

UNIVERSITY OF ONTARIO INSTITUTE OF TECHNOLOGY

CHARACTERIZATION OF NATURAL FIBRE REINFORCED  
BIODEGRADABLE COMPOSITES

By

MARYAM TALIMI

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES  
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE  
DEGREE OF MASTER OF APPLIED SCIENCE

DEPARTMENT OF MECHANICAL ENGINEERING

OSHAWA, ONTARIO

AUGUST, 2011

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UNIVERSITY OF ONTARIO INSTITUTE OF TECHNOLOGY  
FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the faculty of Graduate studies for acceptance, a thesis entitled “CHARACTERIZATION OF LIGHTWEIGHT, BIODEGRADABLE NATURAL FIBRE-REINFORCEMENT REINFORCED COMPOSITES” submitted by MARYAM TALIMI in partial fulfilment of the requirements of the degree of Master of Applied Science.

---

*Supervisor, Dr. Ghaus Rizvi*

*Department of Mechanical Engineering*

---

*Examiner, Dr. Hossam Kishawy*

*Department of Mechanical Engineering*

---

*Examiner, Dr. Remon Pop-Iliev*

*Department of Mechanical Engineering*

---

*Examiner, Dr. Liliana Trevani*

*Faculty of Science*

*Date: 5<sup>th</sup>, August 2011*

---

## **ABSTRACT**

Low cost, light weight, recyclability, and high specific strength of natural fibres make them a good replacement for synthetic fibre such as glass in fibre reinforced plastics (FRP). Green and ecofriendly source of these fibres offer less reliance on oil sources. However, their moisture uptake ability, low thermal stability and quality variations are some disadvantages that restrict their use.

Biodegradable polymers or biopolymers such as polylactic acid polymers (PLA) are polyesters of lactic acid, and originally made from renewable agricultural raw materials e.g. corn starch. Development of new composite products from the existing renewable resources has a strong potential to bring a new biodegradable composite material suitable for the automotive and packaging industry to replace non-renewable petroleum based plastics. These biodegradable composites could degrade completely in soil or by composting process and do not emit any toxic or harmful components.

The purpose of this work is to investigate the effects of increasing natural fibre content, and also adding Biomax modifier on the mechanical properties of poly lactic acid. PLA was reinforced with two different kinds of sustainable natural fibres, cotton, and jute fibres respectively. Biomax strong 120 was used as modifier for PLA/natural fibre composites in order to improve the impact strength and toughness properties. Mixtures of different fibre mass proportions as reinforcement, and PLA as a base resin with modifier additive were compounded in a twin-screw extruder. The extruded materials were processed in a novel compression moulding system to produce test samples. Composites without any modifier content were also produced under the same conditions and used as reference materials.

Addition of plant fibres to the PLA reduces the composites flexural strength, while improves the elastic modulus significantly, compared to neat PLA. PLA 3001D based composites containing 40% jute fibre exhibited the highest stiffness (5.9 GPa) amongst the composites. Investigation of the impact properties of the composites showed that increasing fibre mass proportion leads to an increase in the impact strength of the composites. The impact strength of the PLA/cotton composite is more promising than PLA/Jute composites. The most significant result is that addition of even 3% Biomax Strong 120 had a positive effect on the impact properties of the specimens.

Analysis of the rheological properties of the composites demonstrates that the cotton fibre reinforced PLA has higher complex viscosity than Jute fibre reinforced PLA composites. The DSC results explain that the crystallization temperature increases with increasing the jute fibre content. Furthermore composite's microstructure was monitored using Scanning Electron Microscope (SEM). A better adhesion between the cotton fibres and the PLA matrix than jute fibres and PLA was observed in the SEM images.

## **Acknowledgements**

I am heartily thankful to my supervisor, Dr. Ghaus Rizvi, whose encouragement, guidance and support from the initial to the final level enabled me to develop an understanding of the subject. This work was supported by Auto 21 and collaborated with the researchers from University of Toronto, Ontario. I also thank Dr. Chul Park and Dr. Hani Naguib for their support and advice during the project. I am thankful to Mr. Shiang Law have helped me through the experiments at University of Toronto.

My parents deserve special mention for their inseparable support and prayers. Words fail me to express my appreciation to my husband, Reza, whose dedication, love and persistent confidence in me, has taken the load off my shoulder. Lastly, I offer my regards and blessings to all of my colleagues in UOIT who supported me in many respect during the project.

Maryam Talimi

August 2011

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# **CHAPTER 1: INTRODUCTION**

## **1.1 OVERVIEW**

### **1.1.1 COMPOSITES**

Composites contain two (or more) different phases or components, which have totally different properties from the individual constituents. Generally, a stiff, and strong reinforcement (filler), surrounded in a continuous matrix make a manmade composite. The matrix is usually weaker and more compliant than the reinforcement fibres. The matrix mainly transmits shear stresses at the interface to the reinforcement. In addition, matrix protects the reinforcement from environmental damages and chemical attacks. The coupling between reinforcements and matrix provides the structure with higher stiffness and strength depending upon the fibres [1].

Generally, fibre reinforced plastics (FRP) are stiff, and have high strength. Their properties can be optimized by gaining more alignment of the fibres (esp. continuous) along the load paths. These are the reasons that make composites a successful material for several applications [2].

### **1.1.2 BIOCOSITES**

Bio-composites are composite materials consisting of one or more constituent(s) formed from a renewable resource. The reinforcement could be selected from natural plant fibres such as flax, cotton, kenaf, hemp, jute, and so on. Bio-fibres derived from waste papers, or recycled wood, and also by-products from food crops are in the category of wooden fibres. This definition contains regenerated cellulose fibres such as viscose and rayon as well, because they are also derived from biological origins similar to natural nano fibrils of chitin and cellulose.

Matrices commonly used with natural fibres at the present time are fossil-derived polymers (also called synthetic). Examples of these matrices are thermoplastic polymers such as polypropylene (PP), polyethylene (PE), polystyrene (PS), and polyvinyl chloride (PVC), and thermosets polymers, such as, phenolics, epoxies, isocyanates and unsaturated polyesters. In biocomposites, the ideal matrices are of renewable origin such as from starches, and vegetable oils [1].

After a significant growth in usage of glass fibre reinforced fossil fuel based matrices in the past 80 years, in different applications such as thermal insulation, and in aerospace, many industries became more interested in using bio-composites. Some of the reasons were increased health and environmental concerns, and requirement of lighter materials in order to reduce energy consumption. That was the point where wood plastic composites came to the market. Compared to inorganic reinforcements in thermoplastics, light weight, reduced abrasion of processing equipment and renewability can be counted as advantages of the wood fibre. Use of wood fibre, as reinforcement helps to reduce raw material costs, while improving stiffness and dimensional stability. In addition to reinforcement, matrix phases can also be derived from

renewable resources, hence the sustainability issues related with using synthetic materials in composites can be addressed [1].

### **1.1.2.1 REINFORCEMENT/FILLER**

Strength and stiffness properties of fibres make them suitable materials for reinforcement in fibre-reinforced composite materials. Generally composite properties are governed by the inherent properties of the reinforcement fibres in them.

Comparing stiffness, specific tensile strength, elongation at break of natural fibres with synthetic fibres, makes natural fibres (such as hemp and flax [1]) potential substituent for E-glass fibres. Because of the great importance of E-glass fibres in composite industry, it can be considered as reference reinforcement [1].

The use of natural fibres to reinforce thermoplastics such as polypropylene and polyethylene as an alternative to synthetic or glass fibres has been and continues to be the subject of research and development. The potential advantages of using natural fibres have been well documented and are generally based on environmental friendliness as well as health and safety factors [3]. There are 3 different kind of natural fibres; vegetable, mineral, and animal fibres. Vegetable fibres can be subdivided into wood and non-wood fibres. Based on the origin of non-wood fibres in the plant, they can be classified into leaf, bast, and seed hair fibres. On the other hand subdivision of wood fibres is between softwood and hardwood fibres [1]. All kind of vegetable fibres, (wood or non-wood), however, consist of three major cell wall polymers: lignin, cellulose, and matrix polysaccharides. Cellulose and lignin are embedded into pectins and hemicelluloses (as matrix polysaccharides). Beside these main components, there are a few non-structural components, such as inorganic salts, waxes, and nitrogenous materials [1].

Generally, vegetable fibres' structure can be considered as miniature composites containing millions of fibrous units referred as microfibrils. The microfibril in turn can also be considered as a composite material, in which, the matrix is composed mostly of hemicellulose, lignin, and other polysaccharides, while the fibre component in this form is crystalline cellulose. Fibres with more cellulose substance and high degree of polymerisation display higher tensile strength and also higher modulus of elasticity. The choice of suitable reinforcing fibres from a variety of natural fibres is based on the required stiffness and tensile strength of a composite. Additional criteria for the selection of suitable fibres are thermal property, elongation at break, required adhesion between fibres and matrix, dynamic and long-term performance, price and manufacturing costs.

#### **1.1.2.2 MATRIX**

The fibres in a fibre-reinforced composite are held together by the matrix. Applied forces to the composite, are transferred to the fibres via matrix. Another important function of matrix is to protect fibres from mechanical and environmental damage. In traditional composites, the matrix mainly consists of either a thermoset or thermoplastic polymer. Examples of thermosets and thermoplastics are unsaturated polyester, and polyethylene (PE), respectively.

The bio-composites manufacturers demand that the matrix mainly be prepared from renewable origins, even though the current biopolymer technologies show that synthetic thermoset and thermoplastic polymers dominate commercial bio-composite fabrication. Consequently polypropylene (PP) and polyethylene (PE) are extensively used in wood-plastic composites (WPCs). However, bio-composites based WPC, are now receiving a considerable amount of interest and are in widespread commercial production, especially in North America. Till now large group of thermoplastic biopolymers that have been used mainly for the packaging

industry do not meet the material properties' requirements for other fibre reinforced composites. Their properties such as high processing viscosity and the overly high elongation at failure are harmful for many applications. There is significant need for development of thermoset polymers from renewable origins due to the limitations of thermoplastics. Thermosetting resins derived from vegetable oils have been employed as the building blocks and are usually modified in order to produce cross-linkable molecules, examples being maleates, epoxides, isocyanates or aldehydes. At present, cross-linking of the mentioned monomers is possible only with usage of petrochemical reagents such as polyols isocyanates, phenols, amines and polycarboxylic acids. The ultimate goal is to make best use of renewable resources while achieving the needed material properties. Promising thermosets in bio-polymer industry are derived from by vegetable oils and can be used for coating and thermosetting applications. Even though there are plenty of potential thermoplastic biopolymers derived from natural resources such as starch, polylactic acid, natural rubber, polyhydroxy alkanates<sup>48</sup> and proteins from grains, the majority of large commercial production of thermoplastic biopolymers relies on the development phase with only Cargill's NatureWorks PLA and Novamont's Mater-Bi starch-based thermoplastics [1]. Particularly, two of the main bio-degradable polymers seem attractive for commercial production. These bio-polymers are poly (lactic acid) (PLA) and poly (butylene succinate) (PBS).

PLA is brittle polymer, in other words it has high strength and low elongation at failure [4]. Although mechanical properties of PLA are similar to those of polyethylene terephthalate (PETE), it benefits from lower processing temperature requirements.

PBS, on the other hand, has a melting temperature of about 90–120 °C (similar to LDPE). It is a white crystalline thermoplastic with glass transition point of about -45 to -10 °C (between

PE and PP). The tensile strength of PBS is between PE and PP, and its stiffness properties lie between that of LDPE and HDPE. Potentially excellent PBS processing can be done on polyolefin processing machines at temperatures between 160 °C and 200 °C. The processing outcome can be various products, such as extruded, injection moulded, and blow moulded parts. In addition to these characteristics, availability of its raw materials (butanediol and succinic acid) from bio-based natural resources will be possible in near future [4].

New opportunities are created because of advances in science and technology. Some of these opportunities are in respect to solving specific environmental problems, such as biodegradability, recyclability, and eco-friendliness. Achieving these solutions will help us to save and protect our environment. More recently, in order to find some alternatives to the petroleum based polymeric composites, materials derived from the renewable natural fibres and biodegradable matrices have been developed to be used in packaging applications and automotive industries [5].

Several biopolymers are already being commercially produced in the market, even though they are not intended for regular plastic production. Although there are only a small proportion of the produced biopolymers used in the plastic industry, it would considerably decrease our dependence on materials derived from non-renewable resources. Some examples of available biopolymer resources are as follows:

- Cellulose is the most abundant carbohydrate in the world.
- Starch is found in some plants such as corn, potatoes, wheat, and tapioca. It is mostly used for non-food purposes, like making paper, and cardboard.

- Collagen is the most plentiful protein found in mammals. Gelatin is made from collagen, and has some applications such as sausage casings, and capsules for drugs
- Casein is mainly produced from cow's skimmed milk, and is used in adhesives, protective coatings, etc.

*Poly Lactic acid(PLA)*

PLA is a thermoplastic bio-polymer of lactic acid derived from renewable resources, such as sugarcane, corn starch, or tapioca. The methods of production are either ring-opening polymerisation of the cyclic lactide dimer, or by direct gradual polycondensation of the cyclic lactide dimer. The latter process may lead to low-molecular weight PLA materials. The problem can be solved by some specific procedures. In order to attain higher molecular weight PLA, some developments on polymerization have been done in the industrial scale. These advances make PLA a promising potential for structural materials with sufficient life span and compostability. They also keep mechanical properties at high level, while avoiding rapid hydrolysis even under humid conditions [4].

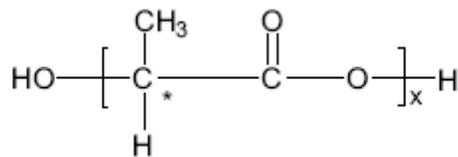


Figure 1. Poly Lactic Acid (PLA) Monomer.

Currently there is a large-scale PLA production facility in North America by Cargill Dow LLC, a joint venture between Cargill Corporation and Dow. The production of PLA in this plant is based on use of corn starch as the resource with an annual production capacity of 140,000 metric tons. Some other manufacturers also supply PLA.

One of the specific conditions which lead PLA to degrade is the presence of oxygen. The degradation of PLA in a nitrogen atmosphere takes place at around 375°C [6].

### **1.1.2.3 ADDITIVE/IMPACT MODIFIER**

PLA is inherently a very stiff and brittle material. A previous study has shown a significant improvement of mechanical properties and processability of the PLA composites by adding plasticizer to PLA [7].

Biomax strong 120 is a petroleum-based ethylene acrylate copolymer. This material acts as an impact modifier for PLA composites, and also has good compatibility with PLA [8]. Few studies show that 1 to 4% loading of biomax strong reduces extruder drive power, melt temperature, while increases energy efficiency. It is also shown that addition of only 1-2% of this modifier considerably increases the toughness [8]. Biomax strong benefits are as following:

- Increase toughness
- Reduce brittleness
- Enhance Flexibility
- Improve impact strength
- Improve viscosity stability
- Improves machine ability and cutting
- Shows good contact clarity

### **1.1.3 ADVANTAGES OF BIO-COMPOSITES**

There are some attractive properties of PLA, which make it a potential future material for commercial packaging applications. Examples being are its production from renewable resources, its good mechanical characteristics, and the capability of recycling or composting of

the material. Incineration and land-filling are the existing methods of disposal for these polymers. The composting process efficiently closes the disposal loop by returning the materials to the soil, the place in which biodegradation takes place [3].

The other features such as greater environmental concerns, public awareness and the reduction of petrochemical based polymers provide a driving force to the growth of new products derived from natural fibre and biopolymer resources. Establishment of laws by governments in some countries encourages people in use of products which are recyclable and/or biodegradable (known as 'green' products).

#### **1.1.4 APPLICATIONS OF BIODEGRADABLE COMPOSITES**

Until the last decade, factors such as high cost, low availability and limited molecular weight had restricted the uses of PLA to medical applications. Some of the examples include surgical implant devices, tissue culture, internal sutures, wound closure, and controlled release systems. Recently, development of new techniques allowed cost-effective production of high molecular weight PLA polymer, hence its application have broadened. Low toxicity, along with its environmentally friendly characteristics of PLA, made it a suitable material for applications like food packaging and other consumer products. The other examples of conventional products which are made by PLA are thermoformed cups, and containers, support trays, electrical/electronic applications (such as housing for laptop computers), candy wrap, optically enhanced films, shrink labels, and various food packaging products [9].

The renewable composites are now attracting applications in a wide range of industries such as automotive, medicine, packaging, Examples of applications of biodegradable composites include the mobile phone and computer cases, casings for monitors.

### 1.1.5 MECHANICAL PROPERTIES OF BIO-COMPOSITES

Combination of many factors has an effect on the composite properties. The mechanical properties of reinforced plastics vary with the kind, shape, relative volume, and orientation of the reinforcing material, and the length of the fibres. Generally, however, the composite properties are derived from the intrinsic properties of the components. How these features help to improve the composite material's properties is mainly governed by factors such as the fibre architecture and the fibre–matrix interface [1].

- Fibre architecture

Fibre architecture covers fibre geometry, fibre orientation, packing arrangement and fibre volume fraction. Many composite properties, particularly mechanical properties can be controlled by these factors. The most important factor is fibre volume fraction ( $V_f$ ), because a large number of the mechanical properties increase with increasing volume fraction up to a certain value. However, this maximum achievable point is affected by other factors like orientation and packing arrangement of the fibres. Ultimately the adopted manufacturing process controls the maximum reachable  $V_f$ .

The plant fibres' geometry is governed by the morphology of the fibre tissue. Extraction and processing of the fibres influence the fibre geometry. The ratio of fibre length to diameter is called as aspect ratio, meaning that long and thin fibres have high aspect ratio, while low aspect ratio corresponds to the shorter and thicker fibres. Generally speaking higher aspect ratios lead to greater reinforcing efficiency. However, it is difficult to retain the fibre aspect ratio during composite processing and manufacturing.

Separation of individual bast fibre at micro-scale, improves the aspect ratio, and consequently enhances the interface between fibre and matrix. Using this process some of the inherent defects of the aggregate fibres are eliminated, and hence up to 50% improvement is achievable.

Another method to improve the performance of bast fibres through manipulating fibre architecture is to align the reinforcing fibre within the matrix. By getting more alignment, the enhancement of packing arrangement leads to higher  $V_f$  and therefore better performance of the reinforcement [1].

- The fibre–matrix interface

The other important factor in the composite performance is the fibre/matrix interface. The externally applied force transfers to the fibres through the shear stresses over the interface. Controlling the ‘strength’ of the interface is imperative. In order to sufficiently transfer stresses to the fibres, good bonding of fibre and matrix is essential. Toughness is another significant mechanical property. It is the ability of an engineering material to resist crack growth, and failure. Propagation of crack occurs in composites because of their heterogeneous structure. Different toughening processes get activated through breaking down the interfacial adhesion under certain conditions. There are various energy absorption mechanisms such as the frictional sliding of debonded fibre fragments within the matrix, fibre fracture and also formation of new crack surfaces [1].

Natural fibres and large number of matrix polymers are generally incompatible. Knowing that, researchers are frequently exploring for methods to improve the adhesion between fibre and

matrix. Some of the many approaches are chemical treatment of the fibre prior to processing and finding compatibilising agents which are included in the composite mix during processing[1].

#### **1.1.6 METHODS TO ENHANCE BIOCOMPOSITE PERFORMANCE**

As already discussed, the composite properties are ultimately affected by the properties of the components. Therefore, the first step in finding a composite with the desired properties for the intended purpose is to select the reinforcing fibres and matrix polymers carefully. Although one should keep in mind that the bio-composite properties may be also influenced and indeed improved by any change in fibre architecture and the fibre and matrix interface. To some level these factors are controlled by the adopted processing technique. The processing method affects the improvement of performance [1].

#### **1.1.7 CHALLENGES AND UNKNOWNNS**

At present, the PLA price relative to the other thermoplastics and its brittle property, especially in thicker materials are barrier to wider application of its composites. In this respect, a recent paper questioned biodegradable composites by stating that considering the overall energy costs; these polymers are not really green as are usually assumed [3]. However, in respect to the development for commercial purposes, PLA is still in its infancy and significant progress in overcoming these drawbacks might be expected in the near future [3].

Furthermore, there are some challenges to the use of natural fibres as reinforcement in composites. These include their moisture uptake and their vulnerability to thermal degradation, if processing temperatures are higher than 200 °C. Introducing some international standards and production methods of natural fibres in order to have consistent materials throughout the year, will help in adoption of natural fibres as polymer reinforcement [3].

## **1.2 OBJECTIVES**

The development of a low cost, light weight, biodegradable natural fibres reinforced composites and novel processing methodology for producing these form the long term objective of the research project. This will lead industries such as the automotive industry to greener environment by decreasing CO<sub>2</sub> emission and offering less reliance on foreign oil sources. This thesis is concerned only with natural fibres (Jute, and Cotton), and biodegradable polymers (PLA 2002D, and PLA 3001D) derived from renewable raw materials.

The immediate objectives of this thesis are:

- i. Adopt a lab-scale compression moulding system and testing methodology to investigate physical and mechanical properties of bio-composites.
- ii. Design and development of series of experimentation to investigate the effect of reinforcement content on the physical and mechanical properties of biocomposites.
- iii. To investigate the physical and mechanical behaviour of bio-composites in terms of matrix grade and natural fibre type.
- iv. Investigation of effect of bio-max impact modifier on the physical and mechanical properties of bio-composites.

## **1.3 METHODOLOGY**

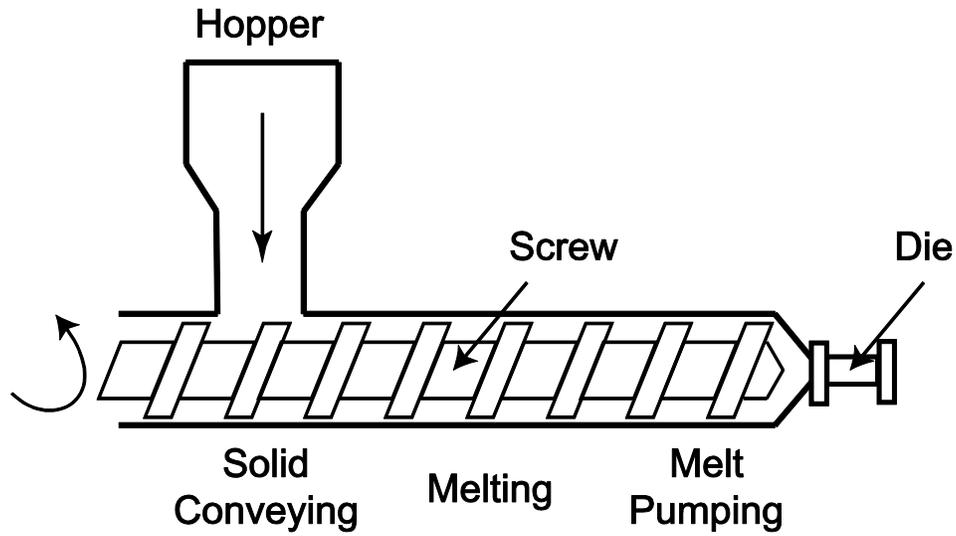
This section describes the manufacturing methodology of bio-composites which includes extrusion, injection moulding, compression moulding. In addition, a review of experimentation methodology for investigation of mechanical and physical properties of bio-composites is also described in this section.

### **1.3.1 MANUFACTURING METHODS**

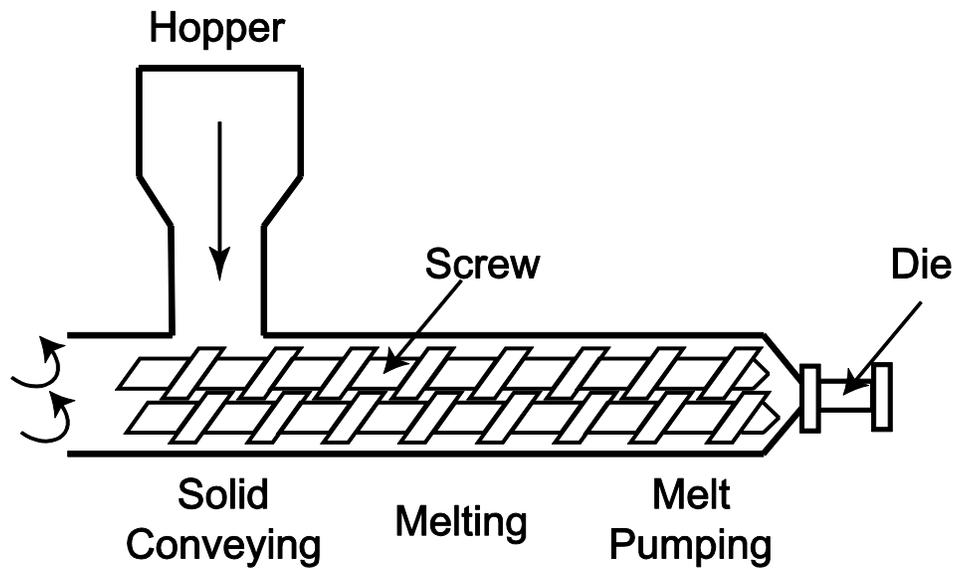
The used techniques to produce biocomposites materials are mostly similar to the existing processing methods for composites or plastics. These manufacturing methods are pultrusion, filament winding, press moulding, hand lay-up, injection moulding, extrusion, compression moulding, resin transfer moulding (RTM) and sheet moulding compounding (SMC). Generally one can say that currently extrusion and injection and compression moulding are the most common processing methods for a large number of biocomposites based on thermoplastics [1].

#### **1.3.1.1 EXTRUSION**

Extrusion is the processing method where polymer (usually in the form of powders or pellets) is continuously fed into a hopper. Following that the material is forced and melted through a metal die by a feedscrew in order to shape a desired form with a fixed cross-section. A motor with a controlled torque and speed is driving the feedscrew. Cooling of the melt right after exiting from the die causes solidification of the material into a continually drawn material. The cross section of the solid piece matches the die form. The die and the feedscrews are designed and made to guarantee that the melt flows in an accurate desired pattern. Extrusion is the most common and important processing method for the production of composites. The ability of creating very complex cross sectioned profiles and also the flexibility to process brittle materials is some of the major advantages of extrusion compared with the other manufacturing methods. Figure 2 shows schematic diagram of a typical single-screw, and twin-screw extruder.



(a)



(b)

Figure 2. Schematics of (a) Single Screw Extruder, and (b) Twin Screw Extruder.

### 1.3.1.2 COMPRESSION MOULDING

Compression moulding is a process that is specifically designed to facilitate the replacement of metal components with polymers (and other composites). Compression moulding is a forming process in which a plastic material is placed directly into an open, heated metal

mould cavity, then is softened by the heat, and forced to conform to the shape of the mould as the mould closes. The mould comprises a matched pair of male and female dies. Curing is performed due to heat and pressure applied to the material. Unlike some of the other processes, the fact that materials are usually measured before moulding prevents the excess flash.

