



UNIVERSITI PUTRA MALAYSIA

***MECHANICAL AND ANTIMICROBIAL PROPERTIES OF
PLA/JACKFRUIT SKIN COMPOSITES CONTAINING THYMOL AND
NANOCELLULOSE***

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ABSTRACT

The aim of this project is to study the effect of different loading of nanocellulose (NC) on the mechanical and thermal properties of PLA/Jackfruit skin based composites and to study the effect of thymol addition on the antimicrobial activity for the composite with and without NC. Jackfruit skin was dried and grinded in order to obtain jackfruit skin powder (JSP) which then undergoes bleaching process. The JSP was then mixed with polylactic acid (PLA) with 10% loading of thymol and 3% and 5% loading of nanocellulose (NC) by using internal mixer, the loading of the JSP was fixed at 30% based on optimum loading discovered by previous study. The PLA/JSP composites were then prepared and tested. The testing that had been carried out including mechanical properties using Instron machine, thermal properties using Thermogravimetric Analysis (TGA) and antimicrobial activity by conducting zone of inhibition against *S. aureus*. It was found that the incorporation of NC into PLA/JSP composites increase the tensile strength with slight reduction at 5% loading of NC. The attempt to incorporate 3-5% NC in the PLA/JSP composites resulted no significant change on the strength due to agglomeration of NC. The tensile modulus increased as the loading of NC increased while the elongation at break decreased. The addition of thymol into the PLA, PLA/JSP and PLA/JSP/NC matrix reduced the tensile strength and tensile modulus while increased the elongation at break. The incorporation of NC also increased the thermal stability of the PLA/JSP composites. However, the addition of thymol into the composites lowered the degradation temperature of the composites. Antimicrobial test demonstrated the capability of the PLA/JSP containing thymol with 5% loading of NC inhibit the growth of *S. aureus*.

ABSTRAK

Tujuan projek ini adalah untuk mengkaji kesan penambahan perbezaan jumlah NC ke atas sifat mekanikal dan sifat haba komposit berasaskan PLA/Kulit nangka dan juga untuk mengkaji kesan penambahan thymol ke atas aktiviti antimikrobial untuk komposit yang mempunyai NC ataupun tidak. Kulit nangka telah dikeringkan dan dikisar untuk mendapatkan serbuk buah nangka yang kemudiannya menjalani pelunturan. Komponen ini kemudiannya dicampurkan dengan asid polylactic (PLA) dan 10% kandungan thymol serta NC sebanyak 3% dan 5% menggunakan Brabender Mixer Measuring. Kandungan JSP telah ditetapkan sebanyak 30% berdasarkan kandungan optimum yang ditemui oleh kajian terdahulu. Komposit berasaskan PLA/JSP ini kemudiannya disediakan dan diuji. Analisis yang telah dijalankan adalah analisa sifat mekanikal menggunakan mesin Instron, sifat haba menggunakan Thermogravimetric Analyzer (TGA) dan sifat antimikrobial yang dijalankan dengan melakukan zon ujian inhibisi terhadap *S. aureus*. Telah didapati bahawa penambahan NC ke dalam komposit PLA/JSP telah meningkatkan kekuatan tegangan tetapi terdapat sedikit pengurangan pada kandungan NC sebanyak 5%. Modulus tegangan meningkat apabila kandungan NC meningkat sementara pemanjangan pada rehat menurun. Penambahan thymol ke dalam matrik mengurangkan kekuatan regangan dan modulus tegangan sementara meningkatkan pemanjangan pada rehat. Penambahan NC juga meningkatkan kestabilan haba komposit PLA/JSP tersebut. Walaubagaimanapun, penambahan thymol ke dalam komposit mengurangkan suhu degradasi komposit tersebut. Ujian antimikrobial menunjukkan keupayaan komposit PLA/JSP yang mengandungi thymol dan 5% kandungan NC menghalang pertumbuhan *S. aureus*.

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LIST OF ABBREVIATIONS

AgNPs	Silver Nanoparticles
ASTM	American Society of Testing and Material
BNC	Bacterial Nanocellulose
CNCs	Cellulose Nanocrystals
DSC	Differential Scanning Calorimetry
FDA	Food and Drug Administration
JSP	Jackfruit Skin Powder
NC	Nanocellulose
NFC	Nanofibrillated Cellulose
PCL	Polycaprolactone
PEG	Polyethylene Glycol
PGA	Polyglycolic Acid
PHA	Polyhydroxyalkanoates
PLA	Polylactic Acid
PVOH	Polyvinyl Alcohol
<i>S. aureus</i>	<i>Staphylococcus aureus</i>
TGA	Thermogravimetric Analyser
ZnO	Zinc Oxide

CHAPTER 1

INTRODUCTION

1.1. Background

Packaging has a very important role in protecting goods from any physical damage, external contamination and deterioration (Wang and Wang, 2017). Synthetic plastics or petroleum based plastics are favored materials for packaging as they are light, cheap, stable and easy to get. Because of that, the production of synthetic plastics using petroleum has increase exponentially over the last few years (Bernstad Saraiva, 2016). Throughout the years the evolution of the packaging materials has become into competition, especially in food application as the increasing demand of consumer for healthy environment concerns which lead the usage of renewable resources for plastics production. As technology advances, different types of bio-plastic or bio-polymer had been discovered by scientist. One of the examples is poly(lactic acid) (PLA) which is discovered by Wallace Carathers in 1932.

PLA is a type of biodegradable plastic that can be produced from natural resources where the raw materials are extracted. Jamshidian (2010) stated that PLA is considered as one of the most valuable bio-polymer. It had been applied into several applications including in food packaging because of its good strength and stiffness (Haafiz et al., 2016). Besides, PLA also shows great biodegradability and biocompatibility compared to other biodegradable polymers (Shameli et al., 2010). However, PLA itself have some drawbacks that can limit the application. Compared to

petroleum based plastics, PLA has poor barrier properties and lower thermal stability (Haafiz et al., 2013). Hughes and co-worker (2012) stated that the limitations of PLA are its brittleness and high polarity and also cost compared to other thermoplastics polymer. To overcome these imitations, combination with natural fibre as filler can reduce the cost of the PLA while nano-fibre usually applied to improve its properties such as thermal resistance, heat distortion temperature and rate of crystallization (Raquez, 2013).

