for the different PLA biodegradation rates in these studies might be the various burial conditions and the population of PLA degrading microorganisms in the soils that were used in the studies.

A longer burial time of 44 weeks was employed in the current study; however, the biodegradation rate is still very low. This may be because of the low population of PLA degrading microorganisms in soil [86, 179, 180]. However, the molecular weight of the PLA may be degraded by hydrolysis in soil. Hence, the effect of biodegradation on the mechanical properties of PLA-SRCs is worth investigating in future.

The biodegradation rate of PLA can be increased at higher composting temperatures (58 \pm 2°C). Several studies investigated high temperature biodegradation and found that pure PLA loses 80% and 94% of its weight at 30 days and 90 days, respectively [113, 130]. Enzymes also play an important role in the biodegradation of PLA polymer [86, 171]. Ohkita and Lee [129] reported that the weight loss percentage of pure PLA was degraded to 0 % after a 10 day enzyme test. Further research on the biodegradability of PLA-SRCs by enzyme test is recommended.

CHAPTER 10. CONCLUSIONS

10.1. Summary of the Findings

This study aimed to design and manufacture biodegradable PLA fibre reinforced composites (PLA-SRCs) that have the advantages of both biodegradable polymer and self-reinforced composite, such as excellent biodegradability and recyclability, and strong interfacial bonding to offer good mechanical properties.

A highly crystalline PLA fibre and an amorphous PLA film were employed as reinforcement and matrix to form the PLA self-reinforced composite (PLA-SRC). The processing temperature window, which is the difference in melting temperature between fibre and matrix, was defined by DSC. Based on the findings from the feasibility study, the study focused on the development of unidirectional PLA-SRCs. The filament winding followed by hot-pressing method was employed to produce the composites. A manual winding machine and a hot-pressing mould were designed and built up to achieve good fibre alignment and even yarn tension. Moreover, the optimisation of the PLA-SRC properties by varying the processing temperature, pressure and holding time was carried out. The main conclusions of this project summarised below.

10.1.1. Comparison between five-stack and four-stack PLA-SRCs

The tensile properties of five-stack and four-stack structure composites were significantly affected by the processing temperature. Tensile strength and strain at break of the five-stack composites decrease with the increase of processing temperature; on the other hand, tensile modulus and stress at yield peak at the processing temperature of 148°C. However, no trend on the tensile properties of four-stack composites by processing temperature can be found. Furthermore, there is no significant difference in the peeling strength between the five-stack and four-stack composites but the incomplete peeling-out and the cohesive fracture surface of the five-stack composites indicate that a better interfacial bonding is achieved in the five-stack composite. Hence, by comparing the properties of five-stack and four-stack PLA-SRCs, it is found that the addition of an interleaved film in the five-stack composites improves the bonding properties and reduces delamination.

10.1.2. PLA-SRC process optimisation

10.1.2.1. Effects on composite morphology

The consolidation degree (fibre wetting) of the PLA-SRCs was evaluated by examining the cross-sectional images. The consolidation degree of the low and mid-temperature composites is improved significantly with the increase of the processing pressure. The consolidation degree of high-temperature composites is significantly higher than that of the low and mid-temperature samples that were made at the same pressure. The low molten viscosity of the PLA at high temperature helps the PLA matrix easily penetrate the fibre bundle, even at low pressure. There is no significant effect on the consolidation degree by the holding time.

10.1.2.2. Effects on mechanical properties

The tensile properties of PLA plastic are significantly enhanced by the addition of the high crystalline PLA fibre into the amorphous PLA film to create the PLA self-reinforced composite. The tensile properties of PLA-SRC after yielding (tensile strength and strain at break) are affected significantly by the processing temperature; the before-yielding tensile properties (tensile modulus, strain and stress at yield) are influenced by the temperature only when the PLA-SRCs were made at low pressures (0.5 and 1 MPa). The processing pressure only influences the tensile properties of the low-temperature composites. However, no significant effect on the tensile properties can be found by the processing holding time.

Furthermore, three different tensile failure modes were defined. Most of the composites made at low processing temperature and/or low pressure failed in Mode A with a large area of matrix delamination due to poor interfacial bonding. The composites that have stronger interfacial bonding failed in Mode B with long pulled-out fibres and local matrix debonding. For failure Mode C, there is no obvious debonding or matrix delamination. The composites start to fail with axial splitting which breaks the matrix and the pulled-out fibres in Mode C are shorter than those in Mode B.

The flexural strength and modulus of the PLA-SRCs produced at the same pressure are improved significantly by increasing the processing temperature. The flexural strength of low and mid-temperature composites is significantly enhanced by increasing the pressure. The processing temperature is also the dominating factor affecting flexural properties of the PLA-SRCs when they are made at low pressure; the differences in flexural strength and deflection are insignificant among the three groups of composites made at various temperatures and at high pressure (1.5 and 2 MPa). There is no significant effect on the flexural properties caused by the holding time.