Although today compression moulding is used for thermosets in the most common applications, the process also can be employed with the thermoplastics. There are various types of reinforcements which can be used in advanced composite thermoplastics. Some of these reinforcements are unidirectional tapes, woven fabrics, randomly oriented fibre mat, or chopped strands. Thermoplastic resins may be loaded into the mould either in the form of pellets or sheet, or the mould may be loaded from a plasticizing extruder. Thermoplastic materials are heated above their melting points, formed and cooled. For both thermosets and thermoplastics, the better the feed material is distributed over the mould surface, the less flow orientation occurs during the compression step.

Compression moulding is a good method to make complex, and high-strength parts. It is also a high-pressure plastic moulding method that is suitable for manufacturing high volume of objects. The process offers so many advantages over the other manufacturing processes, which makes it the best method to produce automotive parts. Some of these advantages are its short cycle time and as a result high production rate. Compression moulding is greatly used to produce larger flat or moderately curved parts such as hoods, fenders, scoops, spoilers, lift gates as well as smaller more intricate parts.

## 1.3.2 MATERIAL PROPERTIES

### 1.3.2.1 MECHANICAL TESTS:

- Impact test

Impact test measures the ability of a material to resist high loadings. This test is a designed method to determine the absorbed energy of fracturing an object at relatively high speed. One of the most significant properties of a composite that a part designer should always keep in mind is impact resistance. It also estimates service life of a part. There are two basic types of impact tests:

- i. The Charpy (Beam) test
- ii. The Izod (Cantilever) test

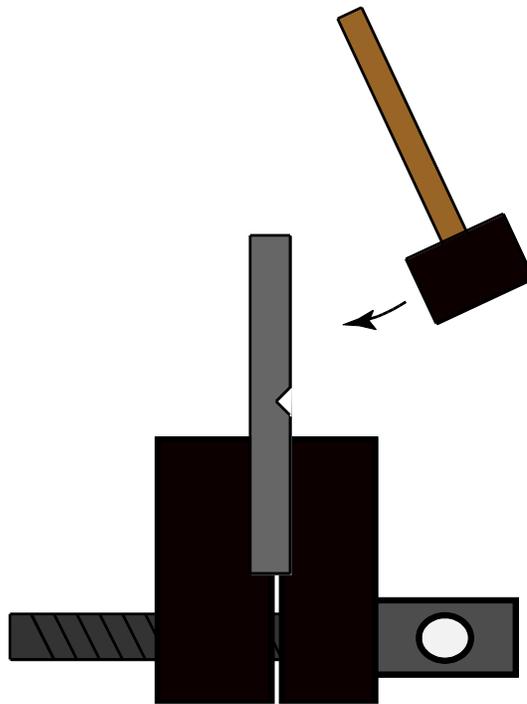


Figure 3. Schematic of an Izod Test.

- Flexural test

Flexural strength corresponds to the highest stress which a material experiences at its point of fracture. The three-point bending (flexural) test determines bending or failure strength, modulus of elasticity, and yield strength. It also monitors flexural stress, flexural strain, and flexural stress strain behaviour of the specimens.

### **1.3.2.2 THERMO-PHYSICAL TESTS:**

- Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry is the most widely used technique to study the changes occurred during heating a polymer. These changes are called ‘thermal transitions’ of a polymer. Examples of the thermal transitions are glass transitions, crystallization, and melting of a polymer.

Two different types of DSC which are currently available include:

- The power compensated DSC and
- The heat flux DSC, which is also known as Differential Thermal Analysis (DTA)

As the power compensated DSC is the most commonly used method, it is going to be described in more details.

Generally the Differential Scanning Calorimetry (DSC) system consists of two pans. It works on the basis of comparing the thermal properties of a sample against a standard reference material which has no transition in the temperature range of interest (alumina). The reference pan is held empty. Small holders contain each one of either the sample or the reference material. The holders are placed in an adiabatic environment as shown below (Figure 4). The temperatures of the holders are monitored using thermocouples, while the electrically supplied heat keeps the temperature of the two holders equal. The computer plots the difference in heat output of the two

heaters against the average temperature. Using this graph one can find the thermal transition temperature such as glass transition, crystallization and melting point of the material. The enthalpies which correspond to the crystallization and melting peak can also be calculated.

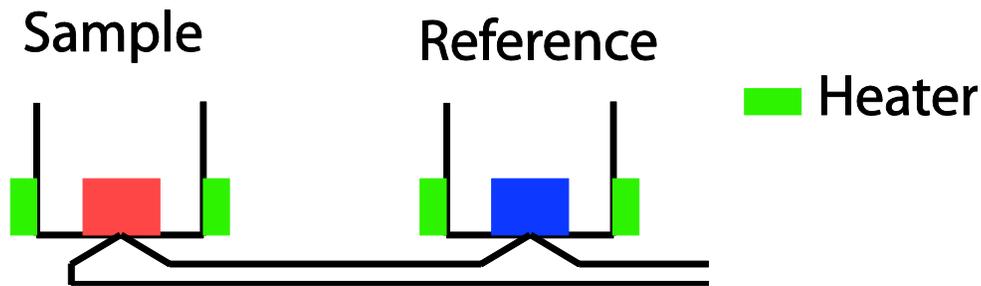


Figure 4. Schematic of Differential Scanning Calorimetry.

- Rheology

Rheology is the science of flow of fluids and deformation of solids under controlled testing conditions. The study of rheological properties can be applied to all types of systems (fluids, semi-solids, and even solid materials) such as polymers and composites. The purpose of the Rheology experiments is to have more understanding of the composites' rheological properties in different practical conditions, and ultimately to develop a better product. Generally these physical properties are a link between the end use product performance and the materials processing steps.

The instruments which can be used in order to measure a material's rheological properties are called Rheometers. Some types of rheometers include the most versatile being controlled stress and/or strain rheometers and capillary rheometers.

Viscoelastic parameters

Complex modulus ( $G^*$ ) is a measure of material overall resistance to deformation.

$$G^* = \text{Stress}^*/\text{Strain} \quad 1$$

$$G^* = G' + iG''$$

Elastic (Storage) modulus ( $G'$ ) is a measure of elasticity of material, or in other words the ability of the material to store energy.

$$G' = (\text{Stress}^*/\text{Strain}) \cos \theta \quad 2$$

Viscous (Loss) modulus ( $G''$ ) is the ability of the material to dissipate energy. The energy lost is in the form of heat.

$$G'' = (\text{Stress}^*/\text{Strain}) \sin \theta \quad 3$$

Tan Delta is a measure of the material damping, such as vibration or sound damping.

$$\tan \sigma = G''/G' \quad 4$$

## 1.4 ORGANIZATION

The organization of the thesis is as follows: Chapter 1 is an introduction to composites, background information on natural reinforced composites, the processing methods such as extrusion, and compression moulding, as well as advantages of using green composites. Chapter 2 contains a literature survey of natural fibre reinforced composites. The advantages and disadvantages of different reinforcement types are presented, and the importance of composites' components derived from renewable raw materials is discussed. This chapter also covers the effects of fibre

modifications on the mechanical properties of biocomposites by other researchers to find out the best fibre-matrix interface. Furthermore, various manufacturing methods for biocomposites by other researchers are discussed in this chapter.

Chapter 3 describes the specifications of the materials used in this experiment. It also contains description of the manufacturing methods developed for making natural fibre reinforced PLA based composites.

Chapter 4 provides a series of experiments carried out in order to measure the mechanical properties such as impact resistance, and flexural strength of the composites, and also to study thermal stability of materials. In this chapter the relation between mechanical properties of the natural fibre reinforced composite and its micro-structure is discussed.

Chapter 5 discusses the results of the processing methods, as well as the mechanical, and thermal properties. In this chapter the relation between mechanical properties of the natural fibre reinforced composite and its micro-structure is discussed.

Finally, the summary and future work of this research is presented in Chapter 6. This includes a conclusion of investigation of the biocomposite's properties and performance. Further studies are needed, in order to develop a detailed design to investigate various types and contents of modifiers and natural fibres on the physical and mechanical properties of PLA based composites.

## **CHAPTER 2: LITERATURE REVIEW**

### **2.1 BIO-COMPOSITES**

#### **2.1.1 COMPOSITES OF NATURAL FIBRES AND SYNTHETIC POLYMERS (WOOD PLASTIC COMPOSITES)**

Plant fibres are produced from renewable agricultural resources. Some of the advantages of these natural fibres when used in automotive industry are reduction of cost, weight, manufacturing time, and safety improvements. As discussed in chapter 1, cellulosic fibres can be divided into bast, leaf, seed, fruit and finally wood fibres. Natural fibre properties are dependent on seed selection, growing and separation methods.

By comparing the tensile strength, elasticity and elongation at failure of hemp and flax fibres with synthetic fibres, Hemp and flax fibres show considerable potentials for competing with E-glass fibres which is a reference material in composite technology [1].

The use of natural fibres to reinforce thermoplastics such as polypropylene and polyethylene as an alternative to synthetic or glass fibres has been and continues to be the subject of research and development. The potential advantages of using natural fibres have been well documented and are generally based on environmental friendliness as well as health and safety factors [3]

There exist several natural fibres such as cellulose, wool, and silk that can be used in composite structures. Wood is an example a natural based composite in which lignin matrix is reinforced with cellulosic and hemicelluloses fibres. [9].

Because of availability of natural/bio-fibres from renewable resources, the use of bio-composites is expanding in recent years. In addition, the bio-fibres are useable in both thermoplastic and thermosetting matrix composites [10,11]. Also, the natural fibres are cost effective and provide significant performance, especially when they are used in biodegradable matrix composites. [10].

For thermoplastics, cellulose fibres such as wood fibres are the most suitable reinforcements, as they are cost effective and they improve specific mechanical and physical properties [9,12]. In addition, recycled papers such as newspapers, which are the most commonly recycled paper, can be extensively used in wood composites. The average household in the developed world generates more than 8 kg of newspaper every month. This amount can be used as natural fibres for different applications such as manufacturing of insulation or other building materials [9,13,14].

### **2.1.2 BIO-POLYMERS AS MATRIX FOR NATURAL FIBER REINFORCED PLASTICS**

Use of fibre-reinforced plastic composites started by a composite made of phenolic resins reinforced by cellulose fibres. The glass fibre was mixed with unsaturated polyester matrix in 1940s. Fabrication, use, and removal of conventional composite structures, such as glass, carbon or ramid fibres with epoxy, phenolics, unsaturated polyester, and polyurethanes, cause a lot of environmental problems and has always been criticized [15].

In 1989, development of a new idea was stated by the DLR Institute of Structural Mechanics. The main idea was to introduce natural reinforcing fibres such as flax, hemp, ramie and cellulose into a polymer matrix derived from renewable resources like cellulose, starch or lactic acid derivatives, etc. These matrices can be from both thermoset and thermoplastic polymer's groups. The most important reason was to successfully overcome the environmental problems caused by the traditional composites. These new fibre reinforced composites (biocomposites) were created in that time, and are still being under more developments [2]. Comparing mechanical properties of classic glass fibre reinforced plastics (GFRP), most recent developed combinations of fibres and matrix, and being ecofriendly, these new biocomposites are excellent substitute for GFRP in several cases. Biocomposites can be processed by many common manufacturing techniques. Some examples are compression moulding, injection moulding, filament winding, etc [2].

Bodros et al. investigated the tensile properties of natural fibre-biopolymer composites using different kind of biopolymers such as polylactic acid (PLA), L-poly lactide acid (PLLA), polycaprolactone and starch thermoplastic (MaterBi\_Z), poly(3-hydroxybutyrate) (PHB), and poly(butylene adipate-co-terephthalate) (PBAT), and poly(butylene succinate) (PBS). The aim of

this study is to verify the possibility of replacing glass fibre reinforced unsaturated polyester resins by biocomposites. At the end it is shown that the 30% flax fibre/PLLA based biocomposites have the highest tensile strengths than the others [15].

PLA has been commonly used for biodegradable packaging materials. There is a great deal of research stating that PLA is also suitable as matrix in biodegradable composites. PLA can be manufactured from renewable resources, such as corn starch. Composites made of PLA are suitable for use in textiles, bio-compatible/ bio-absorbable medical devices, and industrial packaging [16]. PLA is a thermoplastic material and possess high strength and elasticity modulus. There are also reports on the potential of cellulose-based fibres as reinforcement for polymers, as cellulose materials provide a great deal of potential advantages. [17,18] some of the benefits of cellulose materials are renewable source, low cost, ease of processing, suitable fibre slenderness ratio, low weight, high specific stiffness and strength, and biodegradability [19].

HUDA et al studied the physical and mechanical properties of bio-composites. These composites were prepared from (PLA) and recycled cellulose fibres (from newsprint) through extrusion and injection moulding processing. It was found that the tensile and flexural moduli of the PLA based bio-composites were significantly higher than the neat resin composites. Higher elasticity modulus of the reinforcement added to the PLA matrix was mentioned as the main reason of this improvement. The results of the dynamic mechanical analysis also showed that the storage modulus of PLA was higher where cellulose fibres were used as reinforcements. This shows that the applied stress is mostly transferred through cellulose fibres rather than the matrix resin. Results of differential scanning calorimetry and thermo-gravimetric analysis showed that adding up to 30 wt% cellulose fibre to the PLA matrix did not significantly change the

crystallinity, or the thermal decomposition of the PLA. In general, it was shown that the cellulose fibres that are recycled from newsprint are potential reinforcements for the-composites [19].

Graupner et al. investigated the mechanical properties of composites, completely made of renewable resources raw materials. In this study different types of natural fibres and man-made synthesis (Lyocell) fibres have been used as reinforcement. 40% of reinforcement and PLA as matrix together made the composites using compression moulding. The impact strength of cotton/PLA composites was higher than the other composites, while hemp and kenaf/PLA composites possess higher tensile strength values [20]. On the other hand it has been showed that mixture of high tensile strength and Young's modulus with good impact strength of Lyocell/PLA composites make them suitable for some applications [20].

Some research papers have also been done on investigating the influence of adding man-made fibres based on renewable raw materials to PLA on the characteristics of the composites. Examples of these synthesis fibres are viscose, Lyocell or rayon (Cordenka) [21].

## **2.2 ADVANTAGES AND APPLICATION OF BIO-COMPOSITES**

Some uses of natural fibres in industry include thermal insulation, acoustical boards, absorbency products, geo-textiles, tackable boards, animal bedding, etc. Natural fibre reinforced thermoplastics are mostly used for applications in the automotive industry [15]. The reasons of using natural fibres in automotive industry are, lower weight parts due to lower density, good mechanical and acoustical properties, reduction in cost (60-70% less than glass fibre), and moulding time, lower wear, positive effects on agriculture, occupational health benefits compare to glass fibre, and recyclability.

One of the most excellent mechanical properties belongs to hemp fibre compared to several other plant fibres. Hemp has good biodegradation properties, hence meeting the requirements of waste treatment. The most applications of this natural fibre in the automobile industry include interior parts of vehicles [22].

PLA is currently used in so many consumer applications. These products can be made only by a biopolymer, or mixture of it with other polymers, or reinforced with natural fibres. The largest number of products which use PLA is packaging industry. Another large-scale use of PLA is in the textiles made of fibres [23].

Example of natural fibre-reinforced PLA composites which are existed commercially is in automotive application; a spare tire in the Toyota RAUM made from biodegradable composites based on kenaf fibre and PLA [20]. In biomedical, and bioengineering applications animal silks reinforced poly(lactic acid) (PLA) composites are potential materials for patients with bone effects [24].

### **2.3 MANUFACTURING METHODS**

The melting temperature of PLA is 100°C less than that of poly ethylene terephthalate (PET), and this fact has an important effect on the processing conditions of PLA based composites, especially in extrusion and injection moulding. A study by Byrne et al. described the differences in the manufacturing process of PLA and PET [26].

It is also reported that PET was stiffer than PLA at temperatures lower than 0°C, while at room temperature and temperatures up to glass transition, PET is less stiff. Manufactured PLA sheet had less impact resistance compared to PET [25].

Resin transfer moulding (RTM) is a processing technique which can be used to fabricate high quality natural fibres reinforced composites. In a study, use of this processing technique for natural fibres has been explored. Arctic Flax fibres and epoxy resin was used as reinforcement and matrix in this evaluation. Comparison between the obtained mechanical properties of the materials showed that the composite with 50% Arctic Flax has significantly more stiffness (40 GPa) compared to that of plain epoxy (3.2 GPa). Similar pattern can be observed for the tensile strength of composites compared to the neat epoxy. This study verifies that RTM is a suitable processing method for natural fibre composites based on epoxy resins [26].

Attentions are on the sustainable raw materials for both fibre and matrix intended for industrial application, in order to reduce the environmental effect of CO<sub>2</sub> emission. Among all biopolymers, poly lactic acid (PLA) is one of the most adaptable which is commercially available. However, there are limitations on the application of PLA, not only for structural purposes but also semi-structural applications. The reason is the inherent properties of PLA such as low heat resistance and relatively brittleness. This shows that application of PLA at elevated temperature for some industry is not acceptable. Examples of those purposes are automotive industry, electrical- and medical applications. One of the methods to overcome this issue is to mix fibres with PLA. A study by Tokoro in 2007 was done to investigate the methods of improvement of mechanical properties (impact strength, and heat resistance) of PLA by bamboo fibres. In this path, extraction of three different kinds of bamboo fibre from raw bamboo was prepared. Used methods for preparation of fibres include either sodium hydroxide (NaOH) modification or steam explosion in combination with mechanical processing. Results showed that adding short fibres to the composites does not affect the impact strength greatly, while adding medium length fibre bundles had a significant effect on the impact properties. In respect

to thermal stability and heat resistance of composites, bamboo fibre showed a considerable improvement compared to the neat PLA [27].

Fabrication method of long fibre reinforced composites is investigated. In this study jute yarns are used as reinforcement in the thermoplastic composites. A tubular braiding system was used to process micro-braid yarn from continuous jute yarn. Both treated and untreated fibres inserted straightly as axial fibre, while matrix in the form of polymer fibre surrounded the reinforcement fibre. Study showed that this technique (called Micro-braiding) has some advantages such as least or no damage to the jute fibre bundles, if one compares it with commingled yarns [5].

Plackett et al. examined the tensile properties and degradation behavior of jute fibre reinforced PLA composites. Film stacking processing method was used to produce the bio-composites. The results showed that the tensile strength of composites containing 40% of fibres is double of that in neat PLA, while addition of the fibres has no effect on impact strength of the materials [3].

## **2.4 MECHANICAL PROPERTIES OF BIO-COMPOSITES**

Some studies also have been done on the optimization of natural and man-made cellulose fibre- and PLA based composites. Some of these investigations are about biodegradability of the composites, while the others study the mechanical or thermal characteristics of the composites.

There has been a great deal of research on use of flax, sisal, ramie, oil palm, and cellulose as reinforcing components in composites. The mechanical properties of the matrix have been improved significantly in the past. Mechanical and physical properties of a composite made of Mater-Bi\_Z and Y with flax cellulose pulp of 4.5 mm length (10–40 wt %) are tested by Puglia

et al. Romhany et al. used film stacking method to make Mater-Bi and flax fibre at 140 °C. Garkhail et al. showed that the mechanical properties of PHB and flax fibre biocomposites (fibre volume fraction 10–40%) processed using film stacking are higher than the ones made by injection moulding. Press temperature during film stacking is reported to have significant effect on the mechanical properties of the composites. By increasing the press temperature, the wetting of flax fibres as well as the bonding between matrix and fibres is improved. However, having higher temperatures may cause water evaporation and chain degradation of the flax fibres and consequently decrease the mechanical properties [15].

The choice of fibre and matrix is a significant factor in impact strength of composites. For instance, Chuai et al. showed that the reinforcement of polypropylene with untreated softwood fibres results in a significant decrease in unnotched Izod impact strength with increasing fibre content. However, it was also showed that fibre treatment improves surface compatibility with polypropylene and leads to higher impact strength. Carbon fibre-reinforced PLA composites were studied by Wan et al. it was shown that unnotched impact strength was increased with fibre reinforcement up to a 30% fibre volume fraction. Sanadi et al. also mentioned that the unnotched impact strength of thermoplastics decreases when they are reinforced with agro-fibres. Additional fibres create stress concentration regions that increase the chance of crack initiation and accelerate crack propagation [3].

The compression moulded composites made of Ramie fibres and PLA have been studied by Kimura et al. The study showed that composites having the fibre content of 45-65% show the highest tensile strength, as well as bending strength and modulus [28].

Hu et al. developed a fabrication method for biodegradable PLA reinforced with hemp fibre composites. In this survey the mechanical properties of the completely green biocomposite are also studied. Effects of alkali treatment on the hemp fibres show that the best tensile and flexural properties belong to 40% modified hemp/PLA composites [22].

Another research showed that in kenaf/PLA composites, bending strength, tensile strength and modulus have a linear relationship with fibre content (up to 50% fibre content) [21]. Pan et al. [29] manufactured PLA composites with kenaf as reinforcement. The composite was made through melt-mixing and injection moulding. The fibre mass contents range was between 0% and 30%. At the maximum value of fibre content, the tensile strength was improved by almost 30% compared to the PLA without reinforcement. Bax and Müssig studied flax and man-made Cordenka fibre reinforced PLA composites that were made by injection moulding [30]. The mechanical properties of the composites improved while the fibre mass content was increased from 10 % up to 30%. Injection moulded Cordenka fibre-reinforced PLA with a fibre mass content of 25% was studied by Ganster and Fink [31]. They showed that the stiffness and strength of the composites are approximately doubled comparing the composites to the matrix material while the impact strength could be tripled. Shibata et al. used compression moulding to make Lyocell fabric and PLA composites. Tensile modulus and strength of the Lyocell/PLA composites was measured and improvement of the mechanical properties with increasing fibre content was noticed. The impact strength of the composites was significantly higher than that of pure matrix material. The reported results in the cited research show that the kind of fibre is an important factor on the impact and tensile strength properties of PLA composites.

Graupner et al. studied the influence of addition of lignin to the natural fibre reinforced composites on mechanical properties. In this investigation, compression moulding has been used

to manufacture the samples of 40% of cotton fibres, poly (lactic acid) (PLA), and lignin. The data obtained showed that the composites' characteristics are affected by adding lignin as natural adhesion promoter. The SEM also explained the adhesion improve between fibre and matrix in the composites containing lignin compared to those without lignin [32,33]. The tensile, and impact strength of the hemp fibre reinforced PLA composites are reported to be worse than those of neat PLA, while the modulus of elasticity is an exception [6].

## **2.5 THERMAL PROPERTIES OF MATERIALS**

A study by Day et al. has been done on the behaviour of PLA and its clay nano-composites using a differential scanning calorimetry (DSC) [33,34].

The hydrophilic property is the most negative aspect of plant fibres. This issue causes a reduction in the compatibility of natural fibres when mixed with hydrophobic polymeric matrices. This is the main reason for many researchers to focus on solving this problem by improving fibre-matrix interfaces, and also to improve the thermo-physical and mechanical properties of the end products.

Influences of addition of lysine-based diisocyanate (LDI) as coupling agent to bamboo fibre reinforced PLA composites on the composite properties have been studied by Lee et al. The results obtained show an improvement in the tensile properties. Addition of coupling agent also increases water resistance, and interfacial adhesion of the composites, while it causes a decrease in the thermal flow of the materials [4].

Solarski et al. investigated thermal characteristics of PLA filaments using modulated differential scanning calorimetry (MDSC). This method makes analysis and study of different

thermal events more precise. The results of this study demonstrate an increase in the glass transition temperature ( $T_g$ ), and a decrease in heat capacity after hot drawing process [34,35].

Generally the properties of biocomposites are found to be significantly affected by the preparation methods, and conditions. Masirek et al. confirmed this statement by investigation of changes in degradation, and thermal, and mechanical properties of hemp/PLA composites. The study proved that hemp content and addition of plasticizer influences the mentioned properties of composites [6].

Pan et al. studied how different kenaf fibre contents can affect mechanical properties and crystallization behavior of PLA based biocomposites. Composites with various weight fractions (0, 10, 20, and 30 wt %) first were compounded in a single screw extruder, and then injection moulded into the desired shapes. Furthermore, morphology, mechanical, and dynamic mechanical analysis of the composites were performed. The obtained results verified the positive effect of kenaf fibres on the crystallization rate, as well as tensile and storage modulus [35,36].

In 1996, Sodergard et al. studied the effects of adding peroxide modifier to biodegradability of poly L-lactic acid (PLLA). The reason of the change in the biodegradation of the polymer is mostly related to its morphology. Injection moulding was used to prepare the samples of unmodified and modified PLLA. In addition to the changes in weight, and material's molar mass, mechanical strengths of the specimens also have been tested during degradation in soil [36,37].

To search degradation behavior of biocomposites, a study was carried out by Masirek team. The TGA investigations on the hemp fibre-filled PLA composites in nitrogen atmosphere explained that the presence of fibre in the composite is a force to degradation to happen sooner.

And the plasticizer used in this research showed no effect on the composites' degradation behavior [6].

## CHAPTER 3: EXPERIMENTATION

### 3.1 MATERIALS

For the composite production, in this study, different grades of poly lactic acid(PLA), and 2 different kind of fibres were used as the matrix, and reinforcement respectively. In order to investigate the improvement of mechanical properties and process ability of PLA based composites, Bio max strong 120 is used as impact modifier in the composites.

- Poly lactic acid (PLA)

Biopolymers, NatureWorks PLA with 2 different grades (PLA 2002D and PLA 3001D) was chosen as matrix of biocomposites.

Table 1. Properties of Used PLAs.

Polymer	Tensile strength (MPa)	Elongation to break (%)	MFI (g/10min) (2.16 kg, 210°C)	Density (g/cm <sup>3</sup> )
PLA2002D	53	6	5-7	1.24
PLA3001D	48	2.5	10-30*	1.24

\*(2.16kg,190°C)

Both PLAs were obtained from Jamplast Inc., (Ellisville, Missouri, USA). It was supplied in form of pellets. Some of the important specifications of these biopolymer materials reported by the manufacturer are given in Table 1.

- Reinforcements

2 different kind of natural fibres were chosen to be used as reinforcement in this project. Cotton fibres (*Gossypium hirsutum* L.) were supplied by Fibre and Biopolymer Research Institute (Texas Tech University, Texas, USA), in the form of carded cotton slivers. They were cut manually to the average length of approximately 3 mm, as it can be seen from Figure 5. Pictures of used cotton slivers (before, and after cutting) are shown in Figure 5.