Artocarpus heterophyllus or commonly known as jackfruit is a popular fruit found in Southeastern region of Asia. The edible part of jackfruit are consumed fresh or processed into many type of products such as canned products, chip or jam. However, about 60% of jackfruit is inedible made up of the outer prickly rind, central core and non-edible perianth which are considered as waste (Begum et al., 2014). This waste is unutilized as there is no economic value and uncontrolled disposal of this waste can lead to environmental pollution. This waste which mostly made up of cellulose can be extracted and used as filler for bio-polymer material. These filler can be incorporated with PLA in order to improve the thermal stability and mechanical properties of PLA itself as well as reduce the cost of PLA.

Cellulose fibers modified at nanometer size induce much higher mechanical and thermal properties to polymer matrix compared to common cellulose fibers due to their higher crystallinity combined with higher surface area and active interfaces (Mandal and Chakrabarty, 2014). The intra and intermolecular hydrogen bonding is responsible for the stabilization of the thermal properties of cellulose since the existence of this bonding prevents cellulose from melting before thermal degradation. Moreover, these bonds

cause the cellulose to become insoluble in almost all of the solvents by reason of considerable tensile strength that is imparted by the bonds on the cellulose (Gan and Chow, 2018).

An antimicrobial is an agent that inhibit the growth of microorganism or kill the microorganism. Antimicrobial can be divided into two categories where it is used for pharmaceutical means or non-pharmaceutical means. As this agent is applied to packaging, it can increase the shelf life of the food products without adding harmful additives or preservatives into the food product. There are two types of antimicrobial agents which are metal antimicrobial agent and the natural antimicrobial agent. The natural antimicrobial agent consists of organic acids, polymers or enzyme such as oregano essential oil, thymol and lignin nanoparticle while the metal antimicrobial agent refers to nanoparticles of metals or metal oxides such as silver nanoparticle and zinc oxide nanoparticle. These compounds can be incorporated in the PLA and PLA containing natural fibre composites in order to produce active packaging.

1.2. Problem Statement

The usage of biopolymer as a food packaging material can lead to a better ecosystem. However, these biopolymers have one limitation which is the high cost of production. To overcome this limitation, the addition of fibre as a filler from agricultural waste can be practiced. Agricultural waste such as jackfruit skin which made up of high amount of fibre can be used as the filler for the biopolymer matrix. Besides fibre as filler, the incorporation of nano fibre into the matrix is believed can enhance the properties of the polymer.

Nowadays, our society is facing one major problem involving food products. This major problem is the short shelf life of the food products thus lead to food wastage. Food spoilage can be define as a process which deteriorates the food into the point where it no longer safe to consume by human. The major cause for food spoilage is the growth of bacteria that exceed a certain degree which can cause harmful for consumption. The growth of the bacteria depends on many factors such as temperature, pH, nutrients and oxygen. Some methods such as the usage of preservative had been applied in order to increase the shelf life of food. This method however has the downside which changed the texture, smell and taste of the food.

In this study, I propose to make a packaging materials which contains active compound by using bio-based materials which is reinforced with NC. The biopolymer used is the PLA which has JSP as the filler and NC as the reinforcement. The active compound is supposed to kill the bacteria inside the packaging and prolong the shelf life of the food. This antimicrobial packaging system is to ensure that the process didn't change the texture, smell and also the taste of the food. For the active compound in this study, thymol will be used as it had the microbial activity properties against microorganisms.

1.3. Objective

The objectives of this research are;

- i. To study the effect of different loadings of NC on the mechanical and thermal properties of the PLA/JSP composites.
- ii. To study the antimicrobial activity of active PLA and PLA/JSP composites with and without NC containing thymol.



CHAPTER 2

Literature Review

2.1. Biodegradable Plastic

Scientists around world had been searching an alternative plastic ever since it was mass produced and later found to be harmful to the environment because of the long decomposing time. Some of the alternatives that were managed to discover are oxidatively degradable, photodegradable, hydrolytically degradable and biodegradable plastic or polymer (Ezeoha, 2013). Biodegradable plastic or polymer which can be either petrochemical or bio-based may be a solution to major problem in the environment nowadays. Problems involving non-degradable plastics have become serious issues as landfill sites are becoming increasingly scarce and incineration adds to air pollution and global warming. For biodegradable plastic, it can be degraded by microorganisms to carbon dioxide, biomass and water through a process called bio-deterioration, assimilation and bio-fragmentation (Adriaan & Sarah, 2019). Biodegradable plastic especially those that were derived from natural sources such as starch, lactic acid and cellulose is more preferable as they can degrade naturally and faster compared to the petroleum derived counterpart. Table 2.1 list some of the biodegradables that had been utilized nowadays.

Table 2.1: Uses of biodegradable plastics

Biodegradable plastics	Uses
Polyglycolic acid (PGA)	Specialized applications; controlled drug releases; implantable composites; bone fixation parts
Polylactic acid (PLA)	Packaging and paper coatings; other possible markets include sustained release systems for pesticides and fertilizers, mulch films, and compost bags
Polycaprolactone (PCL)	Long-term items; mulch and other agricultural films; fibers containing herbicides to control aquatic weeds; seedling containers; slow release systems for drugs
Polyvinyl alcohol (PVOH)	Packaging and bagging applications which dissolve in water to release Products such as laundry detergent, pesticides, and hospital washables

2.2. Polylactic Acid (PLA)

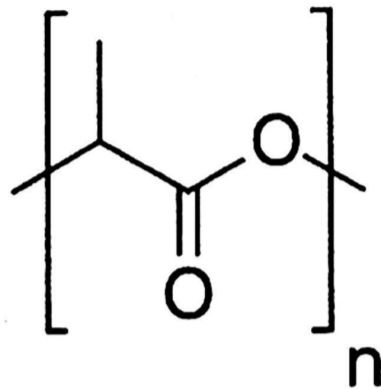


Figure 2.1: Chemical structure of polylactic acid (PLA)