The flexural failure of PLA-SRCs were classified into three modes, which are centre local plastic deformation (Mode A), top layer buckling near support span with centre plastic deformation (Mode B) and delamination near support span (Mode C). Flexural failure Mode A is common for composites that have strong interfacial bonding, such as the composites made at high processing temperatures. However, most of the low temperature and low pressure made composites fail in Mode C with obvious delamination due to the poor matrix penetration. Mode B failed composites show stronger bonding compared to Mode C failed composites.

Mechanical property evolutions have shown that the tensile and flexural properties are highly depended on the consolidation degree of the composite. At high processing temperature, the melt matrix viscosity becomes lower and provides enhanced fibre wetting. Thus, the high-temperature composites have stronger interfacial bonding. Moreover, the processing pressure has a significant effect on the mechanical properties of the PLA-SRCs when they are made at a low processing temperature. This is because high pressure can improve the matrix penetration at low processing temperature, leading to better bonding.

10.1.2.3. Effects on biodegradability

The weight losses of the PLA samples after the burial trials are insignificant. However, the changes in morphologies after burial indicate that biodegradation do happen on the surfaces of the PLA film and composites, but no obvious change on the PLA fibre. This is because the amorphous PLA film is more easily degraded by the microorganisms compared to the crystalline PLA fibre.

10.1.3. A comparison of mechanical properties in other composites

The PLA self-reinforced composite in this study combines the concept of the selfreinforced composite with biodegradable fibre to obtain the advantages from both. Unidirectional PLA-SRCs have also shown enhanced mechanical properties compared with the PLA film. Figure 10.1 compares the tensile modulus, tensile strength and flexural strength of PLA-SRC to the PP and PE self-reinforced composites (PP-SRC
and PE-SRC), as well as common natural fibre reinforced PLA biodegradable composites, such as PLA-flax and PLA-sisal composites. It is worth noting that the composites in Figure 10.1 have similar fibre content, around 40-50%. It can be seen that PE-SRC is the strongest composite among these five materials; it has a longitudinal modulus of 25-35 GPa and a strength of 850-1000 MPa, which are much higher than those of PLA-SRC (tensile modulus of 7-8 GPa and tensile strength of 80-120 MPa) [181]. However, the tensile modulus of PLA-SRC is higher than that of PP-SRC, but lower than the other natural fibre composites. The tensile and flexural strength of PLA-SRC are higher than those of PP-SRC and PLA-flax, although flax and PP fibre normally have higher strength than PLA fibre.



Figure 10.1 Comparison of some mechanical properties of the self-reinforced and natural fibre reinforced composites [90, 98, 107, 181]

10.2. Potential Applications

PLA based materials have been widely used in a various fields, including biomedical materials, packaging, tableware and textiles. The PLA self-reinforced composite in the current project not only keeps the good biodegradability but also improves the mechanical properties of the PLA plastic and provides the benefit of being easy to recycle which is a big challenge for reinforced composites. Based on the features of the PLA-SRC, the following are some potential applications.

Disposable products normally require short shelf life, low environmental impact and low price, because a large amount of these products are disposed of daily to the environment. PLA-SRC is a non-toxic material and has good biodegradability and recyclability; thus, it is suitable for food packaging and other disposable products. Improved tensile and flexural properties of the PLA-SRC also make the composite potential raw material for heavy-duty carrier bags for bulk vegetables, rice, and etc. The carrier bag could be one- or multi-use. Moreover, PLA-SRC can be used for compostable garden bag and bin liner to encourage composting programmes and reduce the impact on the environment.

The unidirectional PLA-SRC in this study is thin and flexible, and has fairly good tensile properties in the fibre direction. Hence, it can potentially be utilised as a strip band in an automatic strapping machine[182]. Applications of PLA-SRC also could be developed in the automobile industry for products such as spare tyre covers, car interior trim, etc.

The PLA-SRC can be used for horticultural products, such as a matrix for controlled release of herbicides and pesticide, sandbags, weed prevention nets, and vegetation ports. Horticultural applications usually require that the material maintains its structural properties when in use, but decomposes into the soil after end-use[182]. Napoothiri et al. [183] also reported the advantages of using a PLA made encapsulation matrix for herbicides. The advantages include low environmental impact, good weed control and increased soybeans growth [183].

10.3. Recommendations for Future Work

It is recommended that further research be undertaken in the following area.

- One of the advantages of a self-reinforced composite is the excellent recyclability after the end-use. To fully recycle thermoplastic polymer based composites, the composites need to be heated up to a temperature that is higher than the melting temperature of the fibre and matrix. However, polymer degradation may occur. Mechanical tests, such as tensile and flexural tests, for the PLA polymer made from recycled PLA-SRCs are suggested for future work.
- In this study, the tensile and flexural properties have been evaluated. Other mechanical properties, such as tearing resistance, impact resistance, can also be assessed in order to expand the potential applications of the PLA-SRC. For example, the evaluation of the abrasion resistance and surface toughness of the PLA-SRC are suggested to further prove the feasibility of the application as strip band. Moreover, dynamic mechanical analysis can also suggest be carried out to evaluate storage modulus, damping properties, etc..
- The winding machine used in this project is capable of producing bi-directional (BD) composites with various fibre contents and fibre layer arrangements at 90°

and 0° . However, the mechanical properties of the BD composite have not been evaluated. These can be tested as part of any future work.