Jute (*Corchorus capsularis* L.) is an important tropical crop and grows in India, Bangladesh, China, Thailand, Nepal and Indonesia. For the bast fibre-reinforced composites, in this research, a jute fibre in the forms of yarn was used as a model system for what might be feasible with a broad range of natural fibres. The fibres were supplied by the Bangladesh Jute Research Institute (BJRI) in Dhaka [37]. The fibres were chopped using a wood refiner machine to the desired length. The mean length of fibres was manually found to be 3mm. Figure 6 shows pictures of jute fibres before and after refining.



(a)



(b)

Figure 5. Cotton Fibre Slivers (a) Before Chopping, (b) After Chopping.



(a)



(b)

Figure 6. Jute Fibre (a) Before chopping, (b) After chopping.

Table 2 summarizes the physical and mechanical properties of used natural fibres (Cotton, and Jute).

Table 2. Natural Fibre's Physical and Mechanical Properties.

Natural Fibre	Tensile strength (MPa)	Young's Modulus (GPa)	Fibre Diameter ( $\mu\text{m}$ )	Density ( $\text{g}/\text{cm}^3$ )
Cotton	625	9	15.0	1.54
Jute	546	8	17.5	1.45

- Additive

Impact modifier (IM), Biomax Strong is a potential additive for improving physical properties of PLAs. Addition of 1-4% of this modifier into PLA showed a significant improvement in the processability of PLA, reduction in needed drive power, a drop in melting temperature, and pressure in the head of the extruder, while increasing energy efficiency are reported as benefits of biomax addition to PLA. Poly lactic acid requires more torque (~30%) as compared to polystyrene or polypropylene. This is the reason that makes biomax strong an excellent additive to PLA.

Biomax strong 120 supplied by Dupont, Canada, was used as impact modifier for PLA in this set of experiments. This material is a petroleum-based ethylene acrylate copolymer which is compatible with PLA. It also improves the impact strength of biomax strong 120 modified PLA even at 2% addition level [8]. This copolymer has a density of  $0.94 \text{ g}/\text{cm}^3$ , Young's modulus of 2

Gpa, a melting temperature of 72 °C and a melt flow index (MFI) of 12 g/10min (2.16 kg/190°C) [38,39].

Different combinations of fibres and matrices, with and without impact modifier were prepared in this study. Samples of neat PLA also are made as reference materials. Table 3 summarizes the mass fractions of the components in each combination.

Table 3. Composites of Different Materials.

PLA Grade	Natural Fibre	Fibre Content (wt. %)	Impact Modifier (wt. %)
2002D	Jute	10	0
		20	
3001D	Cotton	30	3
		40	

In this table, each column describes the options of the components of the composite samples, combining these different choices, 32 are made to use.

### 3.2 EXTRUSION

The resins absorb moisture from atmosphere; hence the first step is to remove any moisture in the raw materials. Therefore, the PLA granules were dried at temperature of 90 °C for 4 hrs. The natural fibres were also dried using a vacuum oven at 80 °C for 12 hrs to reduce the moisture content.

After drying, the material was compounded using twin screw extruder (TSE). The extruder used in this set of experiments is a counter-rotating Conical Twin Screw Extruder (ZSE Leistritz) with screw diameter, length, and L/D ratio of 42 mm, 305 mm, and 7.3 respectively.

Feeding operations were controlled manually. Screw speed was set at 25 rpm and melt pressure varied from 45-50 psi depending on the characteristics of composite's melts. Table 4 summarizes some of the operating conditions of the twin screw extruder.

Table 4. Operation Conditions of TSE.

	Zone 1 Temp. (°C)	Zone 2 Temp. (°C)	Zone 3 Temp. (°C)
2002D/CT/IM	130	180	180
3001D/CT/IM	130	170	170
2002D/JT/IM	140	180	180
3001D/JT/IM	140	170	170

### 3.3 PELLETTIZING

There are a number of techniques available to transform the compounded strands into pellet forms. In general, pelletizing systems can be divided in two categories of cold face, and hot face cutter.

The strand pelletizing system typically consists of a die head, a water bath, an air blowing dewatering unit, and finally a strand pelletizer. The melt passes through a die mounted directly on the end of the extruder, and is formed into the circular cross sectional profile. Right after exiting the extruded strands from the die, the materials were passed through water bath to cool the materials.

In order to prepare the compounded materials for compression moulding, a pelletizing system (Scheer Bay Co. pelletizer, model no BT-25) was used. Prior to entering the strands to the pelletizer, materials were dewatered using a compressed air unit. Figure 7 is a schematic diagram that illustrates the biocomposite's compounding and strand pelletizing process.

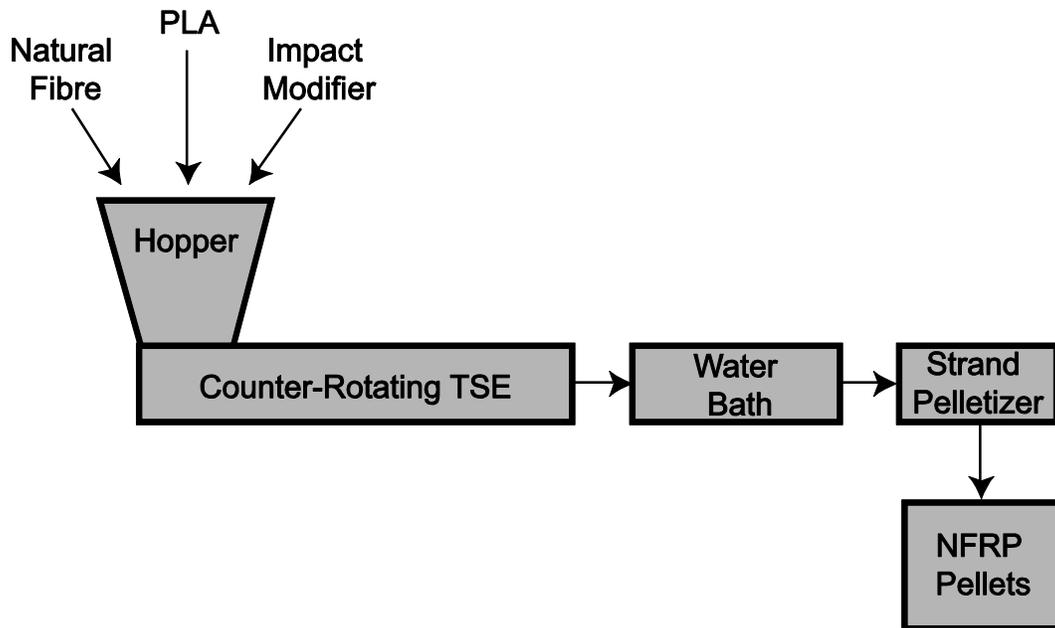


Figure 7. Schematic Diagram of Materials Compounding, and Pelletizing.



Figure 8. Compounded Pellets of PLA 3001D/10% Jute Fibres/3% IM Composites.

One of the most important advantages of this system is that cleaning process between pelletizing two different compounds is very quick. However, increasing the fibre content in the compounded strands to the high levels makes them more brittle, so that the pelletizing process becomes more difficult. In some cases, it is even difficult to keep the pelletizer machine running.

### **3.4 DRYING**

In order to avoid any voids in the final product, the compounded pellets need to be completely dried. In this project drying was done using a vacuum oven. The drying condition for all of compositions was at 90 °C for 24 hrs.

### **3.5 COMPRESSION MOULDING**

In this study a new type of compression moulding was used. Comparing the custom built die-press compression mould and conventional hot press mould shows that the former improves mechanical properties of the composites by increasing fibre alignment.

#### **3.5.1 DESCRIPTION OF CUSTOM BUILT DIE-PRESS COMPRESSION MOULD**

After preparation of compounded materials by use of the twin screw extruder, and then making the pellets by the strand pelletizer as mentioned earlier, a compression moulding was used for preparing the specimens for further investigations. In this respect, a custom-built compression moulding system was adopted for compounding materials of this study. The design of this new compression moulding system helps the fibres in the composites to gain better alignment than the typical compression moulding machines. The directional flow of the fibres in the biopolymer matrix is due to the specific design of the whole system, which will be discussed later in this chapter. The most important advantage of the custom-built compression moulding is to get properties better than what can be gained in conventional compression moulding. Potential manufacture of end use product with this equipment is another benefit.

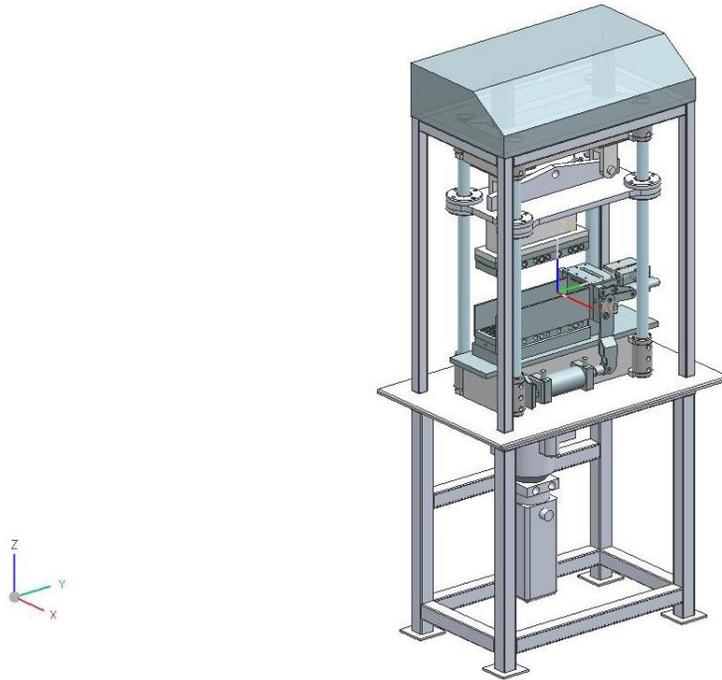


Figure 9. Schematic Diagram of Die and Press in the Custom-Built Compression Moulding System.

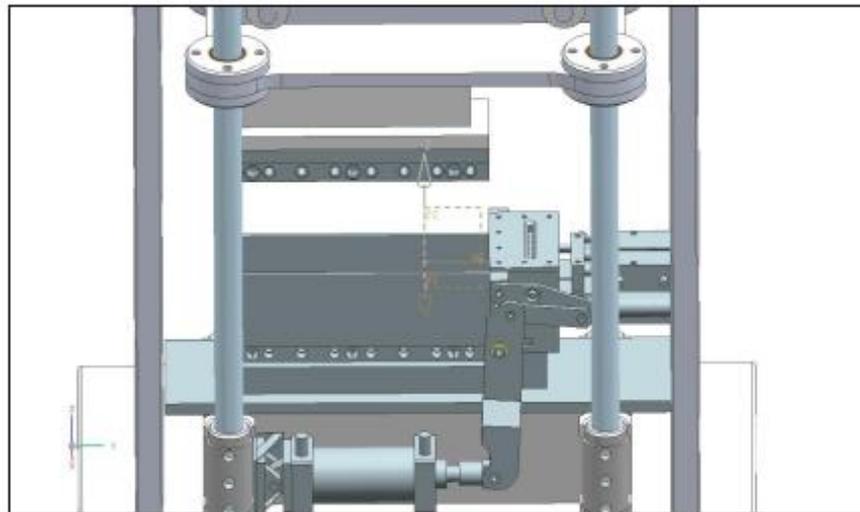


Figure 10. Schematic of Upper and Lower Platens.

Two significant parts of the system are a hydraulically-operated press and a block-die system, while a pneumatically operated melting and mixing system is also available in this

equipment. Figure 9 shows a schematic diagram of the custom-built compression moulding system.

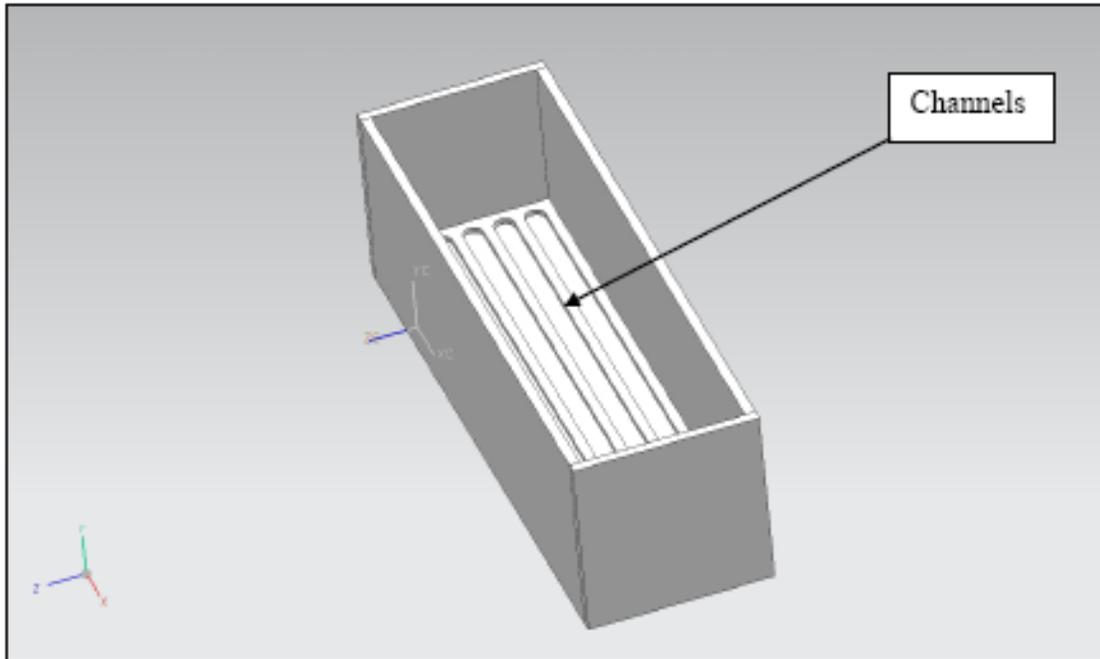


Figure 11. Schematic of Used Die-Press System.

- Press

The press has capability to achieve a usable stroke of eight inches with a maximum loading of 14 tons. Heating and cooling of the materials is controlled by a PID system. Two adjustable parameters in this system are applied force and the flow rate of the hydraulic oil which is related to the closing ram speed. The die consists of an upper platen and a bottom platen as shown in Figure 10. Eight cartridge heaters in the platens make the heating process of the system possible. In this project the heating rate of approximately  $10^{\circ}\text{C}/\text{min}$  was set for production of the specimens, while the cooling rate of  $3^{\circ}\text{C}/\text{min}$  was reached by use of blowing compressed air.

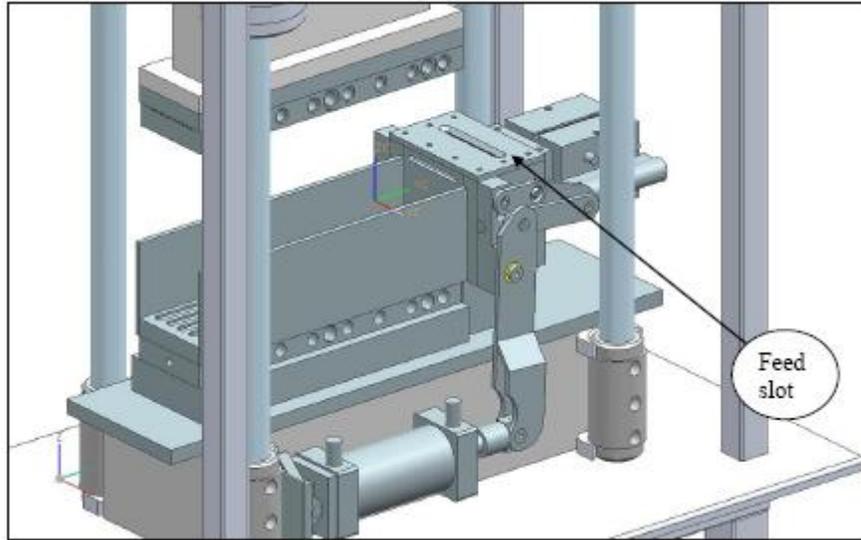


Figure 12. Schematic of the System with Feed Slot.

Five channels (shown in Figure 11) are designed in order to attain good alignment of the fibres during compression moulding. The dimensions of the channels are 1/2 x 1/8 x 14 inches.

A heated chamber is designed for melting the pellets at the right side of the die (Figure 12). A plate moves back and forth to mix the molten materials. The chamber is connected to the die by a feed slot on the side wall of the die. Right after loading the materials into the die through the slot, material is pressed by moving the top platen downwards. This causes the molten materials to flow towards left throughout the channels. As a consequence, the fibres in the matrix achieve better alignment in the longitudinal direction of the specimens. In order to improve the ease of removing materials from the die, both the die platens were sprayed with silicon prior to pressing. Platens are cooled using the compressed air before taking the specimens out, in order to avoid any deformation.

### 3.5.2 COMPOSITE PRODUCTION

As discussed earlier, all of the samples in this project are made using the custom built compression moulding system and by following the mentioned steps. Upper and lower die

temperatures and mixing temperature and time are shown in Table 5. The die closing speed is set at 40 mm/sec, and kept same for all of the composites.

Table 5. Processing Conditions for Bio-Composites.

Mixing time (min)	Mixing Chb. Temp. (°C)	Upper Platen Temp. (°C)	Lower Platen Temp. (°C)
10	180	120	120

In processing all of the compositions the conditions shown at Table 5 were used, but in a few cases, the mixing chamber temperature of 190 °C, and the mixing time of 15 min was employed. The reason was the difficulty in the processing caused by increasing the cotton content. In contrast, composites reinforced with jute fibres did not show such a difficulty, because of the different inherent properties of these fibres compared to cotton fibres. The composites with these different conditions of processing include PLA 2002D reinforced with 30% cotton fibres (with and without impact modifier).



Figure 13. Custom Built Compression Moulding System (a) Open Mould (b) Mould Under

Pressure.



(a)



(b)

Figure 14. Natural Fibre Reinforced Composite (PLA 3001D/10% JF/3% IM) (a) Warm Profiles in the Mould (b) Cooled Profiles After taking Out of the Mould.

As a result, composites containing cotton fibres as reinforcement showed more difficulties in process ability, to the point that compression moulding machine failed to produce the high percentage of cotton fibres (40%). In this respect, higher MFI value of PLA 3001D showed more difficulties as compounded reinforced biopolymers with 30% cotton fibres also failed to be moulded, even at the conditions of using longer mixing time, and higher temperatures.

## **CHAPTER 4: MECHANICAL AND PHYSICAL CHARACTERIZATIONS**

### **4.1 IMPACT TEST**

Investigation of the influence of the natural fibre type, and also natural fibre content (from 10% to 40%) on the impact resistance of the composite materials was studied in this work. The biopolymer grade (PLA 2002D and PLA 3001D) effects on the impact strength of the biocomposites can also be measured by an impact tester. The impact tester is an equipment for measuring the toughness of the composite materials. There are two different types of impact test which can be done for composites; Izod, and charpy impact test methods.

In this study, the impact resistance of the biocomposites was measured using an Izod impact tester. The Notched Izod impact strength of the composites was calculated according to ASTM D256, using a testing Machine, Tinius Olsen, model 892 (Figure 15). For this purpose notches on the specimens were made by a specimen notch maker. Figure 16 shows the used

notch making equipment in this work. Notched samples for impact testing are also shown in Figure 17. Each composite profile was cut to the required length according to ASTM D256.

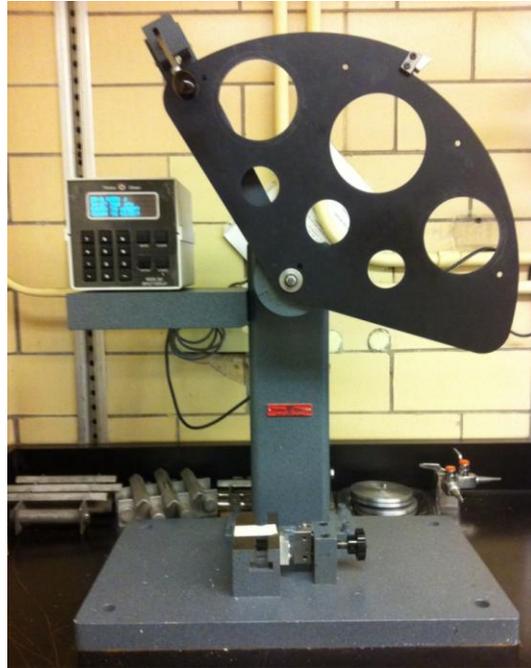


Figure 15. Izod Impact Tester (Tinius Olsen, Model 892).



Figure 16. Specimen Notch Maker.

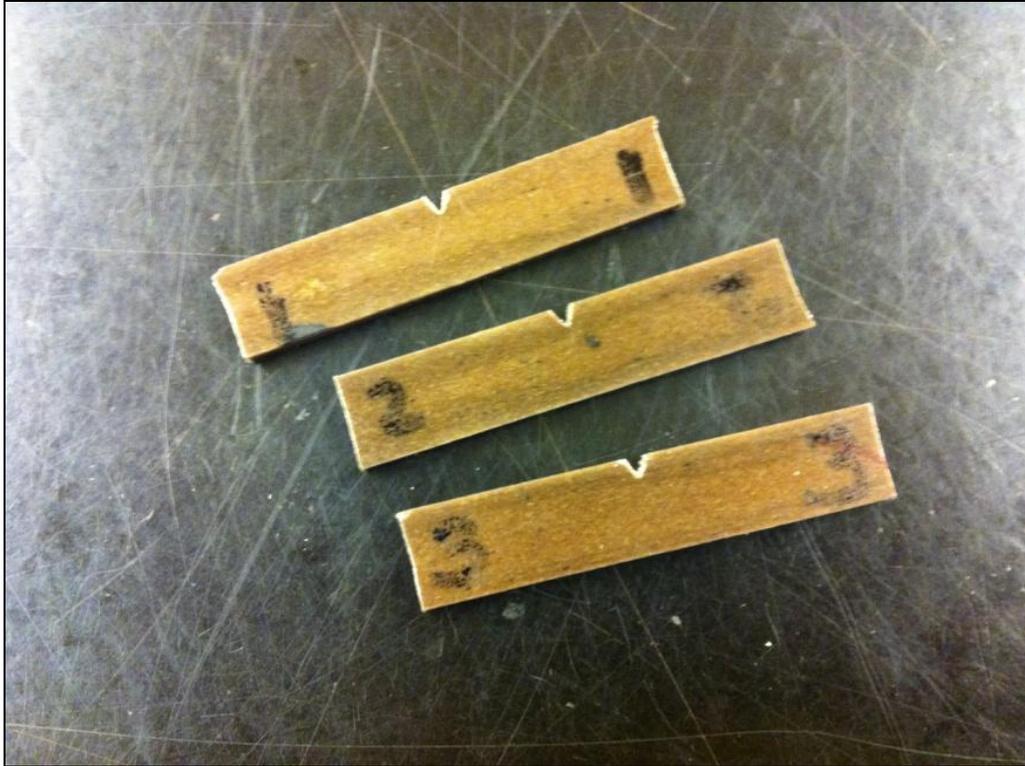


Figure 17. Notched Samples of PLA 2002D/40% Jute Fibre Composite.

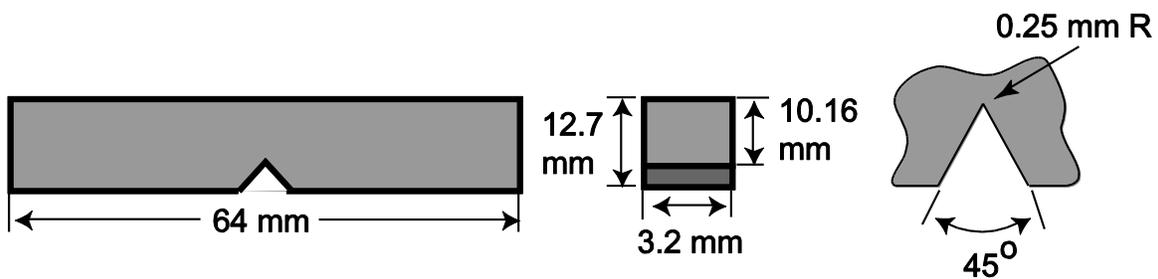


Figure 18. Notched Izod Test Specimen Dimensions.

The result of the performed notched Izod test can be reported either in energy lost per unit of specimen thickness (such as ft-lb/in or J/cm) or in energy lost per unit cross-sectional area at the notch ( $J/m^2$  or ft-lb/in<sup>2</sup>). In this study, the obtained results are in the form of J/m.



Figure 19. Used Disc Saw for Cutting the Samples.

#### **4.2 FLEXURAL TEST**

A mechanical testing machine, LS100 plus with 100 KN load cell, was used to measure the flexural properties according to ASTM D790. The 3-point bending tests were performed at a crosshead speed of 5 mm/min.

Each composite profile was cut to the required length according to ASTM D790. Cross sectional area of three different locations of each specimen was measured using a calliper before the flexural testing, in order to get more accurate data. The dimensions of the samples are roughly 64 mm x 12.7 mm x 3.2 mm. All of the mechanical tests took place at the ambient conditions of 23 °C and 50% RH. For both impact and flexural tests, 6 samples of each composition were tested until the fracture was occurred. System control and data analysis of flexural test were achieved using NEXYGEN MT software, and excel. The used equipment to cut the composite profiles to the desired length is shown in Figure 19.

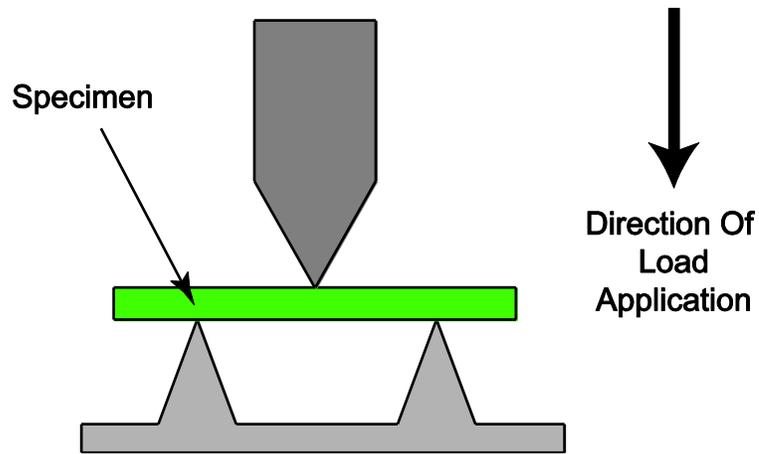


Figure 20. Schematic of Flexural Test.

The obtained results are the average values of five measurements for both of the mechanical tests.

#### 4.3 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Understanding the concepts of glass transition temperature ( $T_g$ ), as well as crystallization temperature ( $T_C$ ) and melting temperature ( $T_m$ ) is an important part in the study of polymers and their applications. Generally polymers behave in a significantly different manner when the temperature drops below  $T_g$  (more brittle) or goes up to higher temperatures than  $T_g$  (more rubbery). Hence to select a material for a specific application it is essential to know the behavior of composites under applied heat flow.