Figure 2.1 shows the chemical structure of polylactic acid (PLA). PLA is produced by extracting the starch from plants such as corn. During the growth of the corn, carbon dioxide from the surrounding is utilized for photosynthesis. During photosynthesis process, carbon dioxide and free energy generated by solar energy convert glucose inside corn plant into starch which contributed to the chain building for PLA. Therefore, PLA is suggested to have the potential in reducing environmental pollution due to the ability to reduce carbon dioxide emissions (Vink, Glassner, Kolstad, Wooley & O'Connor, 2007). Some good things about PLA are biocompatibility, processability, renewability and less energy consumption (Rasal, Janorkar & Hirt, 2010). Compared with another biopolymers like poly(hydroxyalkanoates) (PHAs) and poly(ethylene glycol) (PEG), good thermal processability of PLA give the ability to be manufactured through many types of processing methods such as extrusion, fiber spinning and also film casting (Rhim, Mohanty, Singh & Ng, 2006). Due to the biodegradable and biocompatible characteristics of PLA, it was given approval by the Food and Drug Administration (FDA) in the applications with food contact and became a decent candidate for the application of packaging for short service life goods or fresh food, including blister

packaging, lamination filming and overwrapping (Ingrao et al., 2017). Despite all its advantages, PLA also has some downsides such as brittleness, low crystallization ability and degree and low impact strength (Auras et al., 2004; Rasal et al., 2010). To overcome these downsides, PLA are often incorporated with natural fillers to enhance the polymer matrix which produce composite materials.

2.3. Jackfruit



Figure 2.2: Image of jackfruit

Jackfruit (*Artocarpus heterophyllus*) is a very popular fruit commonly used in South and Southern region of Asia. Figure 2.2 shows the image of jackfruit. It is a specie of tree of mulberry family (Moraceae) and largely grown in Malaysia, Thailand, India, Myanmar, Indonesia and Philippines (Hameed, 2009). Jackfruit is also the largest fruit in the world which contains various types of nutrients including dietary fiber, carbohydrates, vitamins, minerals and antioxidant compounds inside its seeds and bulbs (Zhang et al., 2018). This fruit is one of the readily available and accessible fruit as it can be harvested throughout the year because of it being non-seasonal fruit. It is also due to the fact that it can be eaten unripe, ripe, uncooked or cooked which was supported by Cheok et al, (2018). Jackfruit usually weight around 10-25 kg when matured where for

large size of jackfruit can weigh up to 50 kg. From those weigh, about 50% of the fruit composed of unfertilized floral parts and rind are usually rejected as waste as they are fibrous (Hameed, 2009). As the production of processed fruit increase, the fruit waste will also increase tremendously. Jackfruit peel wastes which did not have any economic value often provide a major problem of disposal for environments. In order to reduce the amount of these wastes, many researches had been done to utilize the potential of the waste in the industry. The fibre that can be extracted from these waste which is a natural fibre is flexible compared to synthetic fibre that is brittle. However, there are some limitations that need to be overcome when using natural fibre. These limitations are poor fibre separation and weak interfacial adhesion between the fibre and the polymer matrix (Beckermann and Pickering, 2008). These limitations can be overcome by altering the surface of the fibre by undergo fibre treatment. Two ways of fibre treatment are bleaching and alkaline treatment. By using bleaching treatment, it altered the link between the carbohydrate and lignin and also removed the non-cellulosic component within the fibre (Kalia et al, 2009). Meanwhile, alkaline treatment can decrease the diameter of the fibre which can increase the contact ratio with the polymer matrix as well as creating a rough topography on the surface that lead to the increase in the adhesion (Kalia et al, 2009).

2.4. Nanocellulose

Nanocellulose (NC) can be described as a biodegradable nanomaterial due to the properties of cellulose which is sustainable, renewable, nontoxic, recyclable and produces low carbon footprint (Dufresne, 2017). Cellulose biopolymers are inexhaustible as plants can produce up to 75 billion tons of cellulose approximately per year (Feng et al., 2018). NC can be extracted from various sources such as wood, cotton and other plant based materials (Khan 2014). One of the extraction process is by acid hydrolysis where the cellulose fibre is mixed with sulphuric acid under constant stirring (Sung, 2017). Intramolecular and intermolecular hydrogen bonding play an important part for the stabilization of the ordering of cellulose chains which leads to the compact microfibrils formation. The presence of hydrogen bond also provides stabilization in term of the thermal properties of cellulose as it prevents the cellulose from melting due to the thermal degradation. Moreover, these bonds also become one of the reason cellulose is insoluble in almost all solvents because of considerable tensile strength that is contributed by the hydrogen bonds (de Oliveira, Bras, Pimenta, da Silva Curvelo, & Belgacem, 2016; Hoi & Martincigh, 2013; Moubarik, Grimi, & Boussetta, 2013). Three type of NC that have been used as key components for the application of cellulose-derived packaging are cellulose nanocrystals (CNCs), bacterial nanocellulose (BNC) and nanofibrillated cellulose (NFC). The division of these NCs depends on their synthesis method, size, source and function (Gan & Chow, 2018). Some researchers currently study the incorporation of NC into biopolymer matrix to enhance the properties of the composites. To date no literature reported on the incorporation of nano-

cellulose into composite materials containing PLA and natural fibre as filler. Table 2.2 shows the current study of the incorporation of NC into biopolymer (PLA).

Table 2.2: Current study of the incorporation of NC into biopolymer (PLA)

Authors	Cellulose	Antimicrobial agent	Method	Finding
Fortunati, Armentano, Zhou, Iannoni et al. (2012)	Cellulose nanocrystals	AgNPs (1 wt %)	Melt extrusion	Antimicrobial activity on E. coli was greater than S. aureus.
Fortunati, Rinaldi et al. (2014)	Cellulose nanocrystals	AgNPs (0.5-1 wt %)	Melt extrusion	Films showed improvement in the properties of barrier.
Luzi, Fortunati, Jiménez et al. (2017)	Cellulose nanocrystals	ZnO nanoparticle (0.5-1 wt %)	Microextruder	The mechanical properties and water vapour permeability showed improvement. No significant antimicrobial activities were observed.