- The PLA-SRCs that were made at high processing temperature show stronger interfacial bonding compared to the low and middle temperature made composites. Some studies indicated that partial melting of the fibre could improve the bonding property. A processing temperature that is much closer or higher than the onset melting temperature of the fibre can be tried to evaluate this concept.
- The biodegradability tests in this study show insignificant weight losses of the PLA samples after burying in the compost soil for 44 weeks. Modifications of the burial test can be made in order to increase the biodegradation rate of the samples. The modifications can include longer burial time, higher and controlled burial temperature, and increased population of the PLA degrading microorganisms in the soil. An enzyme test is also suggested for future work.
- The biodegradability of the PLA sample was assessed by measuring the weight loss and examining the sample surface morphologies. However, the change in molecular weight and mechanical properties after the burial test could also be examined in future.
- The consolidation degree of the PLA-SRC was evaluated by studying the polished composite cross-sections. However, only limited areas of the cross-section have been examined. An X-ray tomography scanner could be utilised to obtain more details about the void content as well as the matrix and fibre distributions.
- Because the PLA-SRC in this study is very thin (about 0.2 mm thickness), it not only brought many difficulties during manufacturing and testing, but also restricted the applications in fields that require thicker composites. PLA-SRCs with greater thickness could be developed in future.

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APPENDIX A

One-way Analysis of variance (ANOVA)

Analysis of variance (ANOVA) is one of the statistical techniques to analyse whether or not significant differences between the means of normal distributed groups exist. ANOVA is based on F-test to compare the ratio of variances between groups and within groups (F_{cal}) with a critical F-value (F_{crit}), which is determined by the significance level (α) and the within-group and between-group degrees of freedom (dof). That is to say, if

$$F_{cal} = \frac{variance\ between\ groups}{varance\ within\ groups} = \frac{mean\ square\ between\ groups\ (MS_b)}{mean\ square\ within\ groups\ (MS_w)} < F_{crit}, \qquad A.1$$

there is no significant difference between groups, vice versa.

One-way ANOVA is used to estimate the differences between the groups where only one factor affects the data In order to estimate the differences between the groups, the following calculations should be done. The basic one-way ANOVA values are summarised in Table A.0.1.

• Overall mean:
$$\overline{Y} = \frac{\sum_{j=1}^{n} (\overline{Y}_j)}{J}$$
 A.2

,where J is the set number of the groups

• Sum of square between groups:

$$SS_b = \sum_{j=1}^n (\bar{Y}_j - \bar{Y})^2 = (\bar{Y}_1 - \bar{Y})^2 + (\bar{Y}_2 - \bar{Y})^2 + \dots + (\bar{Y}_j - \bar{Y})^2$$
A.3

Sum of square within groups:

$$SS_w = \sum_{j,i=1}^n (Y_{ji} - \overline{Y}_j)^2 = (Y_{11} - \overline{Y}_1)^2 + (Y_{12} - \overline{Y}_1)^2 + \dots + (Y_{j(i-1)} - \overline{Y}_j)^2 + (Y_{ji} - A.4)$$

,wherei is the number of data in each group

- Mean square between groups: $MS_b = \frac{SS_b}{dof_b} = \frac{\sum_{j=1}^n (\bar{Y}_j \bar{Y})^2}{J-1}$ A.5
 - Mean square within groups: $MS_w = \frac{SS_w}{dof_w} = \frac{\sum_{j,l=1}^n (Y_{jl} \overline{Y}_j)^2}{J(l-1)}$ A.6
- Calculated F-value: $F_{cal} = \frac{MS_b}{MS_w}$ A.7
- Looking up the critical F-value from the F-test table: $F_{crit:(J-1),J(I-1),\alpha=0.05}$

Source of variation	Sum of square (SS)	Degree of freedom (dof)	Mean square (MS)	Calculated F value (F _{cal})
Between groups	$SS_b = \sum_{j=1}^n (\overline{Y}_j - \overline{Y})^2$	J – 1	$MS_b = \frac{SS_b}{J-1}$	$F_{cal} = \frac{MS_b}{MS_w}$
Within groups	$SS_w = \sum_{j,i=1}^n (Y_{ji} - \overline{Y}_j)^2$	<i>J</i> (<i>l</i> – 1)	$MS_w = \frac{SS_w}{J(I-1)}$	n/a
Total	$SS_t = SS_b + SS_w$	JI – 1	n/a	n/a

 Table A.0.1 Summary one-way ANOVA table