Differential scanning calorimetry (DSC) can be used to determine various properties of a composite. For example it is possible to study fusion and crystallization temperatures as well as glass transition ( $T_g$ ) using this method. Besides these characteristics, chemical reactions such as oxidation can be measured by DSC.

Increasing the temperature of an amorphous solid may lead to glass transition. Generally this event is like a step in the baseline of the heat flow value, because the sample's heat capacity changes during this transition. When the temperature goes up, the viscosity of an amorphous solid will decrease, however no formal phase change occurs.

After the glass transition, the molecules may gain enough energy to move and display a crystalline form. This point is called the crystallization temperature ( $T_c$ ). The transition from amorphous solid to crystalline solid appears as an exothermic peak in the recorded DSC signal. Eventually, the sample gets to its melting temperature ( $T_m$ ), as the temperature increases. Since melting of a material is an endothermic process, it shows itself as an endothermic peak in the DSC curve.

In this study, the melting and crystallization behaviour of the composites were studied using a differential scanning calorimeter (TA instruments 2000 Q20) equipped with a cooling attachment, under a nitrogen atmosphere. The data were collected by repeated heating-cooling cycles. Used thermal procedure was heating the specimen from 25°C to 200°C at a constant heating rate of 10 °C/min. The purpose of first heating cycle is to remove any thermal history of the material coming from the processing cycles. Cooling of the samples from 200 °C to 25 °C were done at rate of 10 °C/min. Isothermal run for 10 min at 25 °C was performed prior to the second heating cycle from 25 °C to 200 °C at heating rate of 10 °C/min. For each composite, 3 samples were tested in order to get more reliable result.

#### **4.4 RHEOLOGY**

Generally polymer processing involves the flow of polymer melts under a pressure gradient, shear deformation, or both. As concentrated polymer solutions and polymer melts behave like non-newtonian fluids, it is essential to be familiar with the exact relationship between stress and strain so as to analyze flow behaviour even with a very simple geometry.

Various techniques can be used to find the relationship between stress and shear rate. As a result the dependence of apparent viscosity to shear rate can be measured over a wide range of temperature. Some of these methods are capillary and Couette rheometry, which their basis is on simple pressure flow, and shear flow, respectively. Other frequently used methods contain cone-and-plate and parallel-plate rheometry. These methods give information in respect to the normal stresses by use of force transducers installed in the direction normal to the plane of shear. Figure 21 shows schematic of different measuring system's geometries.

Parallel-plate rheometer operates at relatively low to moderate range of shear rates to measure viscosity. In contrast, Capillary rheometer is mostly used at high shear rates ( $10^2 - 10^3 \text{ s}^{-1}$ ) to stimulate typical processing operations such as extrusion.

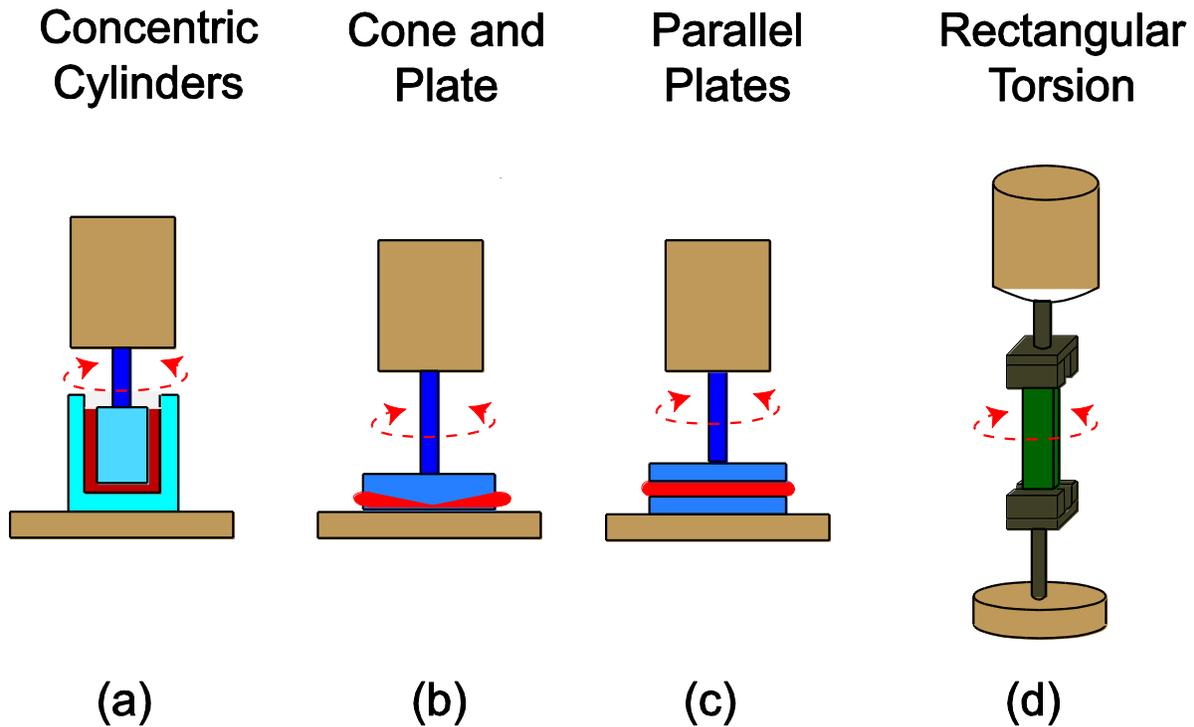


Figure 21. Schematic of Different Measuring Systems (a) Concentric Cylinders, (b) Cone and Plate, (c) Parallel Plates, and (d) Rectangular torsion.

In this study, a parallel-sliding-plate rheometer (TA Instrument-ARES) was used to investigate the rheological properties of the filled biopolymers (shown in Figure 22 ). The instrument is connected to the TA Orchestrator software, in order to plot, and analyse the obtained data from the equipment. The experimentally obtained results help us to analyse the effects of addition of natural fibre to the composites on rheological behaviour of composites.

For all of the composite materials including 2 grades of biopolymer (PLA2002D, and PLA3001D) and different kind of natural fibre, and content (Cotton, and Jute fibre, from 10% to 40%) 2 methods of dynamic strain sweep, and dynamic frequency sweep are performed. Using these experiments, changes in storage modulus ( $G'$ ), loss modulus ( $G''$ ), complex modulus ( $G^*$ ), and viscosity ( $\eta$ ) are measured. In these experiments, composite materials were placed between two parallel plates with diameter of 25 mm, and at a distance of 1 mm. To prepare the samples with 1 mm thickness, the specimen thickness was decreased using hot press equipment. Different experiments can be done using a Rheometer, such as following:

- Dynamic stress or strain sweep
- Dynamic frequency sweep
- Temperature sweep test

Basically, in the dynamic strain sweep, the material response to increasing deformation amplitude (strain or stress) is monitored at a constant frequency and temperature. Using this experiment, the linear viscoelastic region (LVR) of the biocomposites is found. In the other hand, dynamic frequency sweep is observation of the material response to the increasing frequency (rate of deformation) at a constant strain (or stress) and temperature.

For each composite, first the dynamic strain sweep was done in order to find the linear viscoelastic region. Used frequency value in the dynamic strain sweep was 1 Hz, and strain range of 0.01 to 10 for all of the composites.

After finding the strain range related to the linear viscoelastic region, 2 different strain values of 0.1 and 5 was chosen for further experiments (dynamic frequency sweep test). The reason for selection of these strains is to analyse the rheological behaviour of the composites on both regions of linear and non-linear. In this test the angular velocity ( $\omega$ ) was set to change between 1 and 500 rad/s.

Temperature used for each composite material was determined by the compression moulding process temperature. This means that rheology test for all of the materials were at 180 °C, except two composites containing PLA 2002D grade with 30% of cotton fibres (with and without impact modifier). In these 2 cases the temperature was set at 190 °C.



Figure 22. ARES-Rheometer.

In this work, the performed experiments for the composites can be divided into 3 categories:

- Dynamic Strain Sweep (at constant temperature, and frequency of 1 Hz)
- Dynamic Frequency Sweep ( at constant temperature and strain of 0.1)
- Dynamic Frequency Sweep ( at constant temperature and strain of 5)

Dynamic strain sweep, as well as dynamic frequency sweep was used in this work to study the materials rheological properties.

#### 4.5 SCANNING ELECTRON MICROSCOPY (SEM)

Fracture of samples was done after they were immersed in liquid nitrogen, in order to achieve undamaged microstructures. After fracture, samples were sputter coated by platinum using a sputter-coater (Polaron-SC7620). Figure 23 shows the used sputter coater while operating and coating the samples with platinum.



Figure 23. Polaron Sputter Coater (Model-SC7620).

Then using JEOL JSM 6060 Scanning Electron Microscope (SEM), pictures of fractured surfaces of the specimens were taken. Investigation of morphology, studying fibre alignment, adhesion between natural fibres and biopolymers, and finally presence of any possible void has been achieved using SEM images. Figure 24 shows the SEM equipment used in this work.

The operation conditions of the microscope was set at an accelerating voltage of 20 kV and emission current of 79-80  $\mu$ A. For each composite, images with 5 different magnifications of 100, 200, 500, 1000 and 2000x was used. Smaller magnifications are more useful to understand the dispersion of the plant fibres into the polymer matrix, while increasing the magnification helps us to observe the interface of fibre and matrix. Finally, the potential effects of addition of impact modifier on the fibre matrix interaction can be monitored.



Figure 24. JEOL JSM 6060 Scanning Electron Microscope (SEM).

## **CHAPTER 5: RESULTS AND DISCUSSION**

As a reason of increasing environmental concerns, the interest for composites containing components derived from renewable resources has recently grown. Biodegradable polymers and natural fibre-reinforced composites are potential replacement for traditional fibre reinforced polymers. Poly lactic acid (PLA) was reinforced with different kinds of natural fibres (cotton fibres and jute fibres), and also different fibre contents (10% to 40%). Study on the effects of addition of impact modifier on the mechanical properties of these plant fibre reinforced composites are also carried out. The mechanical tests are performed to measure and compare impact resistance and flexural strength of the composites. The rheological properties of these composites were also tested and compared. The samples were produced using a novel compression moulding system following compounding in a twin screw extruder. An optimization of fibre content to get the best mechanical properties (highest impact strength, flexural strength, and modulus of elasticity) for automotive applications is also found in this chapter. The fibre and matrix interface in the composites is also observed for all of the composites using SEM. DSC experiments are used to measure the glass transition temperature, as well as crystallization and

melting temperature of the composites. The ultimate goal of this study is to show whether these natural fibre reinforced biopolymers possess promising properties to replace traditional composites.

## 5.1 MECHANICAL PROPERTIES

To study and compare the mechanical properties of the filled composites, two tests are done for each composition (Impact and flexural tests). In this section results of the experiments and analysis of the obtained results are discussed.

### 5.1.1 IMPACT TEST

As discussed in the previous chapter, impact resistance of the composite materials were measured using the Izod impact tester. Results of notched izod impact test are shown in Figure 25-23 for composites with different mixture of PLA and natural fibres.

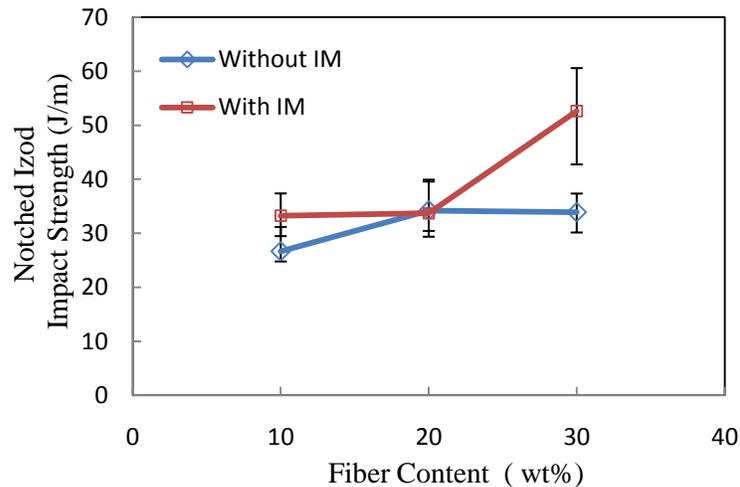


Figure 25. Impact strength of the PLA 2002D/CF/IM composites versus their fibre-mass proportion.

It is apparent that addition of biomax impact modifier increases the impact resistance of poly lactic acid (PLA) reinforced with cotton fibres. It is also shown that increasing fibre-mass proportion from 10 % to 30% in these biocomposites has a positive influence in increasing the impact resistance, especially in composites containing impact modifier. As shown in Table 6 comparing the results of the cotton fibre reinforced PLA 2002D with neat PLA, it is obvious that all of the composites with impact modifier have higher impact resistance than pure PLA. And adding 20% or 30% cotton fibre to this grade of PLA also improves the impact properties of PLA, while 10% addition does not show any better impact properties than pure PLA.

The highest value belongs to PLA 2002D reinforced with 30% of cotton fibres and 3% of impact modifier, and it shows 82% higher value of impact strength than that of pure PLA.

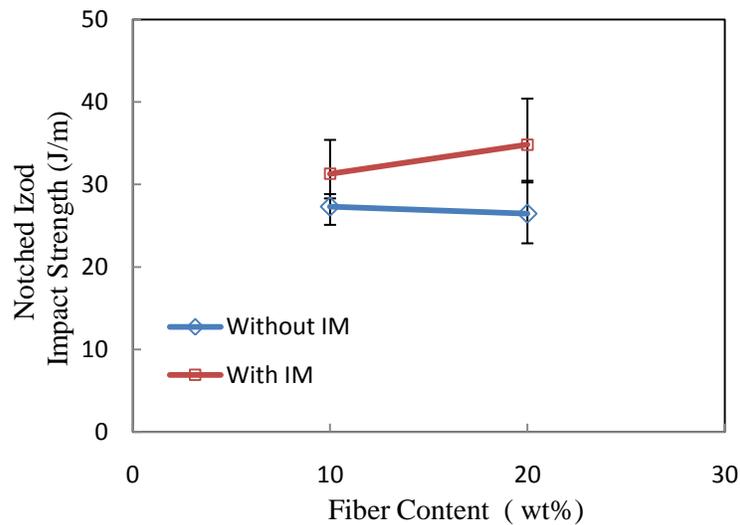


Figure 26. Impact strength of the PLA 3001D/CF/IM composites versus their fibre-mass proportion.

Figure 26 explains that addition of even 3% of impact modifier also increases significantly the impact resistance of the PLA3001D/cotton composites. The impact strength of

cotton reinforced PLA3001D in the presence of IM increases and reaches a maximum value of 34.8 J/m at a fibre-mass-ratio of 20% which is slightly higher than the value for pure PLA.

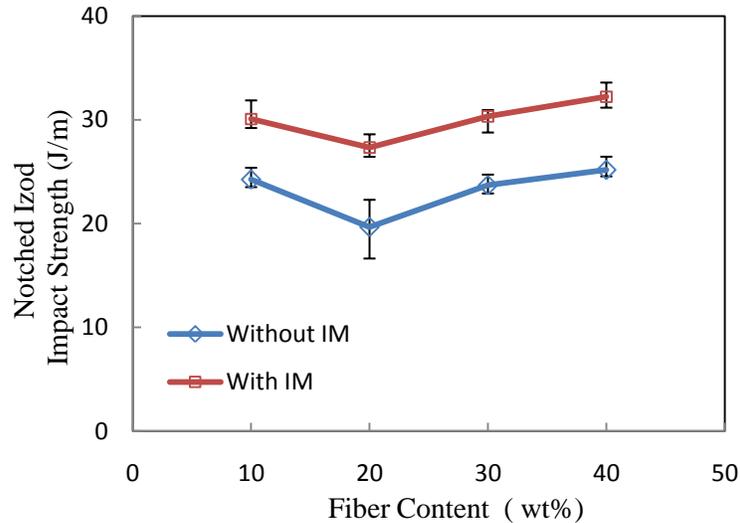


Figure 27. Impact strength of the PLA 2002D/JF/IM composites versus their fibre-mass proportion.

As shown in Figure 27, adding jute fibres to PLA 2002D as reinforcement in this biopolymer affects the impact properties of the composite. The graph shows that from 10% to 20% addition there is a considerable decrease in the impact resistance, while increasing the jute fibre mass proportion to 40% shows a significant improvement in this property. Comparing the graphs for composites with and without impact modifier shows that addition of impact modifier notably enhances the impact properties. The highest value for this set of experiments was observed at composites made of 40% jute fibre with the presence of impact modifier.

Results of further investigation on the mechanical properties of PLA reinforced with jute fibres are shown in Figure 28. In these experiments PLA with the grade of 3001D was used as matrix. Changing the fibre content from 10% to 40% obviously shows an increase in the impact

strength of composites containing impact modifier, while the trend is not seen in the composites without impact modifier.

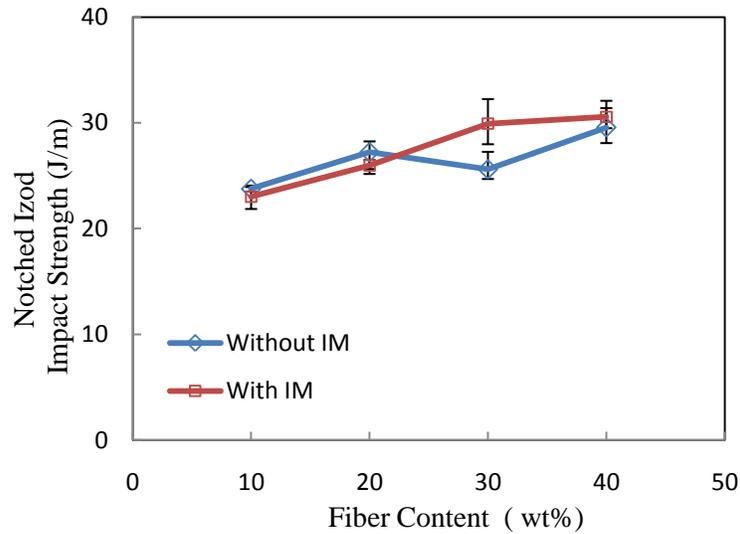


Figure 28. Impact strength of the PLA 3001D/JF/IM composites versus their fibre-mass proportion.

Generally the impact resistance of composites is affected considerably depending on the selection of fibre reinforcement and matrix. As an example, a study by Chuai et al. showed that adding untreated softwood fibres as reinforcement to polypropylene led to reduction of impact strength with increasing fibre content. However, treatment of fibres in order to improve adhesion between fibre and matrix caused either a much smaller reduction in impact resistance or even an increase in some composites with different compatibilising treatment [3].

The decrease of impact resistance between the fibre content of 20% and 30% in the PLA3001D/Jute can be explained by comparing SEM images of these composites (Figure 29). As shown in these pictures some jute fibres are in direct contact with other fibres, and in other words are not completely surrounded by polymer matrix. As a result, less energy was absorbed

during impact. Impact strength values for different types of fibres (Cotton, and Jute) to reinforce PLA 2002D can be found in Table 6.

Table 6. Impact Properties of PLA 2002D Based Composites Reinforced with Cotton and Jute Fibres.

Material	Impact Strength (J/m)	STD
PLA 2002D/Cotton/IM (wt. %)		
100/0/0	28.7	2.8
90/10/0	26.7	2.6
80/20/0	34.2	3.7
70/30/0	33.9	3.2
87/10/3	33.3	3.4
77/20/3	33.7	4.1
67/30/3	52.6	7.3
PLA 2002D/Jute/IM (wt. %)		
100/0/0	28.7	2.8
90/10/0	24.2	0.8
80/20/0	19.7	2.6
70/30/0	23.7	0.7
60/40/0	25.2	0.8
87/10/3	30.1	1.1
77/20/3	27.3	1.0
67/30/3	30.3	0.9
57/40/3	32.2	1.0

An important point to note is that beyond certain fibre content, there is no improvement in the impact properties. This point is different for different composites, and appears to be between higher than 40% of fibres for these composites. Table 6 also demonstrates that the impact strength of the PLA/cotton composite is more promising than PLA/Jute composites.

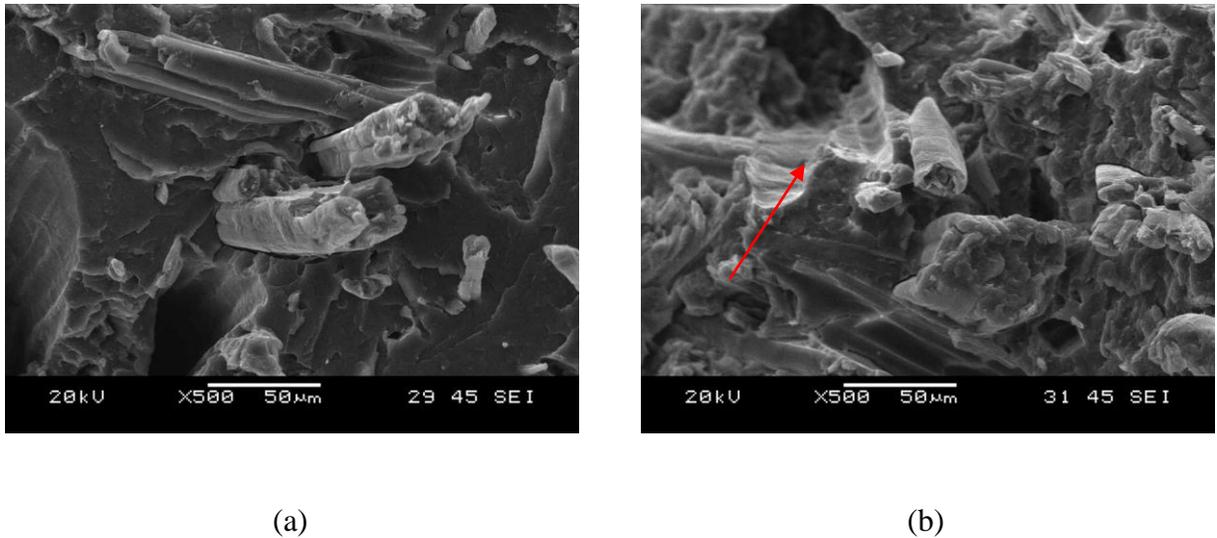


Figure 29. Detailed pictures of the fracture surface of the PLA3001D/Jute composite with a mass proportion of (a) 20%, and (b) 30%.

### 5.1.2 FLEXURAL TEST

The flexural properties of the PLA matrix and natural fibre PLA based composites are explained in this section. Effects of using 2 different natural fibres (jute, and cotton fibre), and different grades of PLA (2002D and 3001D), increasing the fibre content, and also addition of biomax strong impact modifier on the flexural properties of the composites are summarized in the figures of this chapter.

Figure 30 shows how increasing cotton fibre content from 10% to 30% can affect the flexural strength of the composites based on PLA 2002D. As it can be seen from the bar chart, increasing fibre-mass proportion from 10% to 20% increases the flexural strength significantly, when there is no impact modifier in the composite, however increasing the fibre content to 30% led to a decrease in the flexural strength. When impact modifier is included in the composite, the trend is different. As an example, increasing the fibre weight percentage from 20% to 30%

improves the flexural strength, while comparing composites with 10% and 20% plant fibre does not show any difference in this property.

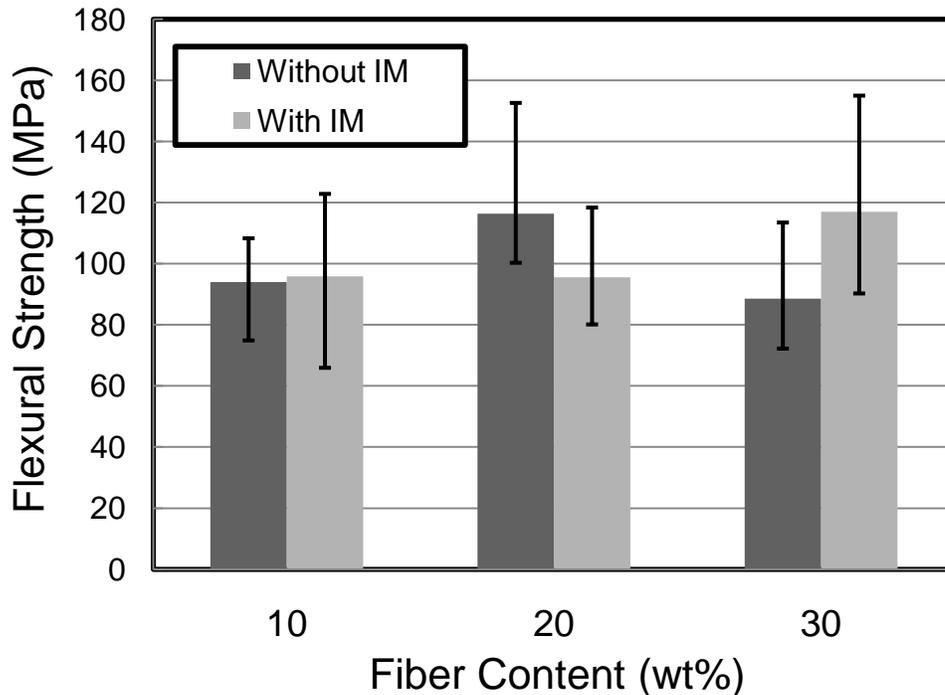


Figure 30. Flexural Strength of PLA 2002D/Cotton Fibre Composites.

Further investigation is also done on the effects of adding cotton fibres to PLA 3001D (with and without impact modifier). Figure 31 shows the obtained results of the flexural test on the composite materials. As it can be seen this figure does not include composites containing cotton fibres more than 20%. The reason is the failure of the compression moulding system to make the samples of high cotton fibre content, as discussed in chapter 3.

This graph shows that as the cotton fibre content goes up from 10% to 20%, the flexural strength of the composites decreases. The reason could be the result of less than sufficient adhesion between the cotton fibres and the biopolymer matrix. As shown in Figure 31, same

trend is observed for composite with and without impact modifier. Comparing results with neat PLA, also shows that increasing cotton fibre mass proportion led to a decrease in flexural strength (Table 7).

Table 7. Flexural Properties of Cotton Fibre Reinforced PLA.