Salmieri et al. (2014b)	Cellulose nanocrystals	Nisin (1 wt %)	Compression molding	Results only showed on the third day. The release of nisin increased continuously.
Salmieri et al. (2014a)	Cellulose nanocrystals	Oregano essential oil	Solvent Casting	Antimicrobial activity was enhanced

2.5. Active Packaging

Active packaging as to inhibit the activity of pathogenic microbes in food has been studied to provide safer food products (Otoni, Espitia, Avena-Bustillos & McHugh, 2016). Food packaging can provide different types of functions such as flavouring, oxygen scavenger, antioxidant, moisture absorber, antimicrobial and ultraviolet barrier. However, the ones with the purpose of giving off biocide substances to food have gained crucial attention because of the ability to lengthen the shelf life of the food as well as reduce the presence of foodborne microorganisms. The major function of antimicrobial packaging is to reduce and later prevent the growth of spoilage microorganisms (Riberio-Santos, Andrade & Sanches-Silva, 2017). There are different approaches that can be applied for the microbial compounds inside food packaging. According to Appendini and Hotchkiss (2002) and Kapetanakou and Skandamis (2016), those approaches can be categorised into three concepts. The first concept is without any contact between antimicrobial compounds and food by putting the antimicrobial

compounds into a separate carrier. The second concept is indirect contact between the food with antimicrobial compounds by having some of the microbial compounds tied to the carrier and the third concept is direct contact of food with the antimicrobial compounds by injecting antimicrobial compounds onto the food surface. All these approaches are illustrated in Figure 2.3.

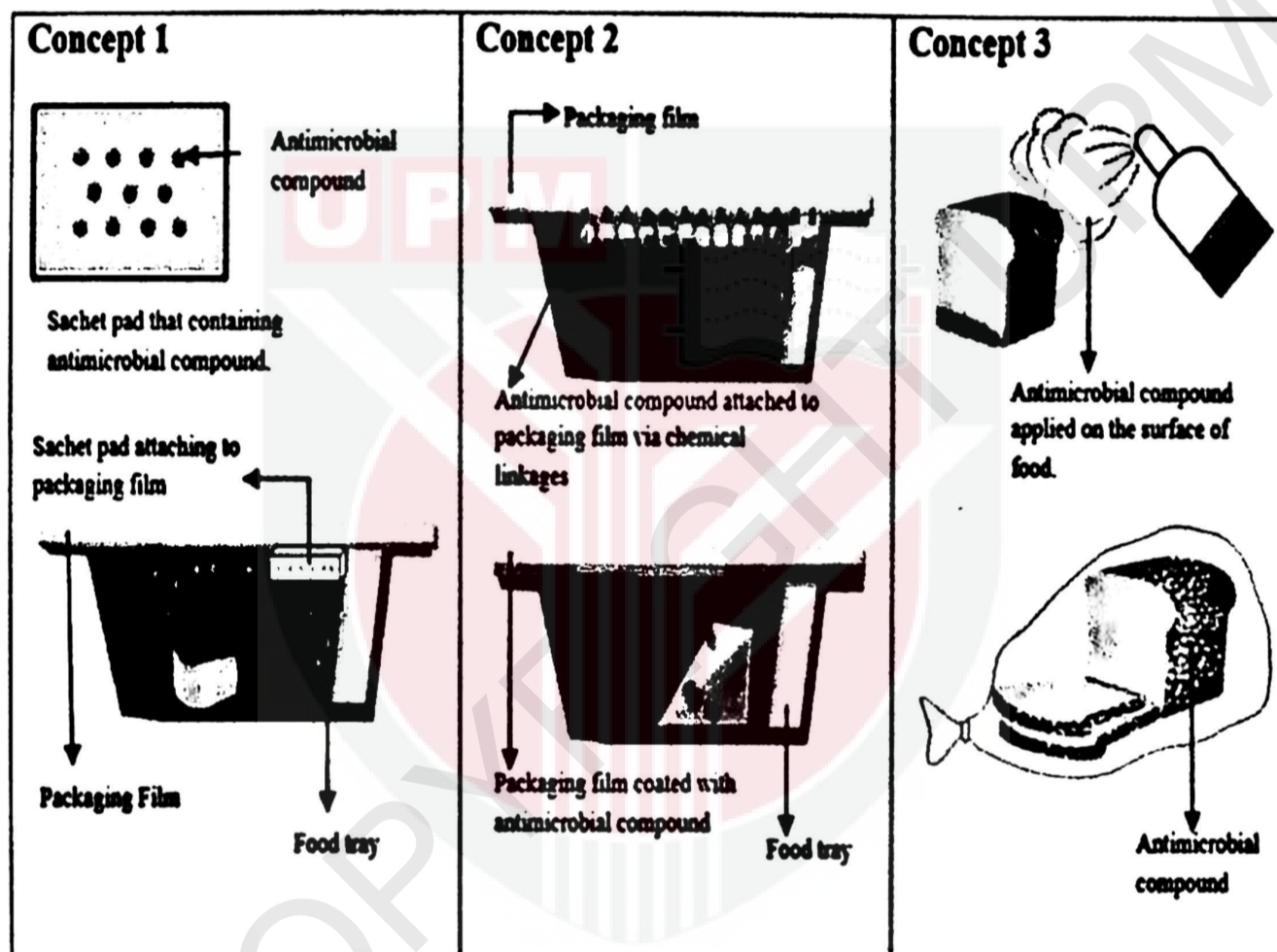


Figure 2.3: Utilization of antimicrobial in food packaging.