Material	Flexural Strength ( MPa)	Flexural Modulus ( GPa)
PLA 2002D/Cotton/IM (wt. %)		
100/0/0	126	3.5
90/10/0	94	3.6
80/20/0	116	4.6
70/30/0	88.6	4.8
87/10/3	95.9	3.2
77/20/3	95.6	3.8
67/30/3	117	5.7
PLA 3001D/Cotton/IM (wt. %)		
100/0/0	131	3.7
90/10/0	106	4.5
80/20/0	85	4.5
87/10/3	95.2	4.1
77/20/3	93.2	4.2

Figure 32 explains the effects of increasing jute fibres on the PLA 2002D based composites. As it can be seen, increasing fibre content from 10% to 20% does not affect considerably the flexural strength of the unmodified composites. But comparing results of composites reinforced with 20% and 30% jute fibre, a significant increase can be observed.

The flexural strength and modulus of neat PLA and PLA/Cotton based composites are summarized in Table 7. The given values explain that addition of cotton fibres reduces the composites strength, while the flexural modulus improves significantly.

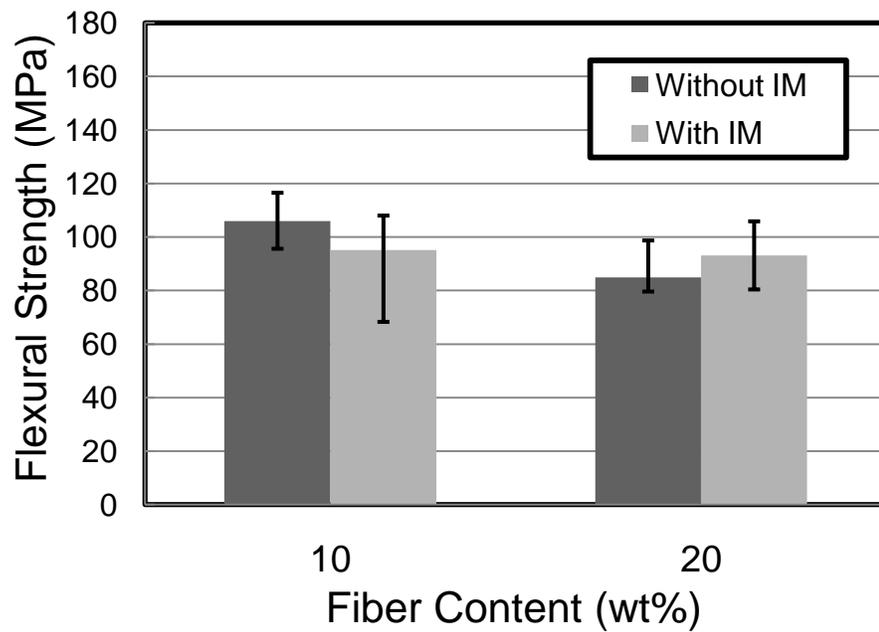


Figure 31. Flexural Properties of PLA 3001D/Cotton Fibre Composites.

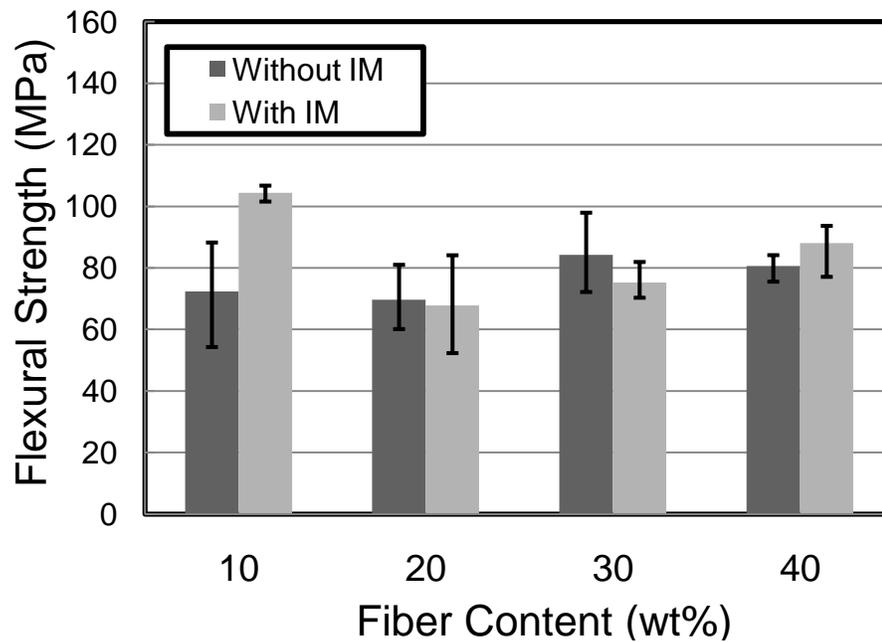


Figure 32. Flexural Strength of PLA 2002D/Jute fibre composites.

The results for 30% and 40% jute fibre content shows that the highest flexural strength is obtained at 30% fibre addition. Investigation on the effects of fibre content on the flexural properties, when the composites are modified with 3% of impact modifier is also presented in this figure. The graph simply shows that increasing fibre content from 20% to 40% led to a gradual increase in the flexural strength of the biocomposites. Whereas changing fibre mass proportion from 10% to 20% does not show the same effect.

Effects of increasing jute fibre content and addition of biomax impact modifier are shown in Figure 33.

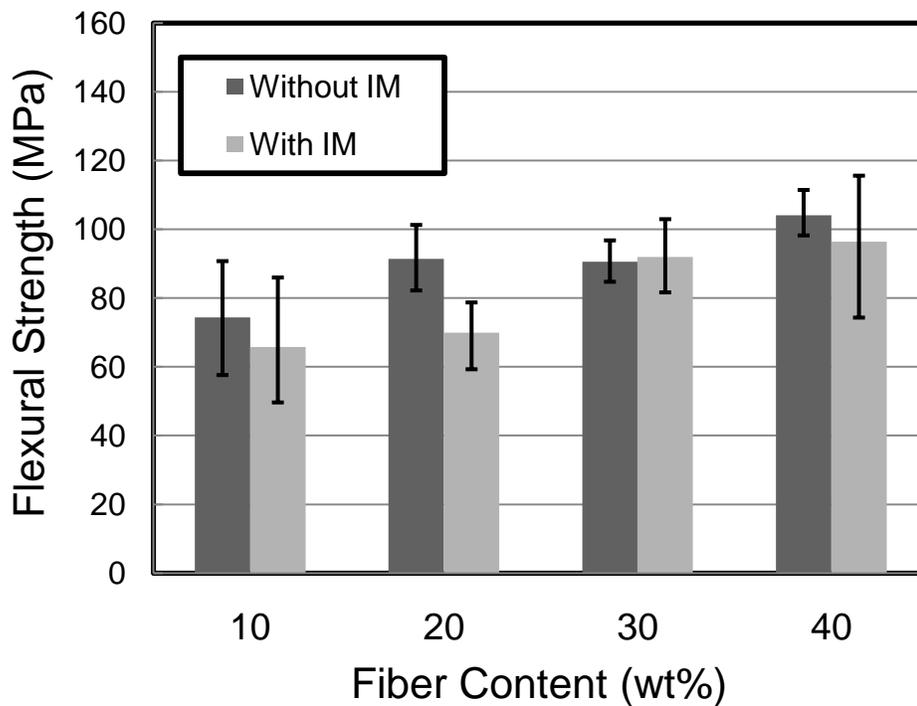


Figure 33. Flexural Strength of PLA 3001D/Jute fibre composites.

The results show that when PLA 3001D is reinforced with more jute fibres, an improvement in the flexural strength of the composites can be gained. The composite shows

same trend when impact modifier is added to the composites. The other observation is that addition of biomax strong 120 did not improve the flexural strength. Error bars on the graphs indicate upper and lower values.

Effects of adding impact modifier, as well as increasing the natural fibre content in composites on the flexural moduli are also investigated.

As shown in Figure 34, increasing cotton fibre up to 30% led to a considerable increase in the modulus of elasticity of the composite materials. The increase in the value of modulus of PLA indicates that the applied stress transferred from the PLA matrix to the stiffer fibre.

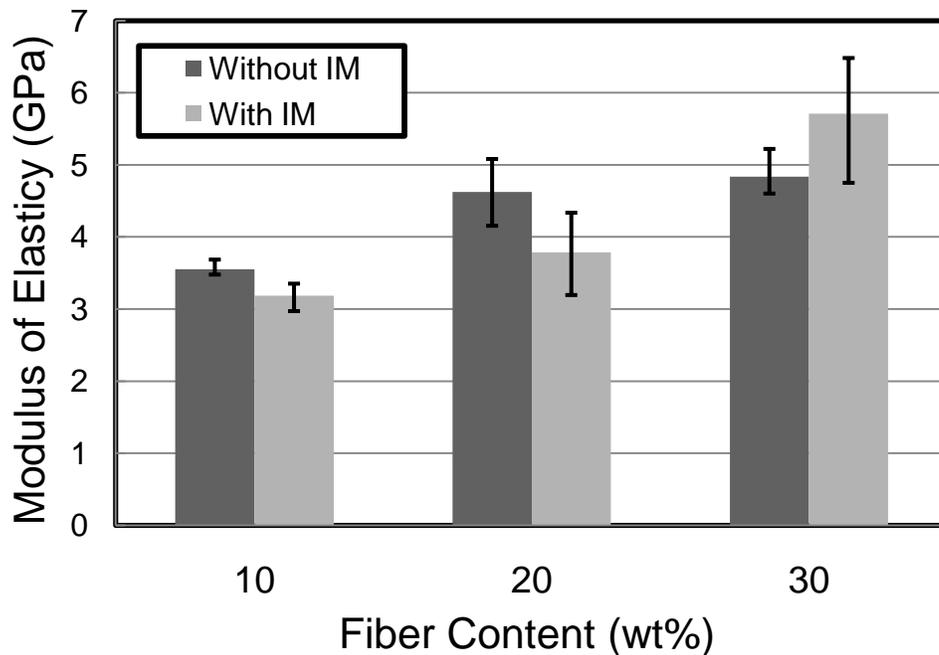


Figure 34. Modulus of Elasticity of PLA 2002D/Cotton Fibre Composites.

Figure 34 also explains that natural fibre reinforced composites which are modified by addition of biomax strong behave similar to the unmodified composites. In the composites containing 10% and 20% of cotton fibres addition of impact modifier caused a reduction in the

flexural modulus, whereas composites with 30% cotton fibres show a different behavior. In other words, addition of only 3% impact modifier to the polymers reinforced with 30% cotton fibre has a considerable effect on the modulus of elasticity of the composites.

To investigate the effects of increasing cotton fibres from 10% to 20% on the modulus of elasticity of composites based on PLA 3001D, Figure 35 illustrates that as the fibre content changes from 10% to 20%, no increase in the flexural modulus can be gained. The other important point in this graph is how the addition of biomax strong led to a reduction in the value of flexural modulus.

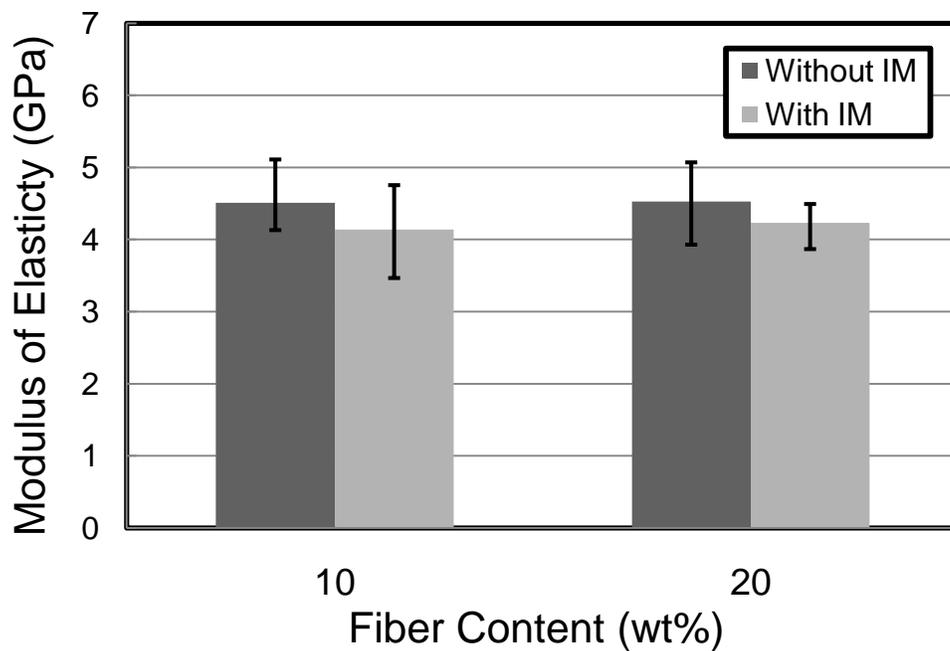


Figure 35. Modulus of Elasticity of PLA 3001D/Cotton Fibre Composites.

Figure 36 indicates how increasing the amount of jute fibres can affect the flexural modulus of composites made of PLA polymer matrix (Grade 2002D). It also shows that influence of addition of biomax strong does not improve the flexural modulus of the composites.

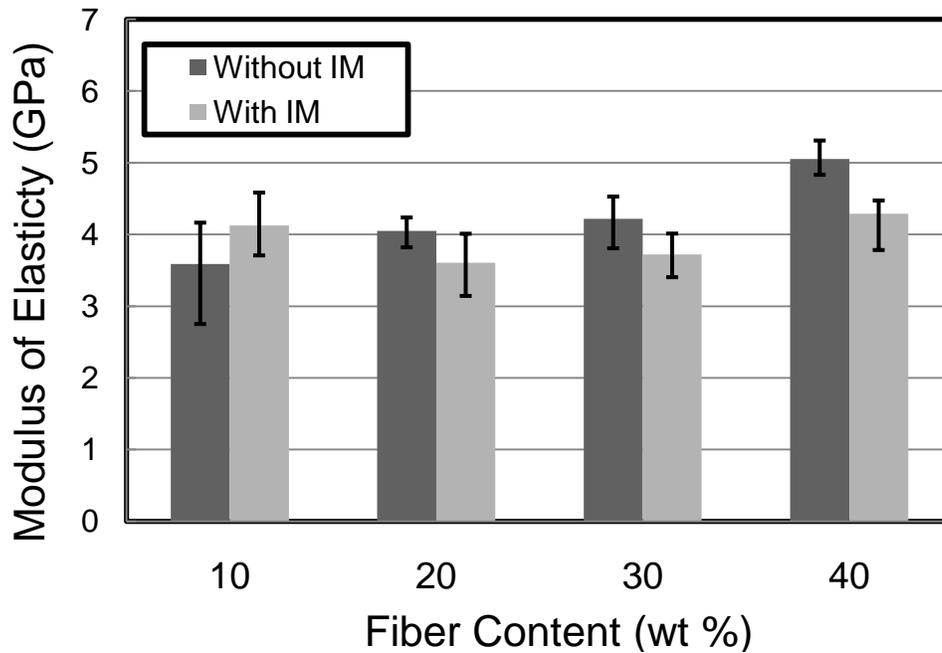


Figure 36. Modulus of Elasticity of PLA 2002D/Jute Fibre Composites.

Using the results shown in the Figure 36, it can be observed that flexural modulus increases significantly by increasing jute fibre mass proportion. Comparing composites with and without biomax impact modifier it is notable that in most of the cases (20% to 40% jute fibres), its addition led to a decrease in modulus of elasticity of the biocomposites. However, an opposite trend is observed in the biopolymers reinforced with 10% jute fibre.

Further investigation on adding jute fibre to a different grade of PLA (3001D) is done. The obtained results from flexural tests are shown in Figure 37. This figure shows that increasing flexural modulus is possible by increasing jute fibre amounts used as reinforcement in the composite samples. Elastic modulus of the composites with biomax modifier also show same trend as the unmodified composites. It can also be observed that presence of biomax modifier leads to a decrease on the composites modulus, except composite with 30% of jute fibre in it.

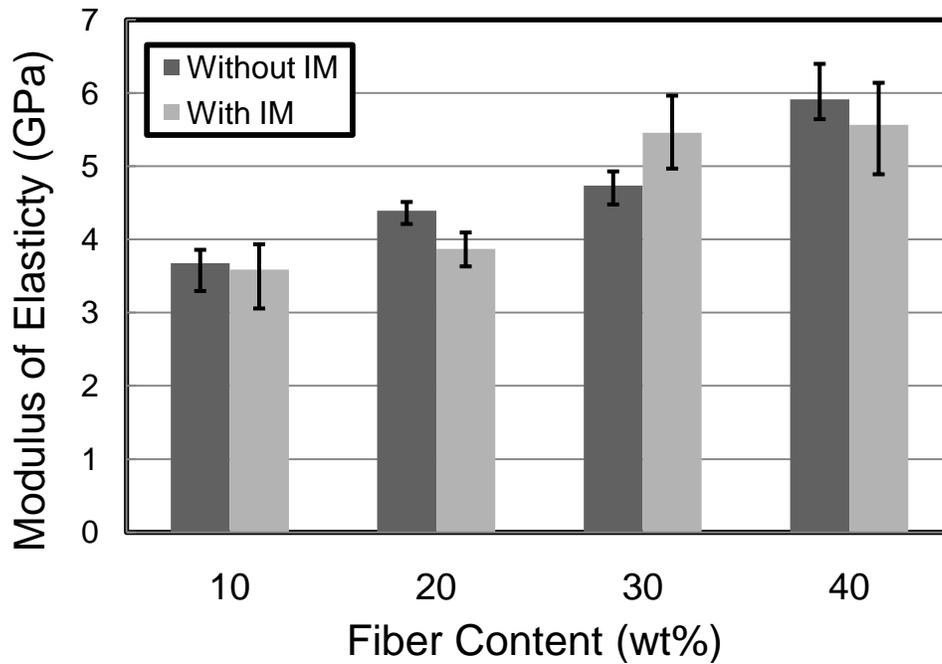


Figure 37. Modulus of Elasticity of PLA 3001D/Jute Fibre Composites.

The pure PLA 2002D has a flexural strength of 126 MPa and a modulus of 3.5 GPa. As presented in Table 8, even the addition of 10% jute fibres increased the flexural modulus. As the amount of fibres in the composite increases (to 40%), the modulus of the PLA increased proportionately, this indicates that the applied stress transfers from the PLA polymer matrix to the stiffer fibre.

The other used polymer matrix (PLA 3001D) shows same trend as PLA 2002D, i.e. increasing jute fibres leads to a significant increase of the composite stiffness. Comparing two grades of PLA indicates that composites of PLA 3001D are stiffer than PLA 2002D. Furthermore, it can be seen that PLA 3001D composites have higher flexural strength. Addition of jute fibre (at 40% fibre mass proportion) improved flexural strength of PLA 3001D.

Table 8 also shows that amongst the jute fibre reinforced composites, the highest flexural modulus (5.9 GPa), and highest flexural strength (104 MPa) belong to PLA 3001D/40% Jute fibre composites.

Table 8. Flexural Properties of Jute Fibre Reinforced PLA.

Material	Flexural Strength ( MPa)	Flexural Modulus ( GPa)
PLA 2002D/Jute/IM (wt. %)		
100/0/0	126	3.5
90/10/0	72.3	3.6
80/20/0	69.7	4
70/30/0	84.2	4.2
60/40/0	80.6	5.1
87/10/3	104	4.1
77/20/3	67.8	3.6
67/30/3	75.3	3.7
57/40/3	88.1	4.3
PLA 3001D/Jute/IM (wt. %)		
100/0/0	131	3.7
90/10/0	74.3	3.7
80/20/0	91.4	4.4
70/30/0	90.6	4.7
60/40/0	104	5.9
87/10/3	65.8	3.6
77/20/3	70	3.9
67/30/3	92	5.5
57/40/3	96.4	5.6

As seen in Table 8, the trend of the flexural modulus of PLA/Jute composites was identical to the trend of PLA/Cotton modulus. For both PLAs, there is a significant increase in flexural modulus in the composites compared to that of neat PLA.

## 5.2 COMPARISON BETWEEN THEORETICAL AND EXPERIMENTAL RESULTS OF MODULUS OF ELASTICITY OF THE COMPOSITES

The theoretical and experimental results were compared using Rule of Mixture (ROM). The properties of a multiphase composite material are a weighted average (usually on the basis of volume) of the properties of the individual constituents. Two mathematical equations explain the relationship between the tensile modulus and the volume fraction of the components for the two-phase composite material. Modulus of elasticity should fall between  $E_1$  and  $E_2$  according to mixture rule as follows:

$$E_1 = E_f V_f + E_m (1 - V_f) \quad 5$$

$$E_2 = E_f E_m / [E_m V_f + E_f (1 - V_f)] \quad 6$$

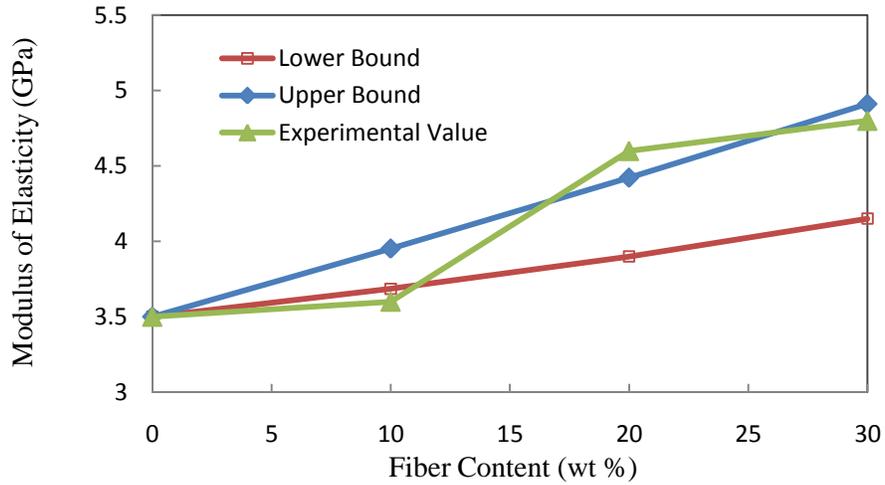
$$\rho_c = \rho_f V_f + \rho_m (1 - V_f) \quad 7$$

Where  $E_1$  and  $E_2$  are the elastic modulus of the longitudinal axis and perpendicular to the longitudinal axis, respectively.

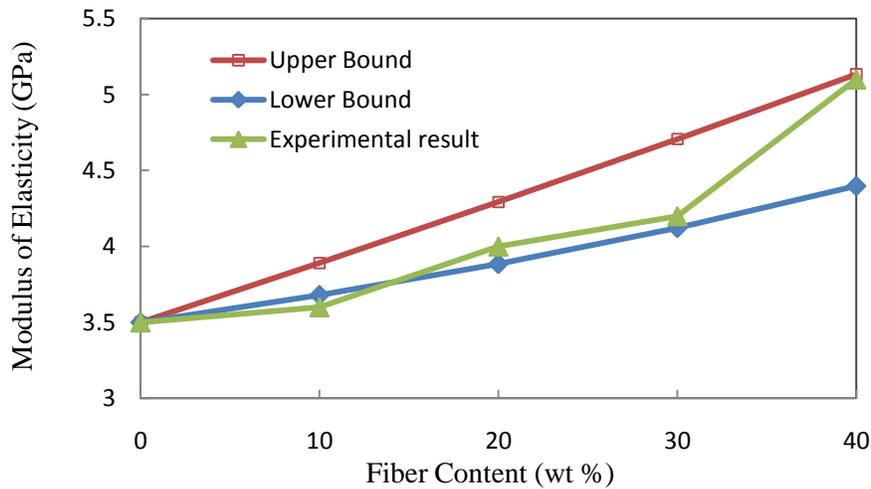
The volume fraction of the fibres ( $V_f$ ) was obtained knowing the mass of the constituents (M), and density of the fibre and matrix and composite ( $\rho$ ). Variation of Young's modulus with volume fraction of jute and cotton fibres demonstrates that rule of mixtures a relationship is followed (presented in Figure 38). The fall-off in modulus at the 20% could be a result of voids created during the composite manufacturing. Degradation of the PLA during processing is another possible reason of the small difference between the experimental and theoretical result.

The increased variation at 20% cotton addition to PLA could be due to the non-uniform mixing during compounding of the fibres and matrix. To get better dispersion of fibres in the PLA

matrix multiple processing was tried, but the polymer degraded, as a result of longer residence time in the extruder. Similar analysis was performed to compare modulus of elasticity of other composites, and satisfactory results were observed.



(a)



(b)

Figure 38. Variation of Young's Modulus of the PLA 2002D Based Composites with Volume Fraction of (a) Cotton Fibres, (b) Jute Fibres.

## 5.3 PHYSICAL PROPERTIES

The thermal and physical properties of composites derived from renewable origin, natural fibre reinforced biopolymer composites were investigated. As discussed earlier jute fibres and cotton fibres were used as reinforcement in the PLA polymer matrix. 2 different grades of PLA were also used (PLA 2002D, and PLA 3001D). Effects of addition of 3% biomax strong impact modifier on the thermo-physical properties of the composite materials also are studied. In this section obtained results of Differential Scanning Calorimetry (DSC), rheological properties, as well as surface morphology are explained and discussed.

### 5.3.1 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

As discussed in chapter 4, differential scanning calorimetry (DSC) is used in this study to investigate any possible effect of natural fibre content, impact modifier, and PLA grade on the thermal properties of the composite. Glass transition temperature ( $T_g$ ), crystallization ( $T_c$ ), and melting temperature ( $T_m$ ) can be monitored on DSC. Enthalpy of crystallization ( $\Delta H_c$ ), and melting ( $\Delta H_m$ ), as well as degree of crystallinity ( $X_c\%$ ) are calculated using the DSC curve.

Thermal scanning was carried out at a programmed rate of 10 °C/min from room temperature to 200 °C under constant nitrogen flow. After that the samples were cooled at rate of 10 °C/min, and data were evaluated by a computer. The first thermal scan used to melt the samples and remove any thermal history from the material. In this chapter, DSC plots were obtained from the second thermal cycle as it provides more accurate result for the thermal transitions such as melting temperature ( $T_m$ ) which is measured from the endotherm peak.

Figure 39 shows the DSC traces for PLA 3001D reinforced with 10% and 20% cotton fibres at second heating cycle to 200°C at a heating rate of 10 °C/min. It will be noted that both

composite materials are characterized by a glass transition temperature ( $T_g$ ), crystallization peak ( $T_c$ ) and melting peak ( $T_m$ ), typical of semi-crystalline polymers. Table 10 summarizes the detailed information of the values for these transitions in addition to crystallization enthalpy ( $\Delta H_c$ ), and melting enthalpy ( $\Delta H_m$ ) obtained from DSC analysis. Estimates of the degree of crystallinity ( $X_c\%$ ) for these two samples are also listed in this table, calculated using a the heat of fusion of the pure PLA crystal.

Comparing the melting enthalpy ( $\Delta H_m$ ) with the value of an infinitely large crystal ( $\Delta H_m^0$ ), the degree of crystallinity ( $X_c\%$ ) of the composites was calculated ( $X_c = \Delta H_m / \Delta H_m^0 \times 100\%$ ). The heat of fusion for a pure PLA crystal was taken as  $\Delta H_m^0 = 93 \text{ J/g}$  [27].

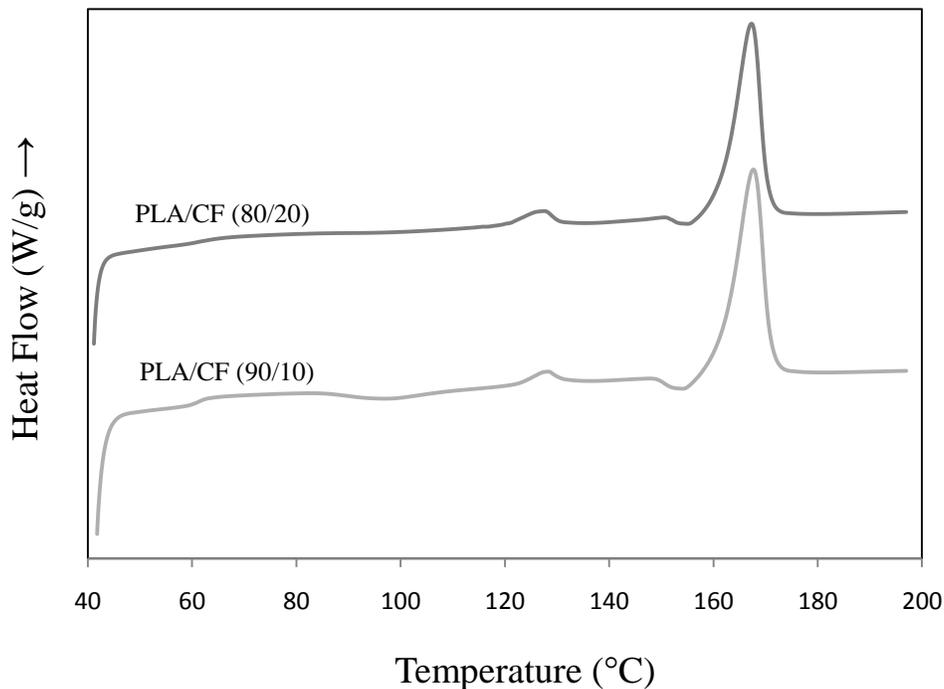


Figure 39. Heat-flow rate vs. temperature of composites of poly (lactic acid), PLA-2002D and different cotton fibre content without impact modifier, at heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$ .

Figure 39 explains that the  $T_g$  values of the composites increase slightly with increasing cotton fibre content, while changes in crystallization temperature is more visible. The obtained results for these two composites show that increasing crystallization temperature occurs when the natural fibre mass-proportion goes up. On the other hand, the melting peak does not change obviously with the addition of cotton fibre to the PLA matrix. Table 10 shows a small increase in the crystallization enthalpy and degree of crystallinity by adding more cotton fibre to PLA 3001D.

As mentioned earlier, crystallization of a polymer is another phenomenon which can be identified with the DSC plot. Above the glass transition point polymers have a lot of energy to move and form new arrangements. In other words, when they reach the right temperature, they gain enough mobility to move into well-ordered arrangements, which are called crystals. When this phenomenon happens and polymers make these crystalline orders, they give off heat. This event can be observed in Figure 58 as big dip in the plot of heat flow versus temperature.

In Figure 40 the PLA reinforced with 10% cotton fibre shows a smaller crystallization peak ( $\Delta H_c = -6.948$  J/g), and it shows a cold crystallization peak appearing at around 106.2°C. This indicates that the crystallization of this PLA (3001D) sample does not complete in the cooling cycle at 10°C/min.

Furthermore, the crystallization temperature of PLA shifts to a slightly higher temperature when higher content of cotton fibre is incorporated in the composite, indicating that the crystallization rate of PLA is improved with the presence of cotton fibre. The figure also explains that composites with more cotton fibre show higher melting point.

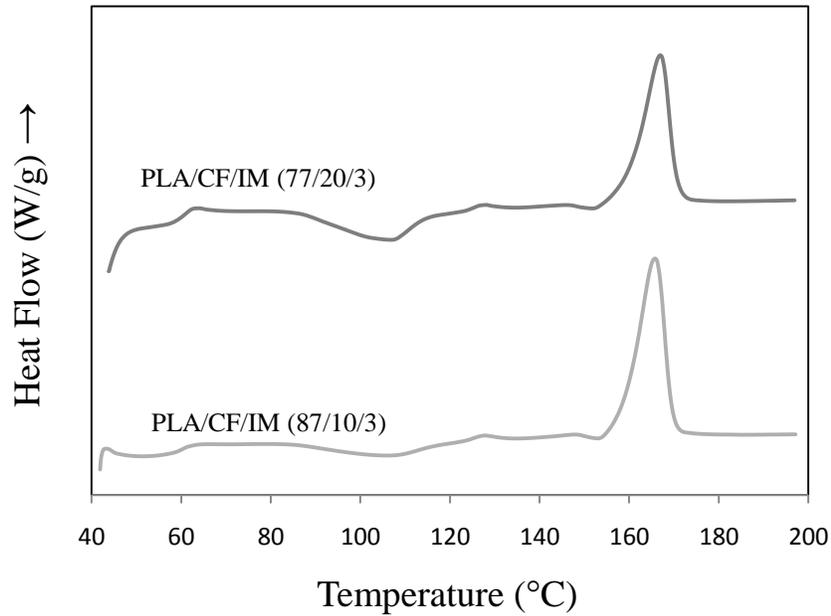


Figure 40. Heat-flow rate vs. temperature of composites of poly (lactic acid), PLA-2002D and different cotton fibre content with 3% impact modifier, at heating rate of 10 °C/min.

Figure 41 shows the effects of increasing jute fibre on the thermal properties of the poly lactic acid (PLA 2002D) based composites. As the DSC curves show, the glass transition peak shifts to the higher temperatures as the jute fibre content increases. The other significant point of these graphs is that using more jute fibre as reinforcement leads to a considerable increase in the crystallization temperature of the composites. However, the crystallization enthalpy decreases with increasing jute fibre mass proportion. No cold crystallization peak is seen in the DSC heating curves of the neat PLA (PLA 2002D), signifying that PLA almost fully crystallizes during the cooling cycle at 10°C/min. Table 9 includes the details of the values of the obtained results from the DSC curves.

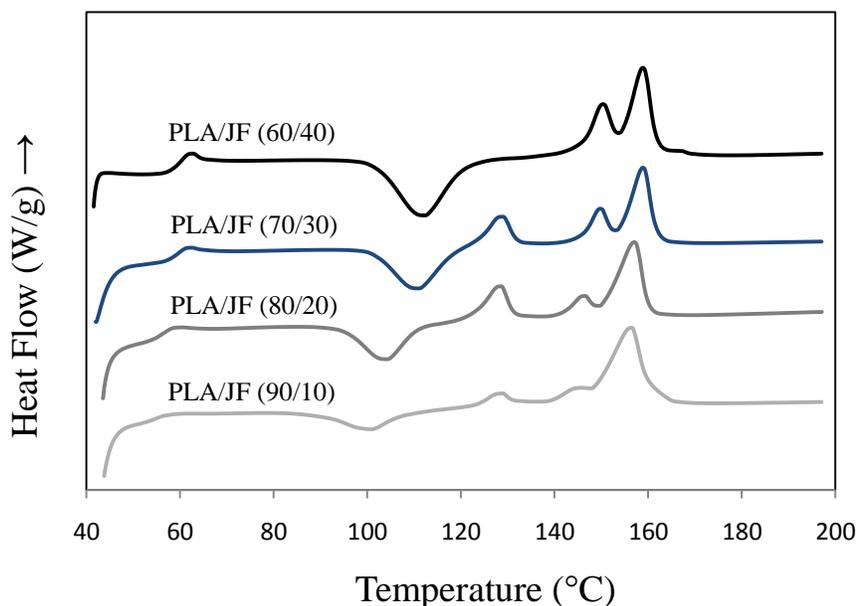


Figure 41. Heat-flow rate vs. temperature of PLA 2002D/jute fibre composites at heating rate of 10 °C/min.

Moreover, the melting temperature of the composites shows a little increase when higher content of jute fibre is used in the composites.

Table 9. Detailed Information Obtained from DSC Thermal Analysis of PLA 2002D Based Composites.

Material PLA 2002D/JF/IM (wt. %)	T <sub>g</sub> (°C)	T <sub>c</sub> (°C)	ΔH <sub>c</sub> (J/g)	T <sub>m</sub> (°C)	ΔH <sub>m</sub> (J/g)	X <sub>c</sub> %
90/10/0	57.6	100.78	6.463	156.32	24.7	6.9
80/20/0	57.9	104.35	13.67	156.94	20.09	15
70/30/0	60.7	111.3	17.3	158.86	20.29	19
60/40/0	60.8	112.28	24.85	158.63	28.68	27
87/10/3	60.3	110.54	19.52	159.07	23.64	21
77/20/3	60.6	113.7	24.54	162.2	28.36	23
67/30/3	60.9	117.3	13.81	161.1	22.3	15
57/40/3	60.9	119.6	14.42	159.1	22.32	16

Effects of adding impact modifier and also increasing jute fibre content on the glass transition temperature, crystallization, and melting temperature of the composites are shown in Figure 42. As it can be seen from the figure, crystallization temperature increases with increasing the jute fibre content. While the glass transition point shows a slight change with increasing the jute fibre. Comparing the transition temperatures between composites with and without impact modifier explains that presence of biomax strong has a positive effect on increasing the glass transition temperature. The same trend is observed for crystallization and melting temperatures of the composites. In other words, addition of impact modifier leads to an increase in these values.

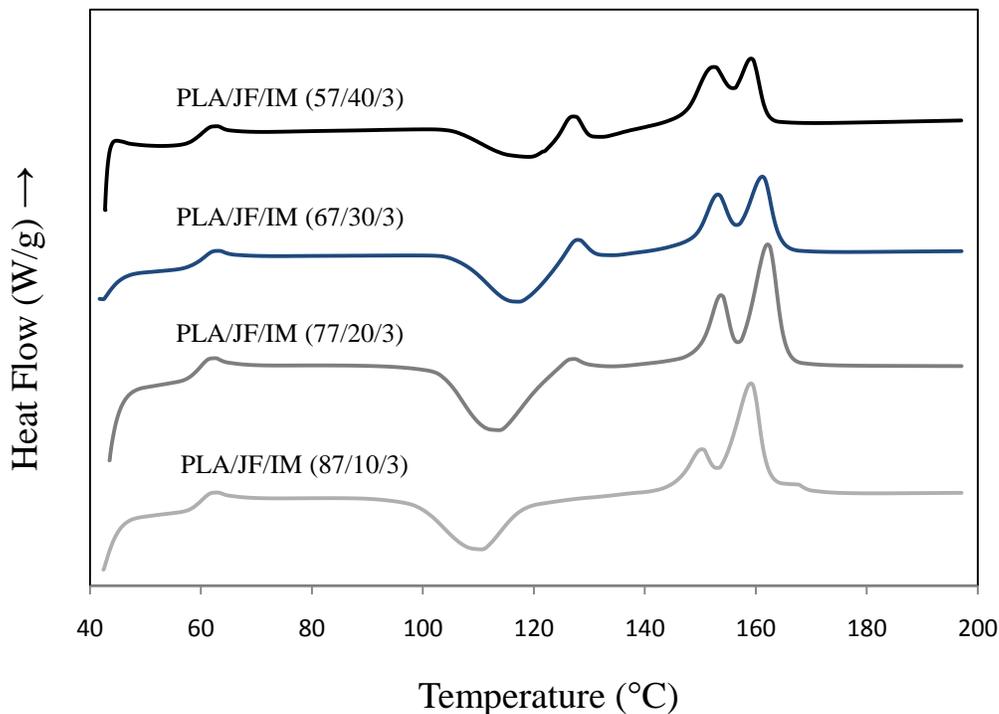


Figure 42. Heat-flow rate vs. temperature of PLA 2002D/jute fibre/impact modifier composites at heating rate of 10 °C/min.

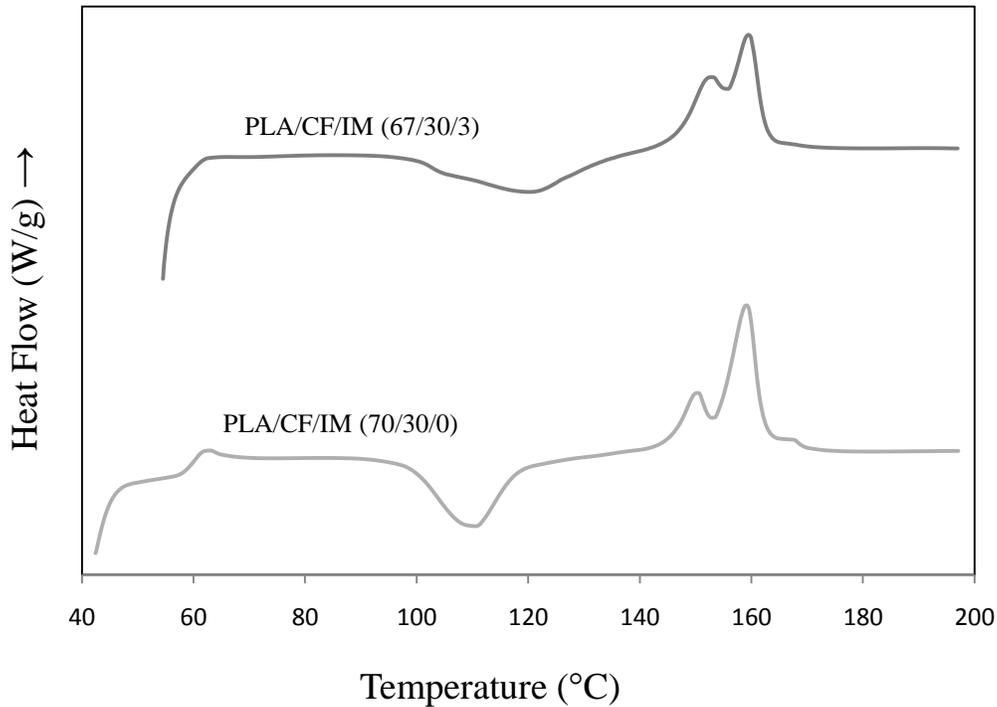


Figure 43. Heat-flow rate vs. temperature of composites of poly (lactic acid), PLA-2002D and 30% cotton fibre with and without impact modifier, at heating rate of 10 °C/min.

Figure 43 specifically shows the effects of addition of 3% biomax impact modifier to the composites on the thermal transition temperatures. The composites contain PLA 2002D reinforced with 30% cotton fibres. Adding impact modifier shifts the glass transition temperature, crystallization, and melting peaks to the higher values.

Furthermore, to investigate the impact modifier effect on the thermal properties of PLA 2002D/jute fibre composites DSC curves are shown in Figure 44. By keeping the jute fibre content constant while adding 3% of biomax strong 120, composites does not show any difference in glass transition and melting temperature in these two composites.

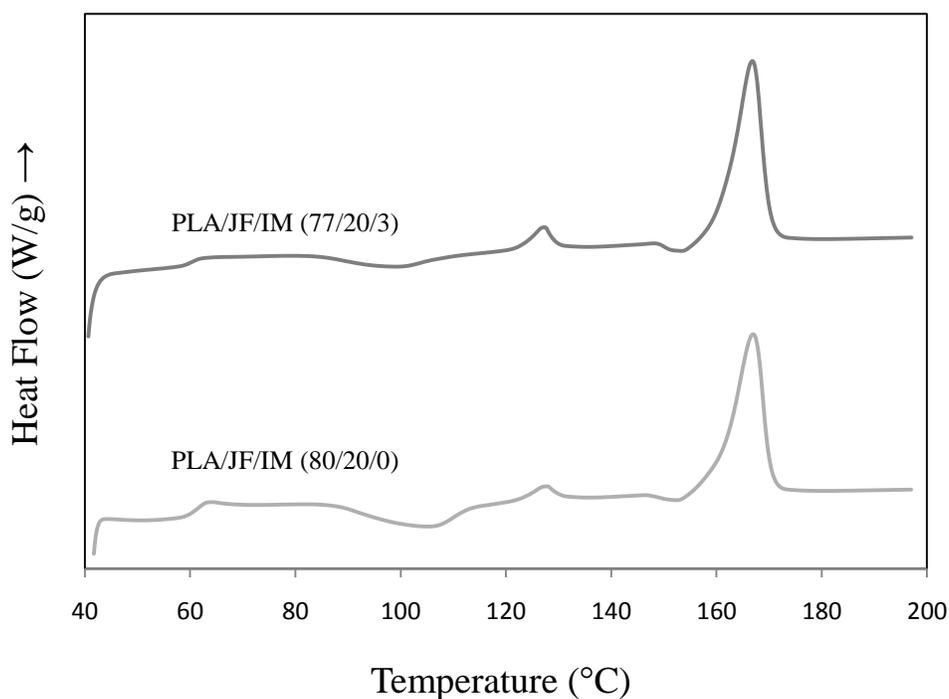


Figure 44. Heat-flow rate vs. temperature of composites of poly (lactic acid), PLA-3001D and 20% jute fibre with and without impact modifier, at heating rate of 10 °C/min.

Table 10. Detailed Information Obtained from DSC Thermal Analysis of PLA 3001D Based Composites.

Material PLA 3001D/cotton/IM (wt. %)	$T_g$ (°C)	$T_c$ (°C)	$\Delta H_c$ (J/g)	$T_m$ (°C)	$\Delta H_m$ (J/g)	$X_c$ %
90/10/0	63.63	97.11	2.768	167.7	42.51	2.98
80/20/0	64.27	101.4	2.946	167.3	35.39	3.17
87/10/3	62.49	106.2	6.948	165.8	36.44	7.47
77/20/3	62.22	106.7	12.81	166.9	31.81	13.8

Table 10 shows that as the cotton fibres content increase the degree of crystallinity of the composites also increase. Generally when a semi-crystalline polymer goes under the

measurement conditions discussed in chapter 4, DSC thermogram (second heating cycle) shows a glass transition, crystallization exotherm and melting endotherm peaks. According to Figure 45 the glass transition temperature of neat PLA ( $T_{g,PLA}$ ) is found to be 63.4 °C, and the melting temperature of 171.8 °C. In this figure the monitored cooling and second heating processes are represented.

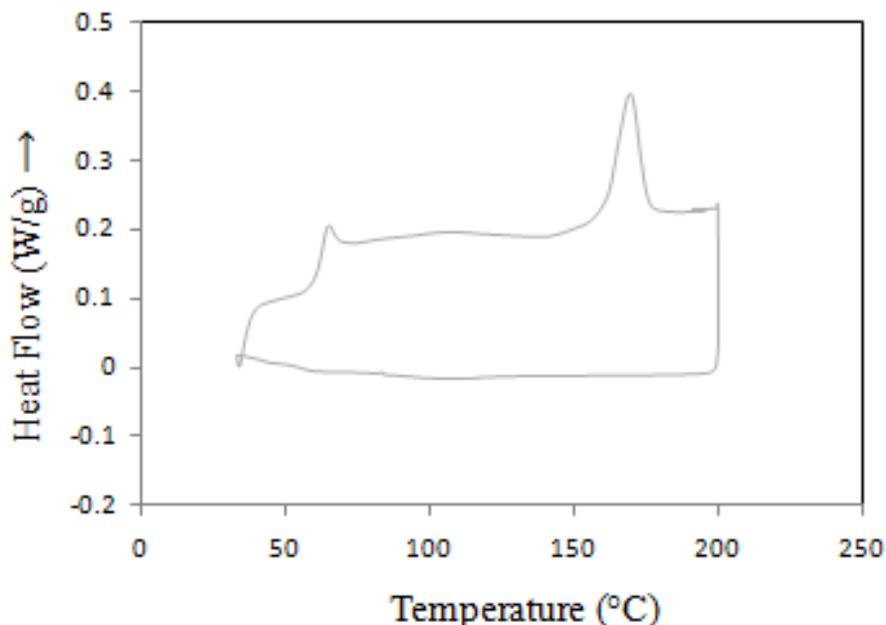


Figure 45. DSC curve of PLA 2002D showing cooling and heating cycles at 10 °C/min ramp.

Two important factors control the crystallization process in the polymeric composites. First main factor are the additives which have a nucleating influence on the crystallization, improve the crystallization, and so they effect positively on the degree of crystallinity. Second factor are the additives, which effect negatively on the crystallization process. They decrease the movement and diffusion of polymeric molecular chains to the surface of the growing polymer crystal in the composite materials. Consequently they result in a reduction in the crystallization rate. Due to the nucleation effect of cotton fibres, the crystallization rate was improved

noticeably with increasing the natural fibres content Table 10. However, the increase of the crystallization temperature for these composites is a little. The reason could be the decreased polymer diffusion caused by presence of these fibres in composites [30].

As it is observed from the flat heat flow in the cooling cycle of the DSC curve, the PLA sample does not crystallize during cooling at 10 °C/min ramp. Instead, when 20% of jute fibre adds to PLA, the sample crystallizes a little in the cooling cycle. However, the major crystallization occurs during second heating thermogram, as indicated by the exotherm peak in Figure 46.

The observed dip of crystallization occurs because a small amount of heat is needed from the outside to keep the temperature of the polymer rising. From a DSC plot such as shown in Figure 46, the crystallization temperature, the enthalpy of crystallization for the polymer can be determined. The latent energy of crystallization phenomenon can be identified by measuring the area of the dip. It is clear that if the tested polymer is 100% amorphous such a dip would not be seen. Crystallization process is an exothermic transition because the polymer gives off heat when the crystallization happens. For this sample, the crystallization occurs between 103 and 129.8 °C, with peak temperature at  $T_c = 113.7$  °C. The enthalpy of crystallization ( $\Delta H_c$ ) is measured to be  $\Delta H_c = 24.54$  J/g, based on the exotherm heat flow. The degree of crystallinity  $X_c$  is determined to be  $X_c = \Delta H_c / \Delta H_m^0 = 23$  %, using 93 J/g as the enthalpy of melting of an infinitely large PLA crystal [27].

A big peak which can be observed in the plot is due to the extra heat flow during melting. An additional piece of information which can be determined from the plot (shown in Figure 46) is the melting peak. The melting enthalpy can also be measured by measuring the area of this

peak. Because melting of the polymer occurs when the heat is added to the material to make it melt, hence this phenomenon is seen as an endothermic transition.

Therefore, for this sample, melting of this regained crystallinity follows immediately, indicated by the endotherm with peak temperature  $T_m = 162.2 \text{ }^\circ\text{C}$  and melting enthalpy  $\Delta H_m = 28.36 \text{ J/g}$  (Figure 46).

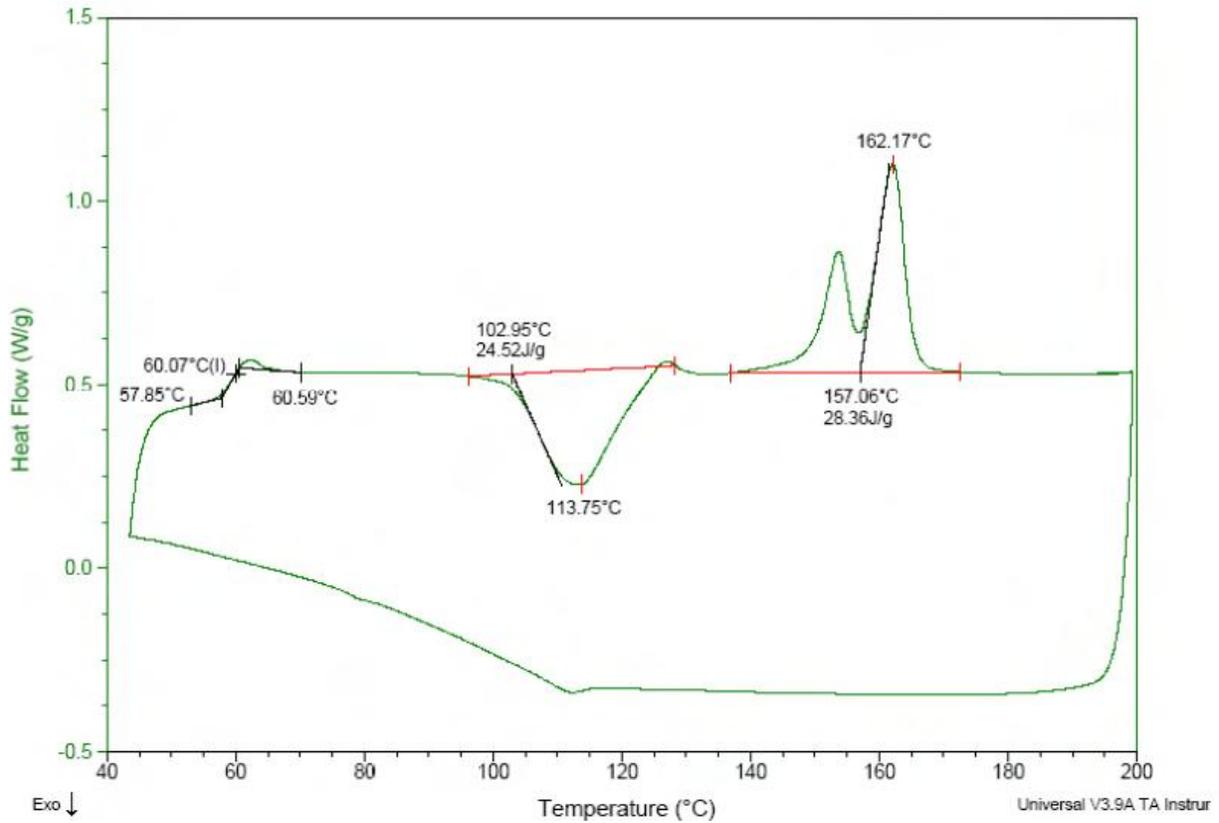


Figure 46. Detailed Information on the DSC Curve of PLA 2002D/20% Jute Fibre/3% IM Composite.

### 5.3.2 RHEOLOGY

As it has been discussed in chapter 4, in this work, the rheological properties of composites such as storage modulus ( $G'$ ), loss modulus ( $G''$ ), complex coefficient of viscosity

( $\eta^*$ ), and viscosity ( $\eta$ ) of the composites are determined using dynamic strain sweep, and dynamic frequency sweep tests. The influences of addition of natural fibre to the composites on rheological behaviour of composites are investigated. The linear viscoelastic region is also determined for different composites with different fibre contents, and PLA.

The general purpose of the rheology experiments is to have more understanding of the composites melt rheological properties in different practical conditions.

- Dynamic strain sweep

In dynamic strain sweep test the materials response to increasing deformation amplitude (strain) can be monitored at a constant temperature and frequency value. The most important purpose of this test is to identify linear viscoelastic region.