2.6. Thymol

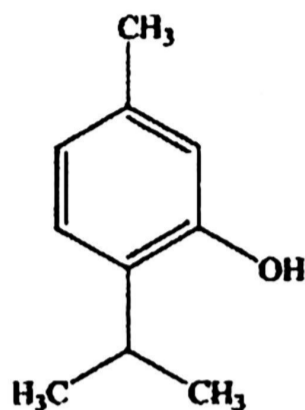


Figure 2.4: The chemical structure of thymol

Thymol (2-isopropyl-5-methylphenol) is the main monoterpene phenol construct in the essential oils extracted from plants belongs to the Lamiaceae family (Licata et al., 2015). Figure 2.4 shows the chemical structure of thymol. The essential oils have been utilized in food industry since ancient times as preservative agents and flavouring due to their antimicrobial and antioxidant properties (Lee, Umamo, Shbamoto & Lee, 2005). Thymol also shows high potential to be used in the food industry as it is already considered as “Generally Recognized as Safe (GRAS)” category by the US Food and Drug Administration (Paola Persico et al., 2009). It is also suitable for food applications as it have migratory release properties that can provide continuous microbial activity from package to the food (Tawakkal, Cran & Bigger, 2014). Beside used in food industry, thymol also utilized in commercial formulations for its repellent effect on *Culex pipiens pallens*, a type of mosquitoes (Park, Choi, Kim, Kim & Lee, 2005) and also has toxic effect on their larvae (Zahran & Abdelgaleil, 2011). These studies show that thymol could be useful in search for natural insecticides.

2.7. Mechanical Properties

Mechanical properties of a material are the properties that involve a reaction to an applied load. Mechanical properties is one of the most important properties in determine the purpose and suitability of the materials. Besides, mechanical properties also used to classify and identify types of the materials. The common properties considered are strength, hardness, impact resistance and ductility. Mechanical properties of materials are affected by branching, degree of crystallinity, molecular weight and crosslinking. Rate of stressing, molecular orientation and filler also affects the mechanical properties of the materials (Zweifel et al, 2009).

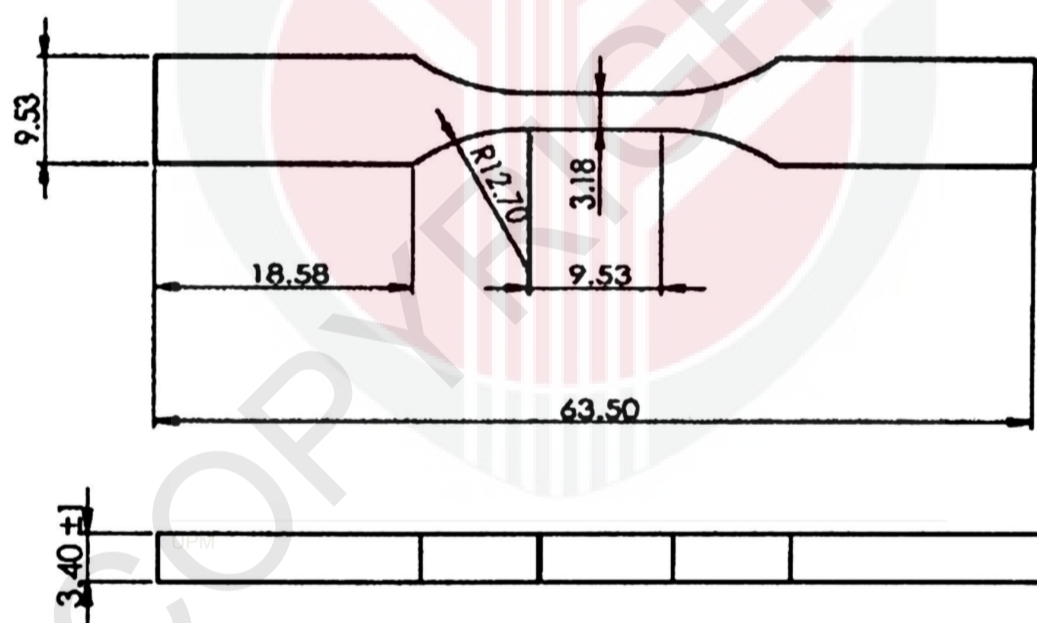


Figure 2.5: Dimension of ASTM D638V

In this study, tensile properties are being observed including tensile strength, tensile modulus and elongation at break. Tensile strength is the breaking strength of a specimen under application of a force capable of breaking the specimen, at a constant rate of extension or load (Chakraborty, 2012). Tensile modulus is resistance

measurement of the material to elastic deformation where low modulus value material will stretch a lot when pulled (David and Michael, 2019). Elongation at break is the ratio between changed length and initial length after breakage of the specimen (Djafari Petroudy, 2017). All the tests are done using ASTM D638V. Figure 2.5 shows the dimension of ASTM D638V.



2.8. Thermal Profile

The thermal properties of thermoplastic materials are as important as the mechanical properties. Unlike metals, thermoplastics are very sensitive to changes in temperature (Campo, 2008). These properties are extremely dependent on the molecular structure of the materials. The number and distribution of side chain, length of the macromolecular chain and crystalline structure of the material have a great effect onto the thermal properties. Klein (2011) stated that the examples of thermal properties (e.g. TGA and DSC) which related to thermoplastics are heat and temperature conductivity, specific volume and phase transition temperature.

Thermogravimetric Analyser or TGA is one of the common test that can be conducted to determine the thermal properties of a material. TGA is an analytical technique that determined the thermal stability of a material and its fraction of volatile components by monitoring the change of weight which occur as the material is applied heat at a constant rate (Rajisha et al, 2011). The basic parameter that are measured in TGA are mass, temperature and time. Figure 2.6 shows the example of TGA curve.

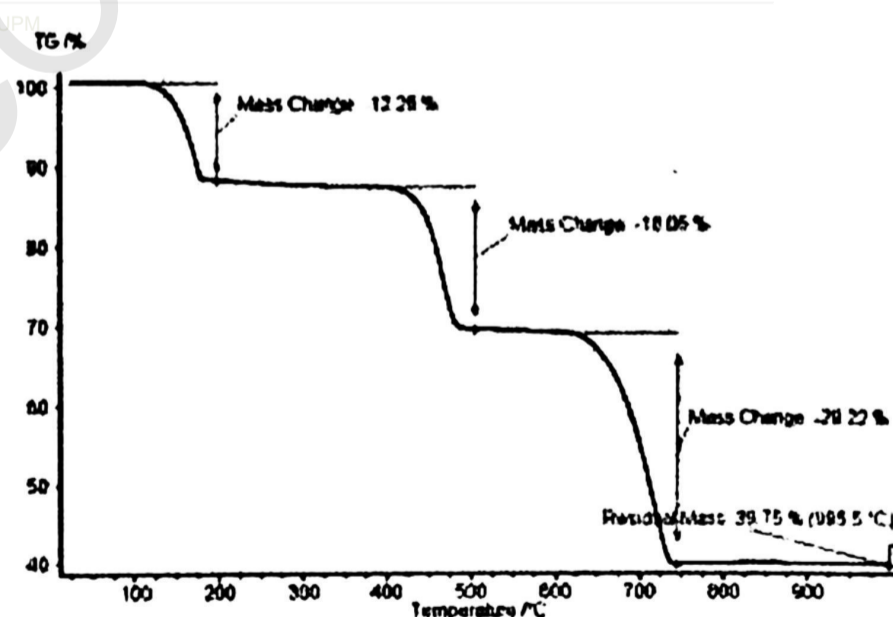


Figure 2.6: Example of TGA curve

CHAPTER 3

METHODOLOGY

3.1. Introduction

This chapter discusses the materials used and methodology involved in order to carry out the experiment. Steps in preparing jackfruit skin powder as the filler for the composite and nanocellulose were also discussed in this chapter. The methodology section covers the processing the PLA and jackfruit skin based composite, addition of NC at different loading and thymol as the antimicrobial agent. The process continued by producing a composite sheet with the hot press before undergo analysis activity for mechanical, thermal and antimicrobial. The equipment used for this experiment are shown in the Appendix. Figure 3.1 describes the process flow diagram of this study.

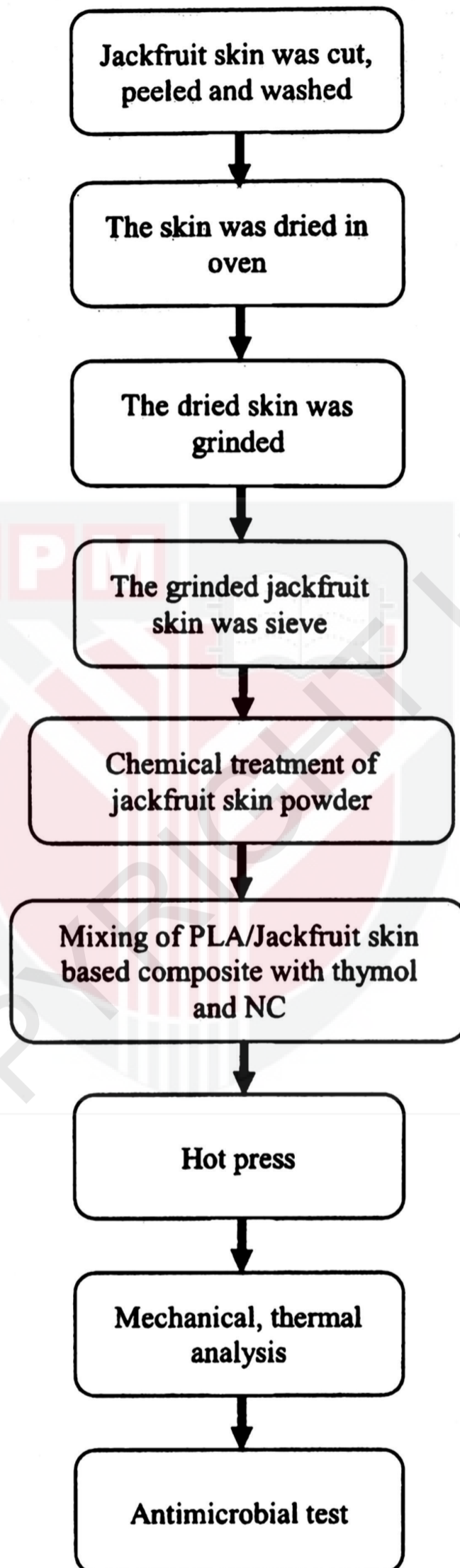


Figure 3.1: Process flow diagram

3.2. Materials and Method

Jackfruits were purchased from Pasar Borong, Selangor Malaysia. The fruits were then washed and peeled to obtain the skin before it was chopped, dried, grinded and sieve to obtain the jackfruit skin powder. Polylactic acid used was Polylactic acid 7001D Ingeo™ produced by NatureWorks LLC, USA. The specific gravity, glass transition temperature and melting temperature range of PLA were 1.24, 59°C and 145-160°C respectively. Thymol was purchased from R&M Chemicals (Essex, United Kingdom) (Molecular Weight = 150.22g/mol) a white crystalline substance. NC was purchased from Zeopnano Sdn. Bhd. where it was extracted from empty fruit bunch. Sodium chlorite (NaClO_2) (90.44g mol^{-1}) and acetic acid (CH_3COOH) (60.05g mol^{-1}) are purchased from Iz Enterprise, Malaysia.

3.3. Preparation of Jackfruit Skin Powder

Jackfruit was cut in half before the skin was separated from the other parts. Then, the skin was cut into rectangular segment which was washed and dried inside an oven (Memmert, Germany) at 70°C for 72 hours. The drying process is completed when the weight of the jackfruit skin remain constant. The dried jackfruit skin was then ground using grinder. All the jackfruit skin powder was inserted into a sieve shaker (Retsch, Germany) to get a constant size of 500 μm .

3.4. Chemical Treatment of Jackfruit Skin Powder

The jackfruit skin was underwent a bleaching treatment. First, 10g of jackfruit skin powder was washed with tap water in order to remove foreign material and dust. The skin powder was then soaked in a 300ml of hot distilled water inside a 500ml beaker.

Then, the beaker was put into a 70°C water bath (AliranTek, Malaysia) inside a fume hood. 2ml of acetic acid and 4g of sodium chlorite were added into the beaker every 1 hour until the jackfruit skin powder turn white in color. The mixture was stirred using a glass rod before covered the beaker with aluminum foil. The jackfruit skin powder was then washed with distilled water until the odour of chlorine dioxide and yellow color absent.

3.5. Preparation of Nanocellulose Powder

NC in slurry form with a total of 900ml was poured into centrifuge tube at 30ml each before put into a freezer (Haier, China) at -35°C for 24 hours. Then, the frozen NC was put into freeze dryer (ScanVac, Denmark) until all the ice absent. The NC was then chopped using stone mortar into a smaller size.