Figure 47 to Figure 54 explains how the storage modulus ( $G'$ ) of the composites changes by increasing the shear strain. As it can be seen increasing the shear rate from 0.01% to 10% leads to a decrease in storage modulus of the composite materials. It is also observed that storage modulus increases when higher natural fibre is used in the composite material.

Furthermore, these graphs show that the linear viscoelastic region is seen in the shear strain range of 0.01% to 0.1%. In other words in this section of the graphs the storage modulus does not change with increasing the shear strain. However, increasing the fibre content does not have any effect on this region.

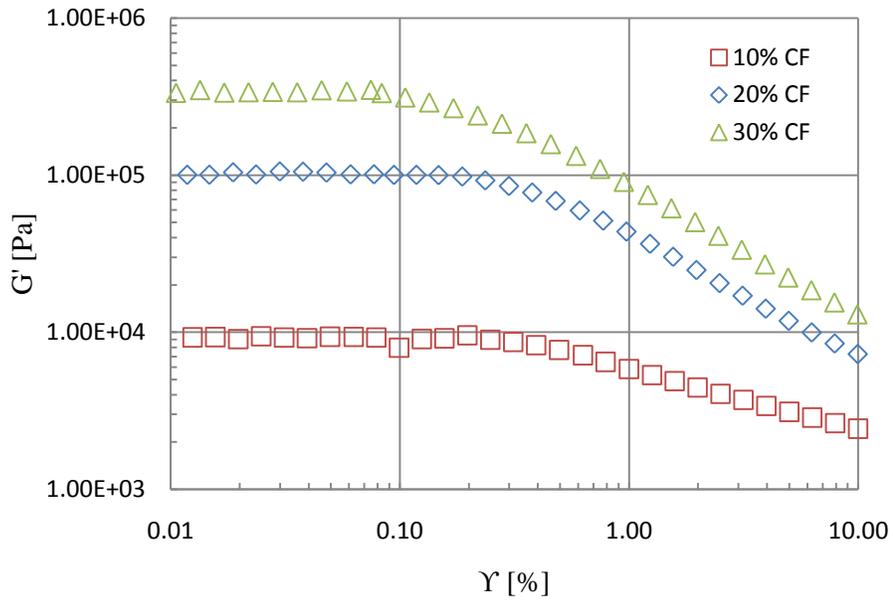


Figure 47. Storage Modulus of PLA 2002D Based Composites with Different Cotton Fibre Content, vs. Shear Strain.

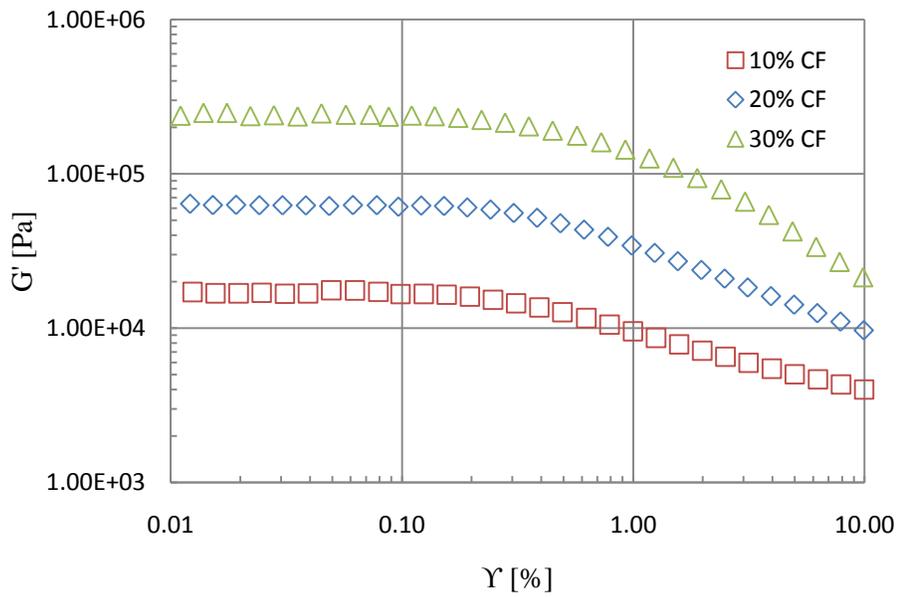


Figure 48. Storage Modulus of PLA 2002D Based Composites with Different Cotton Fibre Content and Impact Modifier, vs. Shear Strain.

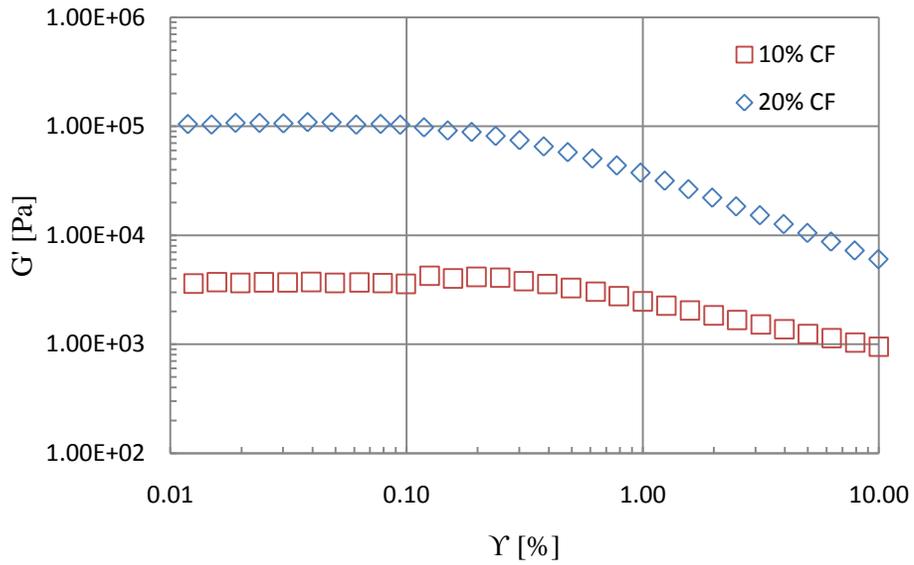


Figure 49. Storage Modulus of PLA 3001D Based Composites with Different Cotton Fibre Content, vs. Shear Strain.

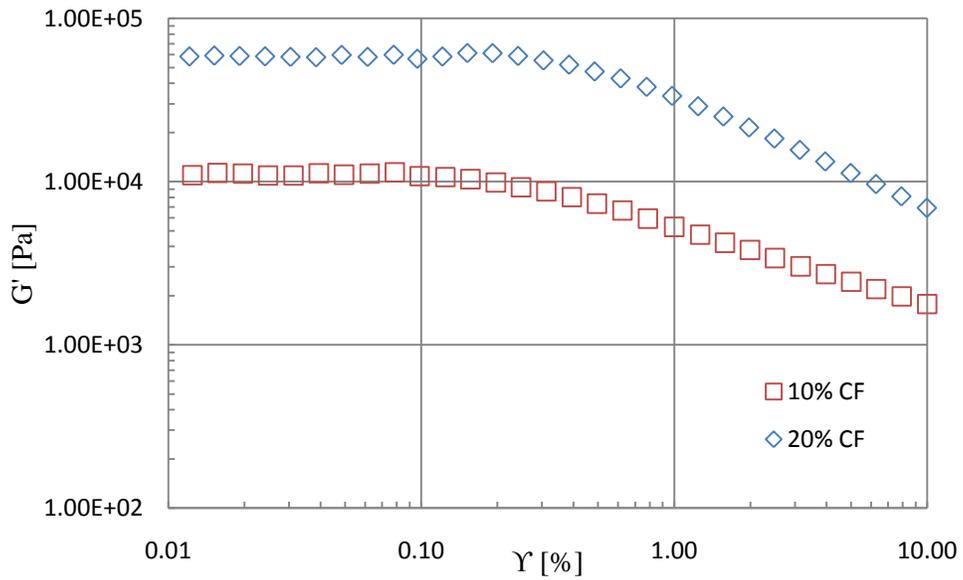


Figure 50. Storage Modulus of PLA 3001D Based Composites with Different Cotton Fibre Content and Impact Modifier, vs. Shear Strain.

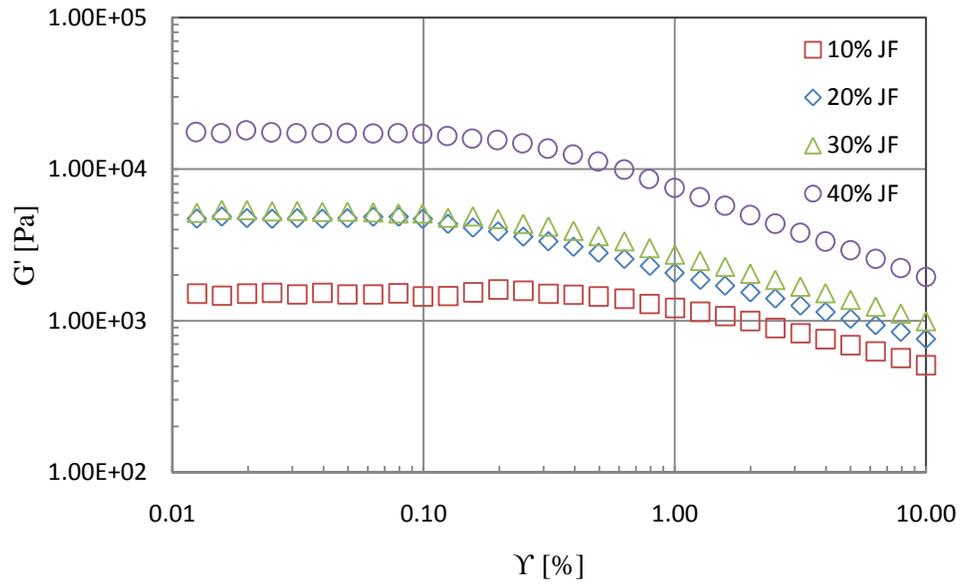


Figure 51. Storage Modulus of PLA 2002D Based Composites with Different Jute Fibre Content, vs. Shear Strain.

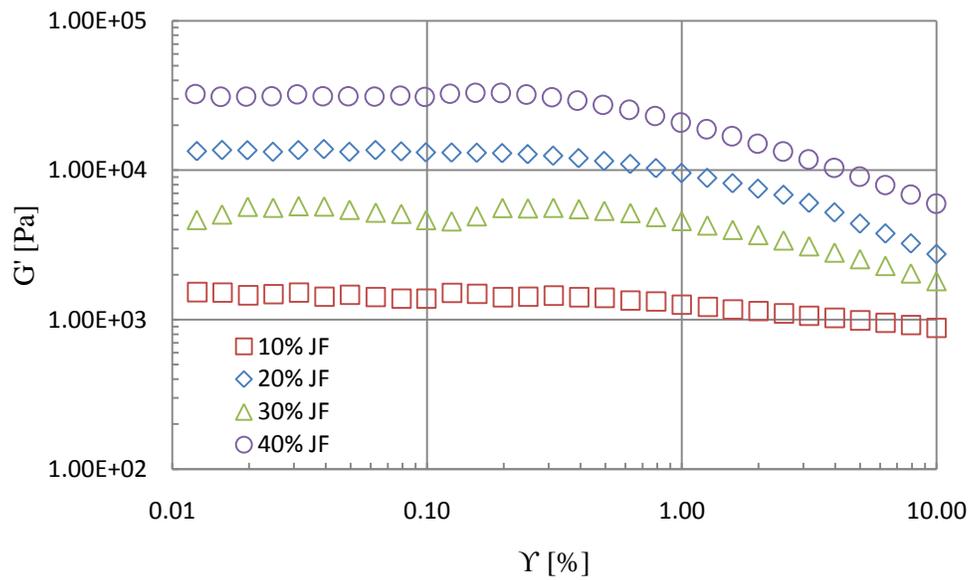


Figure 52. Storage Modulus of PLA 2002D Based Composites with Different Jute Fibre Content and Impact Modifier, vs. Shear Strain.

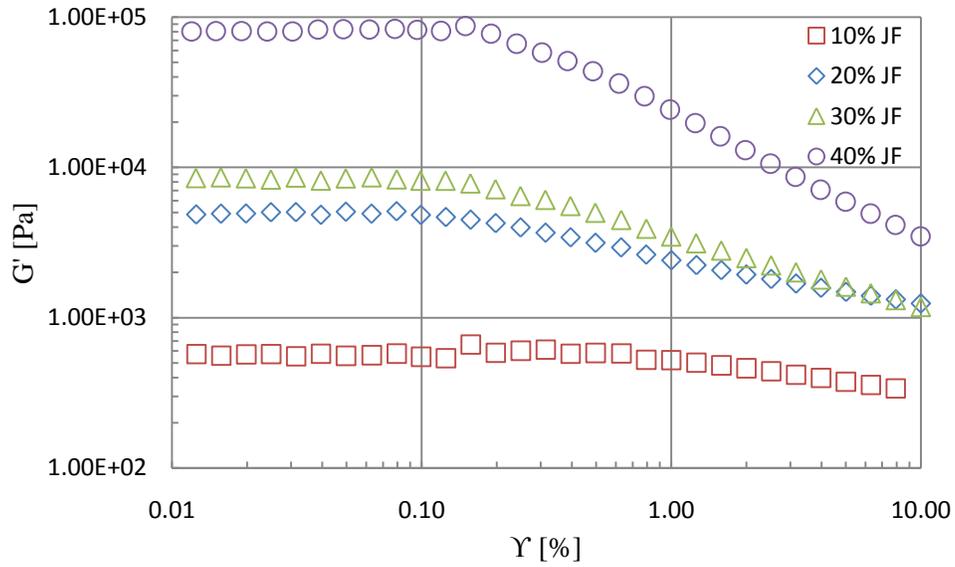


Figure 53. Storage Modulus of PLA 3001D Based Composites with Different Jute Fibre Content, vs. Shear Strain.

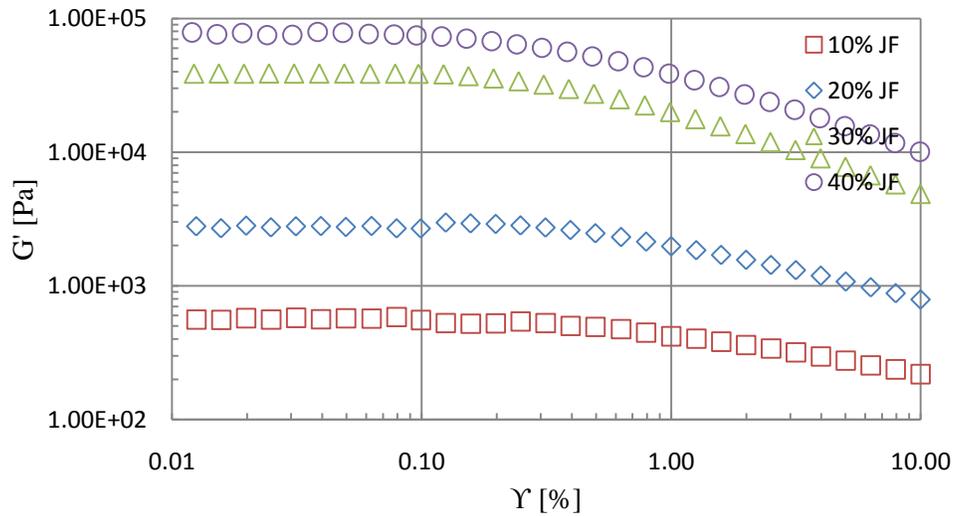
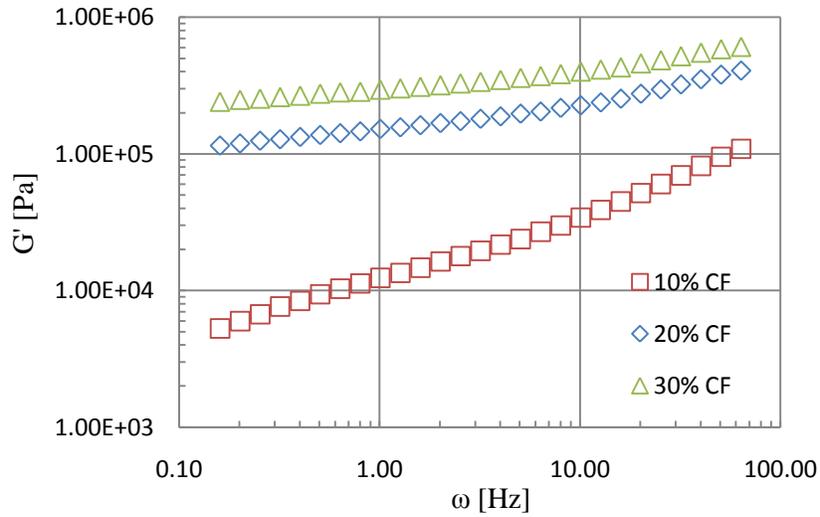


Figure 54. Storage Modulus of PLA 3001D Based Composites with Different Jute Fibre Content and Impact Modifier, vs. Shear Strain.

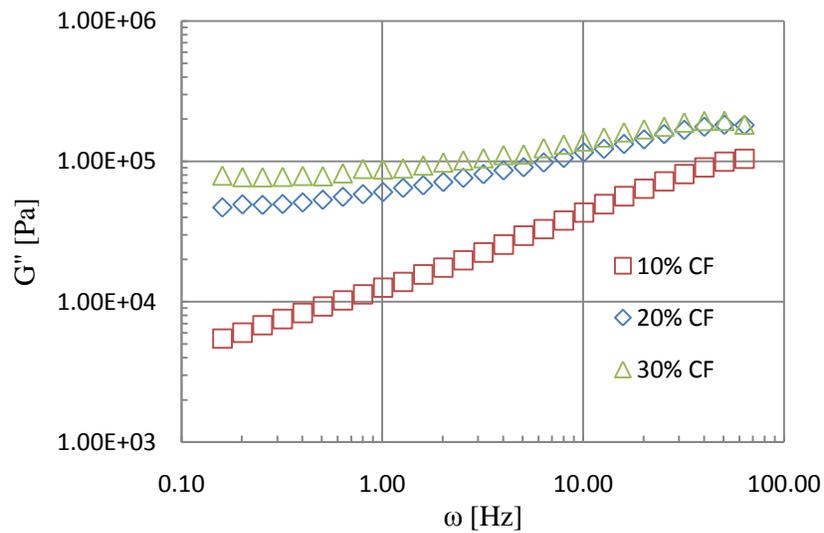
After determining the LVR, two strain values of 0.1% and 5.0%, in the linear region and non-linear region, respectively selected for the dynamic frequency sweep test.

- Dynamic frequency sweep

Figure 55 in this section explain the changes in storage modulus ( $G'$ ), loss modulus ( $G''$ ), and complex coefficient of viscosity ( $\eta^*$ ) of the Cotton fibre reinforced PLA composites versus angular frequency ( $\omega$ ) at constant shear strain of 0.1%.



(a)



(b)

Figure 55. Storage Modulus (a), and Loss Modulus (b) vs. Angular Frequency for Composites of PLA 3001D/Cotton Fibre.

As expected increasing the angular frequency increases the storage and loss modulus, while it decreases the complex coefficient of viscosity. Indeed, increasing the angular frequency increases the applied strain rate on the material, and as a result decreases the viscosity. This fact explains that natural fibre reinforced PLA composites show similar behaviour as if they have not been reinforced with natural fibres.

Furthermore, as the fibre content increases in the composites, the storage modulus, loss modulus, and the viscosity increase (Figure 55 to Figure 58).

The most significant result of the graphs is that the mentioned properties suddenly change by increasing the cotton fibre content from 10% and 20%. While the difference between the composites with 20% and 30% cotton fibre is less.

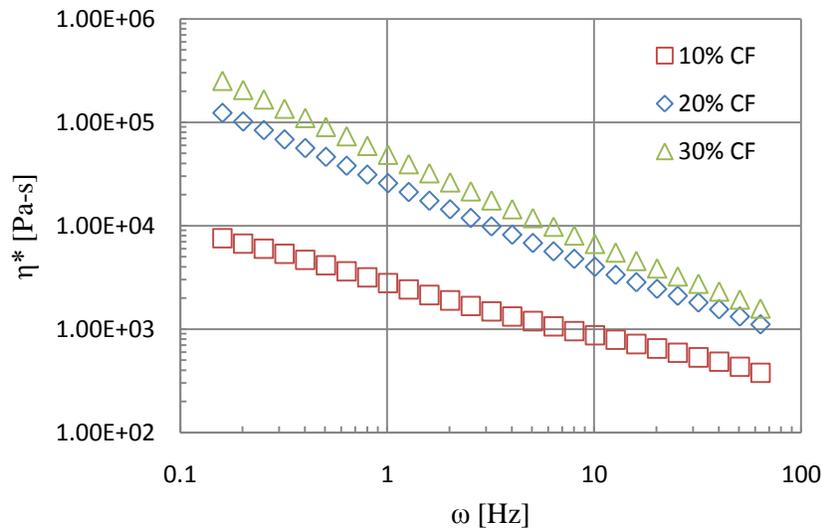
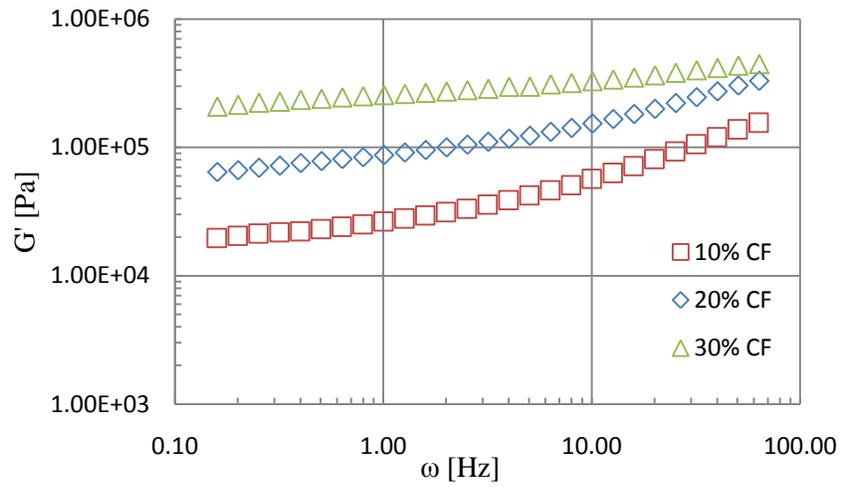
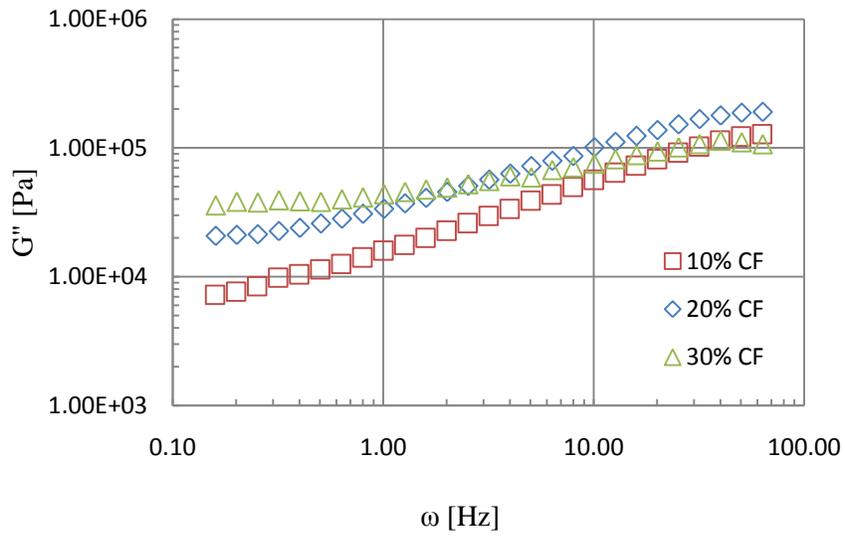


Figure 56. Complex Viscosity vs. Angular Frequency for PLA 2002D/Cotton Fibre Composite.



(a)



(b)

Figure 57. Storage Modulus (a), and Loss Modulus (b) vs. Angular Frequency for Composites of PLA 2002D/Cotton Fibre/Impact Modifier.

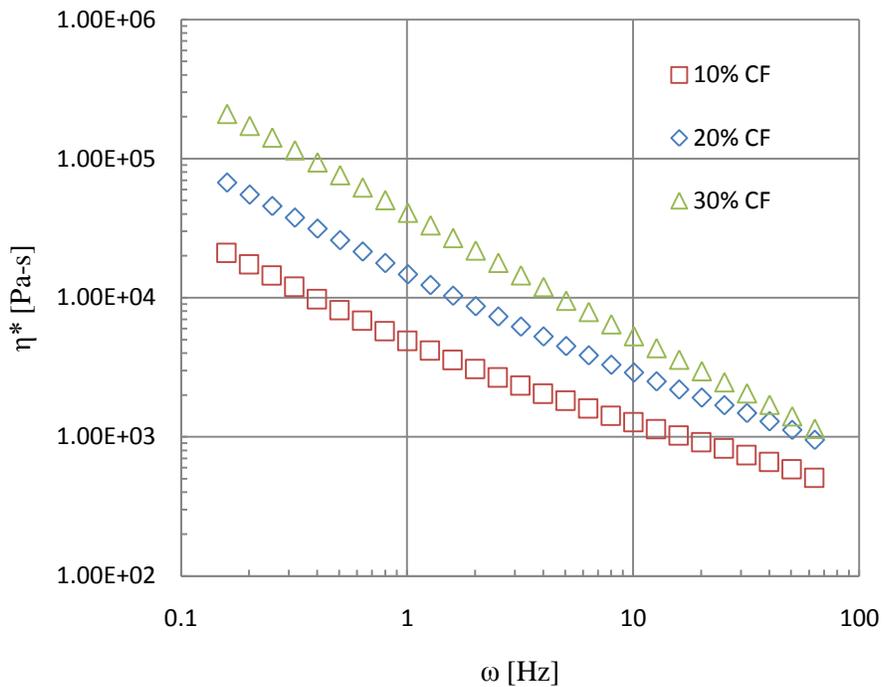
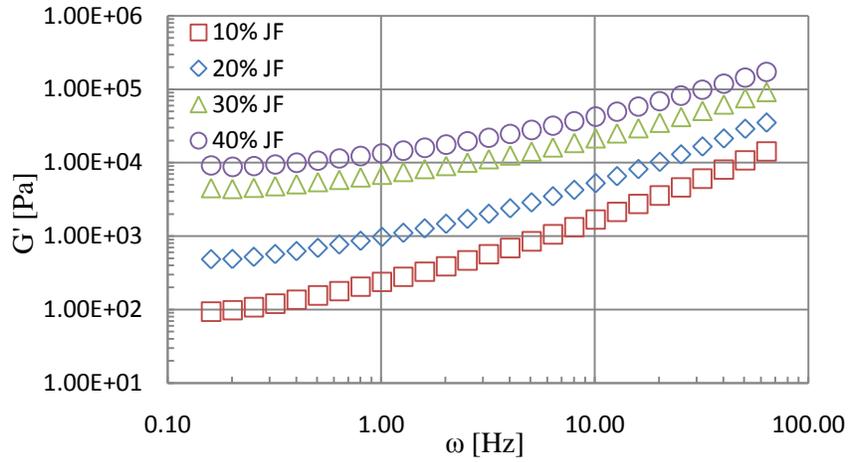


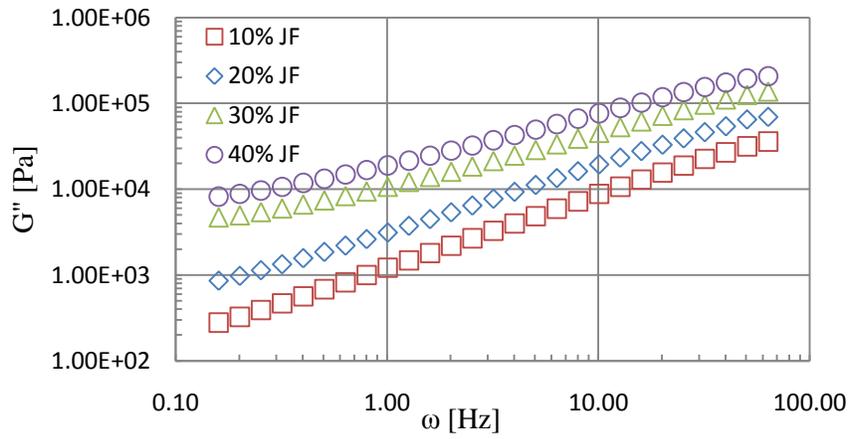
Figure 58. Complex Viscosity vs. Angular Frequency for PLA 2002D/Cotton Fibre/Impact Modifier Composite.

As it can be observed from Figure 56, and Figure 58, addition of 3% biomax strong modifier does not show any change in the complex viscosity.

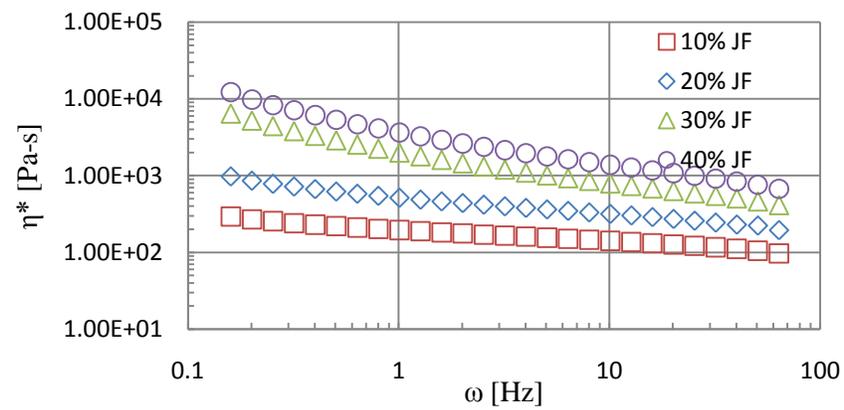
Same experiments are also done on composites made of jute fibre, impact modifier and PLA 3001D at constant shear strain of 5%. Figure 59, and 54 illustrates that the storage and loss modulus ( $G'$ ,  $G''$ ) of these composites increase by increasing angular frequency ( $\omega$ ), while the complex viscosity ( $\eta^*$ ) decreases. Furthermore, addition of jute fibre shows similar trend to the addition of cotton fibre.



(a)

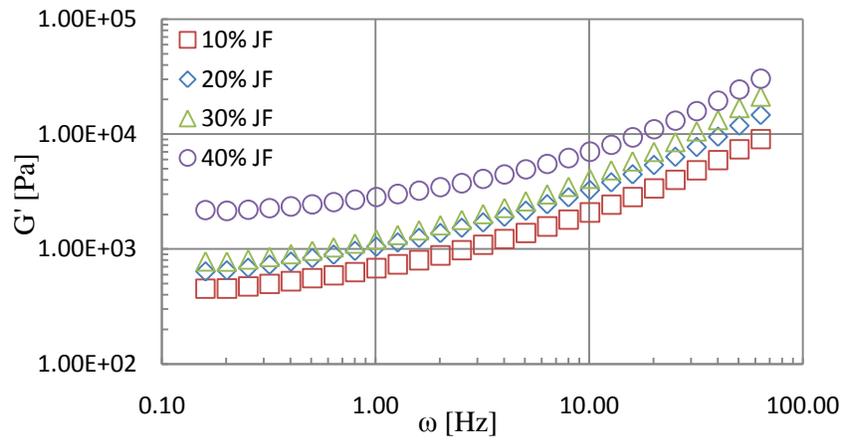


(b)

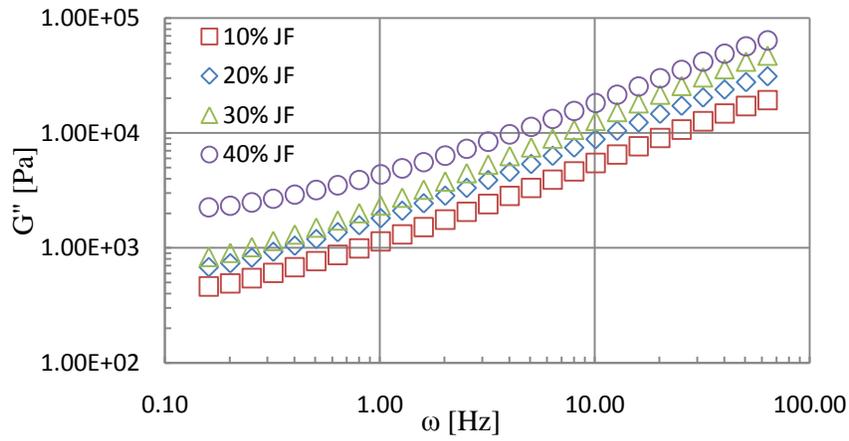


(c)

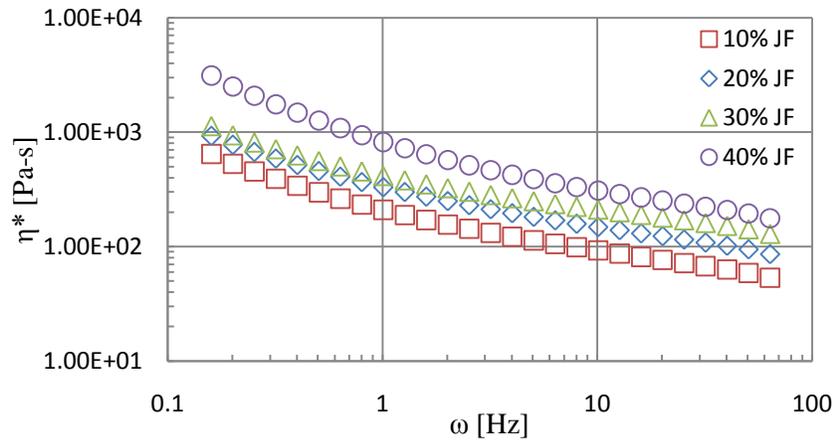
Figure 59. Storage Modulus (a), Loss Modulus (b), and (c) Complex Viscosity vs. Angular Frequency for Composites of PLA 3001D/Jute Fibre/Impact Modifier.



(a)



(b)



(c)

Figure 60. Storage Modulus (a), and Loss Modulus (b), and (c) Complex Viscosity vs. Angular

Frequency for Composites of PLA 2002D/Jute Fibre.

Figure 61 shows how increasing shear strain affects the complex viscosity of the PLA 2002D reinforced with 30% cotton fibre. As expected at higher shear strain values the viscosity reduces.

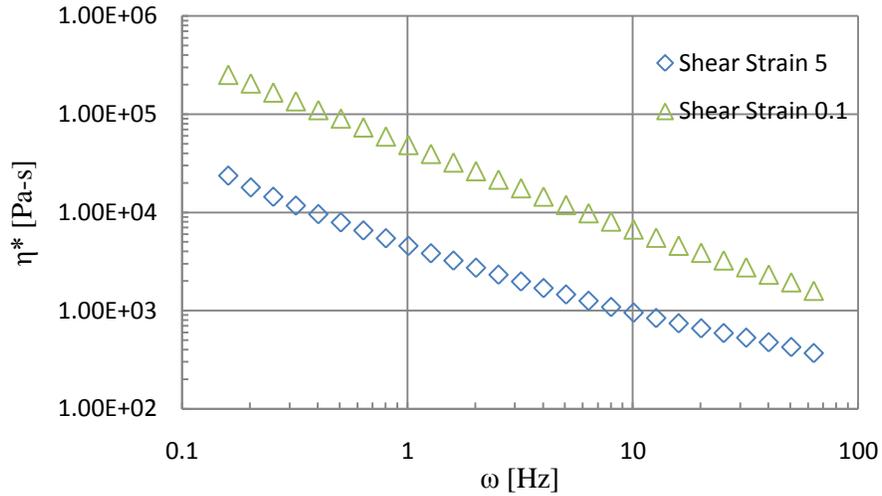


Figure 61. Complex Viscosity vs. Angular Frequency in PLA 2002D/30% Cotton Fibre Composite.

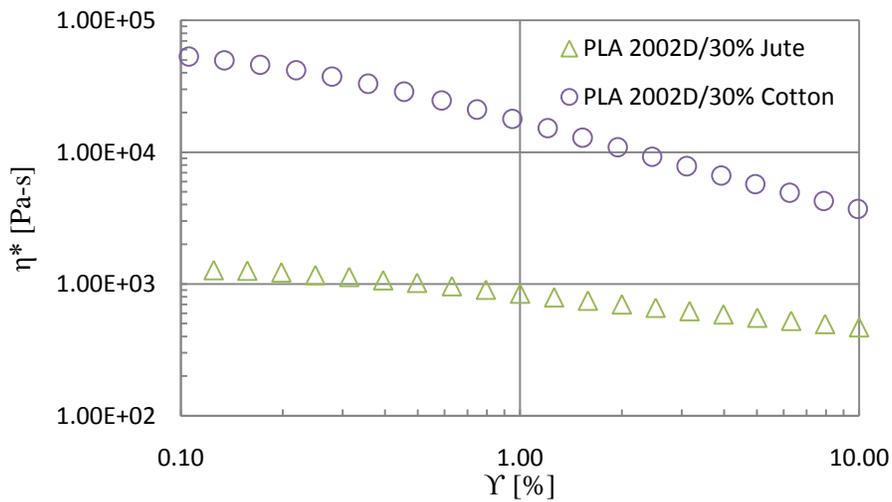


Figure 62. Comparison of Complex Viscosity of PLA Composites Reinforced with Cotton and Jute Fibres.

As it can be seen from Figure 62, PLA composites reinforced with cotton fibres have much higher viscosity value, which illustrates more difficulties in respect to process ability of these biocomposites.

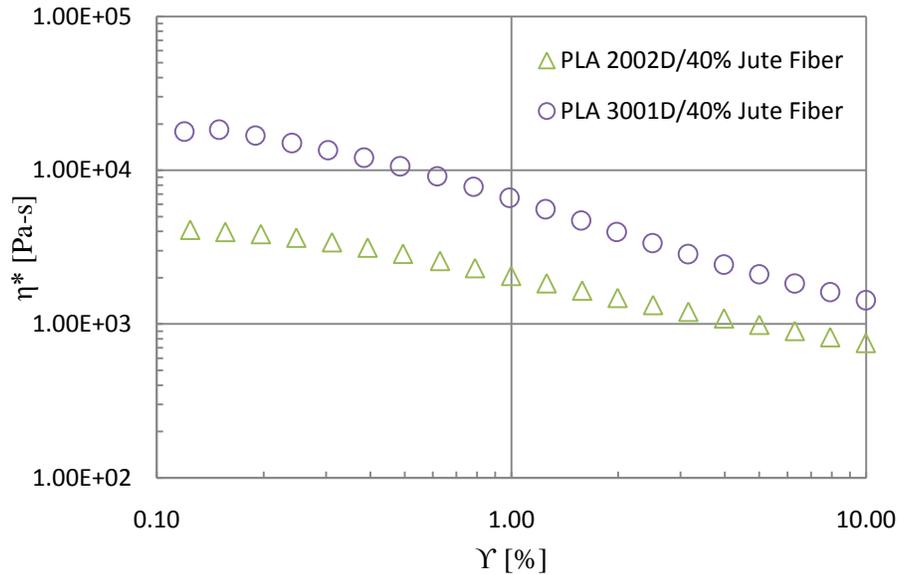


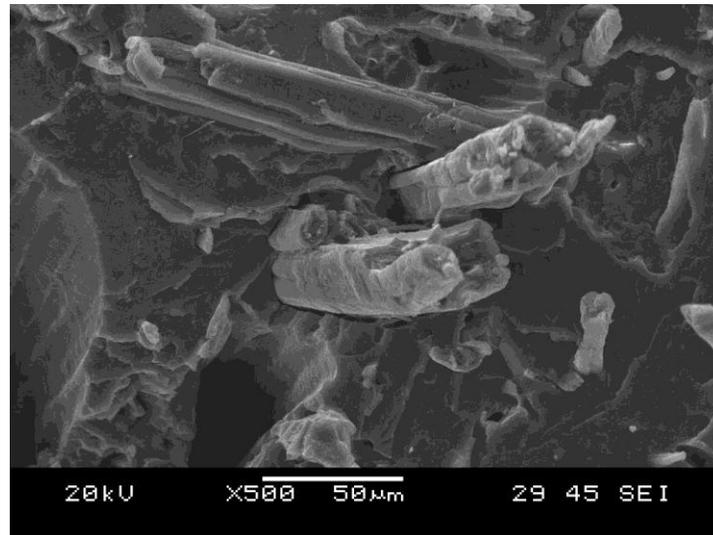
Figure 63. Comparison of Complex Viscosity of PLA 2002D and PLA 3001D Composites Reinforced with 40% Jute Fibres.

In order to show the comparison between viscosity of the two used PLA grades (200D, and 3001D) Figure 63 is presented here. As expected the PLA 3001D has higher viscosity than the other grade, which explains the harder processability of the composites based on this biopolymer, especially during compression moulding.

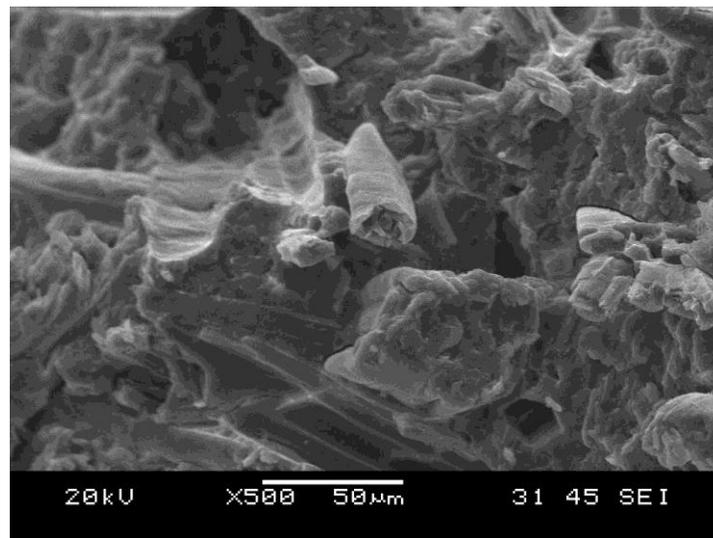
### 5.3.3 MORPHOLOGY

To evaluate the microstructure of fractured surfaces of pure PLA and its composites the SEM images of the fractured surfaces of pure PLA and the composite specimens are presented in Figure 64-63.

Pulled out fibres and the corresponding holes are visible in the images (Figure 64). Furthermore it can be observed that the surfaces of pulled out fibres are clean. The observations agree with the literature for the PLA/Flax and also PLA/Cordenka composite. This indicates a poor adhesion between the fibres and the matrix.



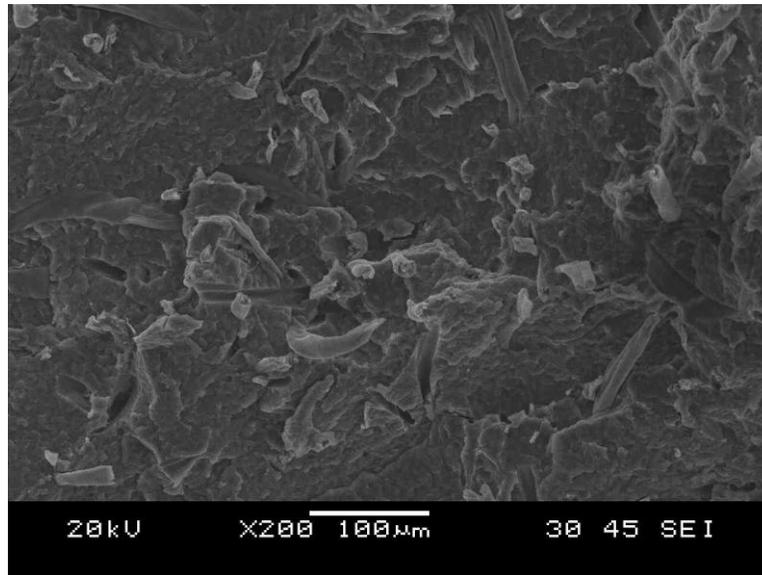
(a)



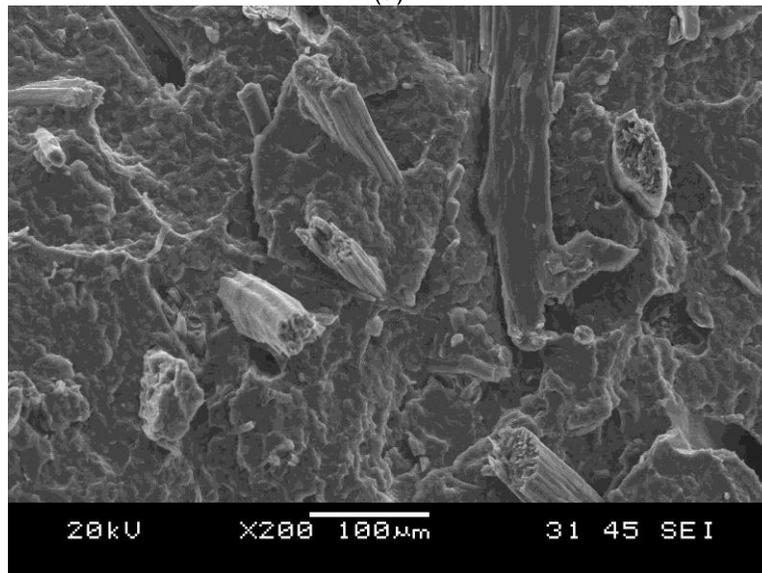
(b)

Figure 64. Detailed Pictures of the Fracture Surface of the PLA/Jute Composite with a Fibre Mass Proportion of (a) 20%, and (b) 30%.

Comparing the SEM images of PLA reinforced with 10% cotton, and jute fibres (Figure 65) shows that the pulled out jute fibres are much longer and cleaner than the pulled out cotton fibres. It suggests that the adhesion between PLA matrix and jute fibres is worse than PLA and cotton fibre.



(a)



(b)

Figure 65. Detailed pictures of the fracture surface of composites with a mass proportion of 10%:

(a) PLA/Cotton composite, (b) PLA/Jute composite.

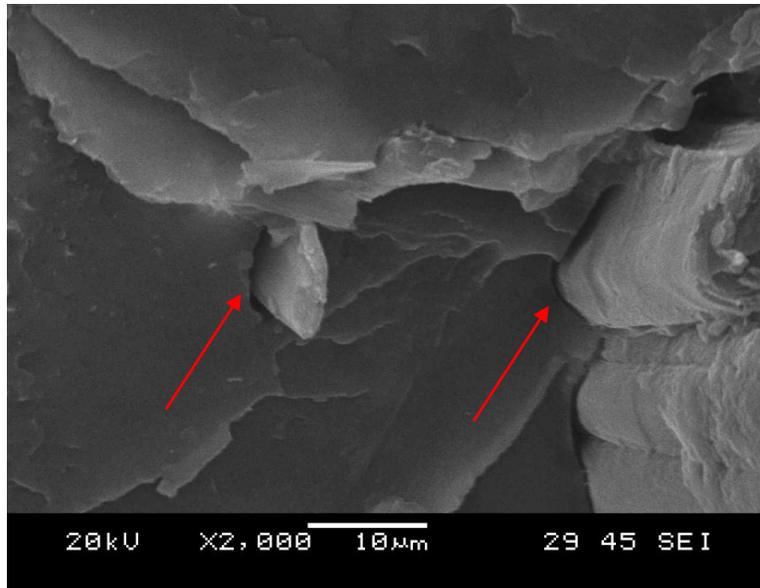
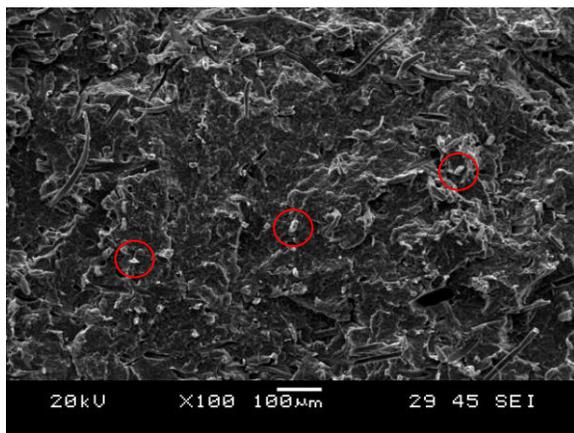
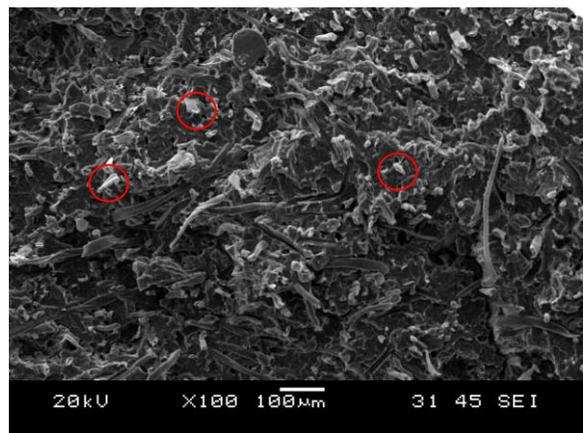


Figure 66. Detailed pictures of the fracture surface of the PLA/Jute composite with a mass proportion of 20%.



(a)



(b)

Figure 67. Detailed pictures of the fracture surface of PLA3001D/ Cotton/IM composites with a fibre mass proportion of: (a) 10%, (b) 20%.

Figure 66 shows the gap between the matrix and the jute fibre. The gap occurred either during debonding in fracture, or because of poor composite production. Both reasons result in a poor interaction between fibre and polymer matrix in the biocomposite. It can also be observed that there are some fibres in direct contact to other fibres, in other words they are not completely surrounded by polymer matrix.

Figure 67 shows the dispersion of cotton fibres in the PLA matrix. As it can be seen from the pointed cotton fibres, the composites possess a good fibre alignment, which is due to the use of the new custom built compression moulding.

## **CHAPTER 6: SUMMARY OF RESULTS AND FUTURE WORK**

### **6.1 SUMMARY**

Biodegradable natural fibre reinforced biocomposites have the potential to replace petroleum based polymers. In this study, two different kind of natural fibres (cotton, and jute) with the average length of 3 mm were used as reinforcement. Selected biopolymer matrices were two PLA grades of 2002D, and 3001D. Biomax strong 120 was also used as modifier for PLA/Natural Fibre composites in order to improve the impact strength and toughness properties. After drying the raw materials using a vaccum oven in order to remove moisture, the fibres and the PLA were mixed and compounded in a twin screw extruder. Following pelletizing and drying, the compounded materials were moulded using the new compression moulding system. The lab-scale compression moulding was designed in order to increase the fibre alignment in the composites. A testing methodology also was developed to investigate thermal and mechanical properties of bio-composites.

The pure PLA 2002D has a flexural strength of 126 MPa and a modulus of 3.6 GPa. As presented results explain, addition of cotton fibres reduces the composites flexural strength, while the elastic modulus improves compared to the neat PLA. Composites reinforced with cotton fibres have higher flexural strength, and modulus of elasticity compared to the composites reinforced with jute fibres. PLA 3001D based composites have higher stiffness than PLA 2002D based composites. PLA 3001D based composites containing 40% jute fibre exhibited the highest stiffness (5.9 GPa) amongst the composites.

Investigation of the impact properties of the composites showed that increasing fibre mass proportion leads to an increase in the impact strength of the composites. The impact strength of the PLA/cotton composite is more promising than PLA/Jute composites. The most significant result is that addition of even 3% Biomax Strong 120 had a positive effect on the impact properties of the specimens.

Analysis of the rheological properties of the composites demonstrates that the cotton fibre reinforced PLA has higher complex viscosity than Jute fibre reinforced PLA composites. As a consequence they are more difficult to be processed. As expected the PLA 3001D has higher viscosity than the other grade, which leads to harder processability of the composites based on this biopolymer, especially during compression moulding.

Thermal properties of the biocomposites were studied using DSC equipment. The results explain that the crystallization temperature increases with increasing the jute fibre content. However the glass transition point shows a slight change with increasing the jute fibre. Moreover, comparing the transition temperatures between composites shows that presence of biomax strong has a positive effect on increasing the glass transition temperature. In the case of

PLA/Cotton fibre composites, increasing fibre content leads to an increase in crystallization temperature, while addition of IM does not show any specific trend on the thermal properties of the materials.

SEM images show that the pulled out jute fibres are much longer and cleaner than the pulled out cotton fibres. It suggests that the adhesion between PLA matrix and cotton fibres is better than PLA and jute fibre, which confirms the better impact properties of these composites. Furthermore, the SEM results of the composites illustrate good fibre alignment in the composites, achieved by using the developed compression moulding system.

## **6.2 FUTURE WORK**

- Optimizing the jute fibre content in the PLA composites to get better mechanical properties.
- Optimizing the Biomax Strong 120 content to produce biodegradable composites with improved properties.
- Incorporation of compatibilizers or coupling agents to optimize the interface between the fibres and the matrix in order to improve mechanical properties of these composites, such as toughness.
- Optimization of the processing parameters for compression moulding such as mixing chamber temperature, mixing time, and temperature of the platens to produce foamed WPCs with improved properties.

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