3.6. Preparation of Composites Containing Nanocellulose and Thymol

The jackfruit skin that had undergoes treatment process was grinded by using grinder. Then, the grinded jackfruit skin was inserted into sieve shaker to get a constant size of powder. The size range for the powder is 250µm. The PLA will first be dried for 24 hours at 60 °C before insert into a mixer. Meanwhile, the slurry NC was put into a freezer at -35°C overnight before put into freeze dryer to remove all the presence of ice. During the mixing process, the operating temperature must be at 160°C to make sure that the PLA is completely melt as the melting point of PLA is around 150°C (Sung et. al, 2017). The mixing time was set at 10 minutes but the jackfruit skin powder and NC will be added into the hopper 2 minutes after the PLA melted. Thymol was added at seventh minute to avoid the thymol from vaporized during mixing process. The

equipment used for the mixing process was Brabender Measuring Mixer, Germany. A total of 50g of sample is used to mix the composite.

Table 3.1: The composition of the composites

Sample	PLA	Jackfruit skin	Nanocellulose	Thymol
1	100	-	-	-
2	97	-	3	-
3	90	10	-	-
4	70	30	0	-
5	67	30	3	-
6	65	30	5	-
7	87	-	3	10
8	60	30	0	10
9	57	30	3	10
10	55	30	5	10

To form the composite sheet, the mixed composite was put into a frame mould. Then, it was inserted into a hot press machine (Gotech, Taiwan). The composite was preheated at 150°C for 2 min before pressed for 3 min at the same temperature. The composite was then left to cool at room temperature before cut into dumbbell shape of ASTM-D638 Type V for the mechanical testing.

3.7. Mechanical Properties

The dimension of the dumbbell shape composite (ASTM-D638 Type V) is measured to perform the test. 5kN Universal Instron Machine, USA was used to perform the tensile analysis with the cross head speed of 5mm/min. Tensile modulus, tensile strength and elongation at break were obtained from the plotted graph. For each sample, a total of 5 specimens were tested.

3.8. Thermal Analysis

Thermal properties of composite were analyzed using thermogravimetric analysis. Pyris 1 Thermogravimetric Analyser (PerkinElmer, America) was used in this analysis. To prevent any contamination from occur, the pan of the instrument was clean with dilute solution of HCL. All samples are heated from 50°C to 500°C with a heating rate of 10°C/min. The evaporation temperature and degradation temperature of composites are obtained from the graph of weight vs temperature and derivative weight vs temperature.

3.9. Antimicrobial Activity

For antimicrobial testing, disc of diffusion test will be conducted. The test was carried out by placing the films containing antimicrobial agent, which in this case is thymol, onto a plate which microbes were growing in LB broth. The microbe culture was standardized to 0.5 McFarland standards which approximately 10^8 cells. Streptomycin standard were used for the *S. aureus*. The plates were inverted and incubate at 30-37°C for 24 hours until sufficient growth occurred. *S. aureus* was used as it was one of the common food-borne disease (Hennekinne, 2012).

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Mechanical Properties

4.1.1 Tensile Strength of PLA/JSP Composites

Figure 4.1 shows the tensile strength of PLA and PLA/JSP composites containing thymol at different loadings of NC in range from 0 to 5%.

The tensile strength of pure PLA is the highest with 53.17MPa. This value is the same as the value reported by Tawakkal et al. (2014). For PLA composites containing 3% of NC loading, the value of the tensile strength is 36.68MPa and 20.21MPa for the composites without and with thymol loading respectively. The value for the PLA containing 3% NC without thymol is lower than the reported value by Sung et al. (2017) which is 56.2MPa. The different in value of the tensile strength might be due to the agglomeration of the NC inside the matrix.

In general, the results demonstrated that when the loading of NC in the PLA/JSP and PLA/JSP/thymol based composites increased, the tensile strength of the composite increased but with slightly reduction at the loading of 5% NC. The improvement percentage for the tensile strength of PLA/JSP composites were 19.1% and 8.6% for 3% and 5% loadings of NC respectively while for the PLA/JSP/thymol composites, the percentage of improvement were 24.6% and -3.8% for the 3% and 5% loadings of NC. The results in this current study had a similarity with a research conducted by Sung et al (2017) who incorporated NC extracted from coffee silverskin into PLA matrix. The

results demonstrated that the tensile strength of the composites reinforced with the NC increased at the loading of 3% and decrease at the loading of 5% NC. Haafiz et al. (2013) stated that the observed trend might be due to the agglomeration of NC particle *via* Van der Waals force. The improvement of the tensile strength may be because of the rigidity and stiffness in NC due to the extensive intra and inter molecular hydrogen bond (Mandal and Chakrabarty, 2014). However, poor interfacial adhesion between both the matrix of the polymer and the filler will lower the tensile strength of the composite. According to Cao and co-workers (2016), the NC particles tend to agglomerate to form bigger clusters rather than binding to the PLA.

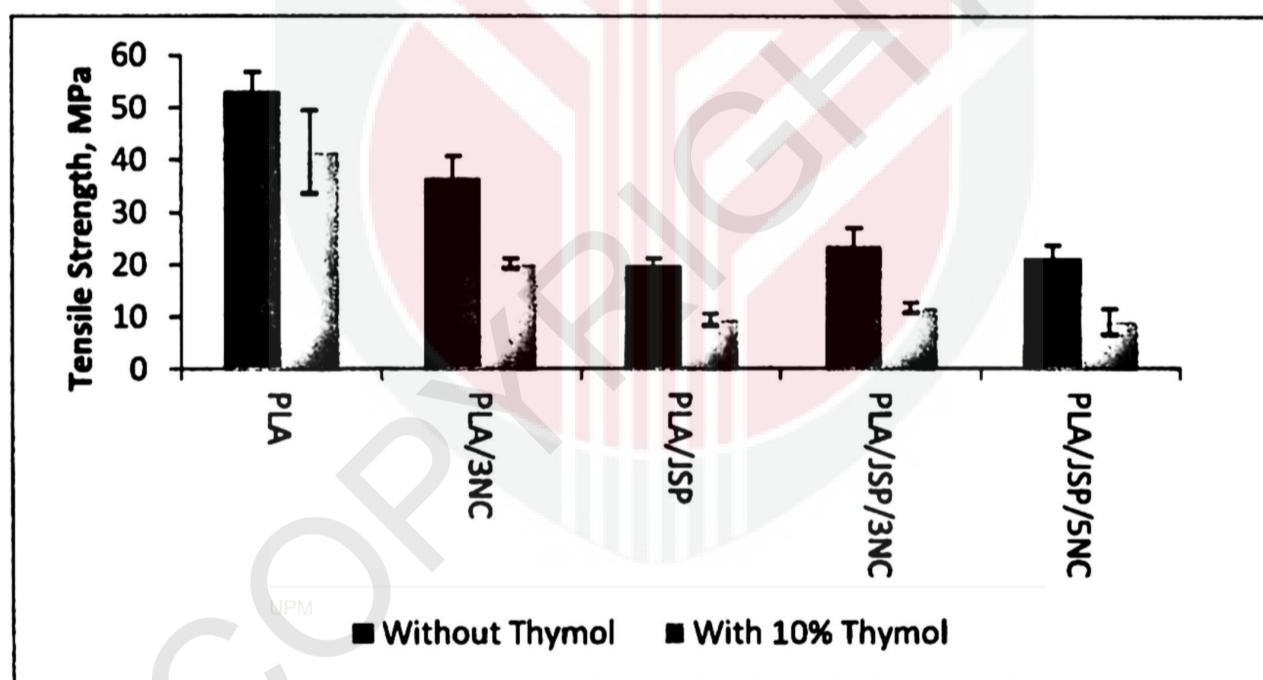


Figure 4.1: Tensile strength of PLA and PLA/JSP composites containing thymol at different loadings of NC

Figure 4.1 shows that the PLA/JSP composites have a higher tensile strength than PLA/JSP/thymol composites. The reduction of tensile strength in term of percentage was calculated to be 52.5%, 50.3% and 57.9% for the composite with 0%, 3%

and 5% loading of the NC. Previous studies done by Marzuki (2018) also reported some reduction of tensile strength as the thymol is added into the polymer matrix. The reduction reported by Marzuki (2018) for the PLA/JSP containing 10% loading of thymol is 12.2%. The addition of thymol into the matrix has effect the intermolecular forces of the polymer matrix (Kramer, 2009). Thymol within the polymer matrix may hinder the chain-to-chain interaction of the polymer and reduce the cross linking which resulted in decrease of rigidity of the polymer (Kavoosi et. al, 2013).

4.1.2 Tensile Modulus of PLA/JSP Composites

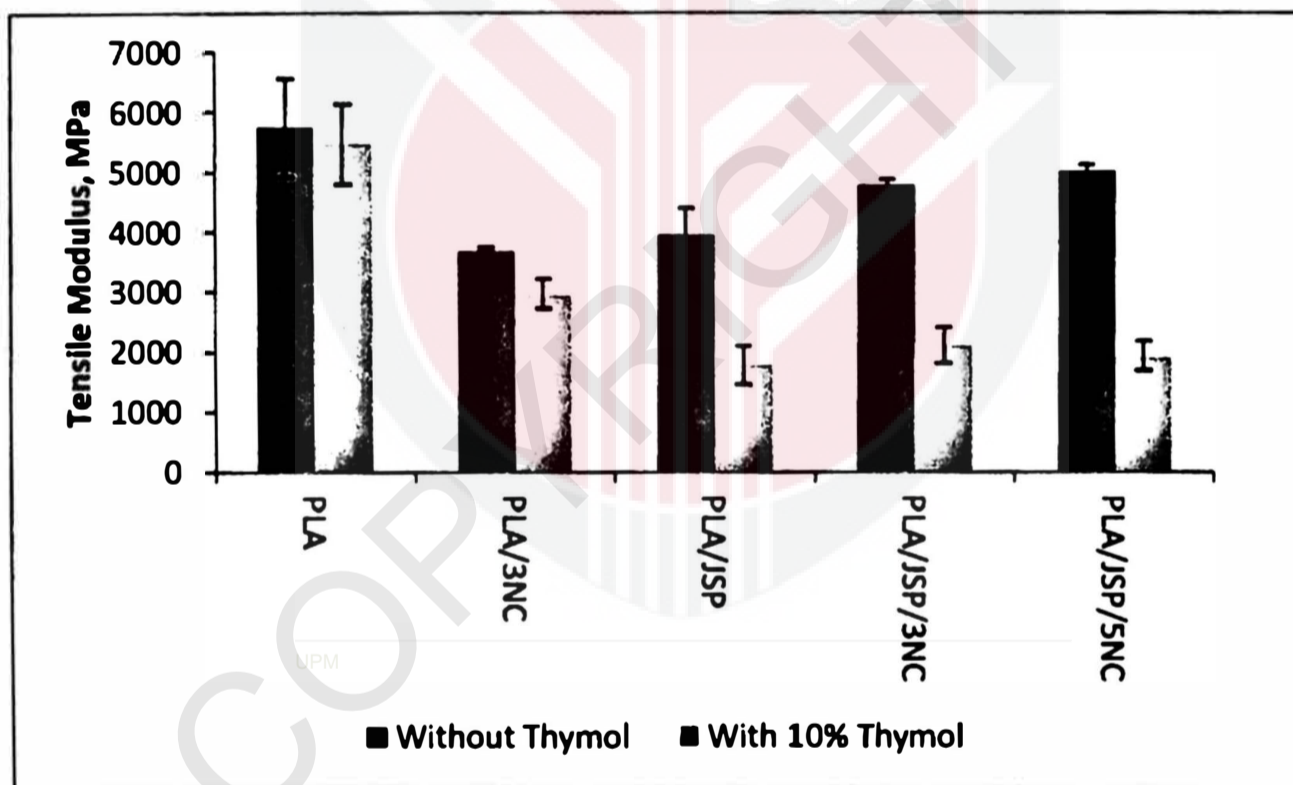


Figure 4.2: Tensile modulus of PLA and PLA/JSP composites containing thymol at different loadings of NC

Figure 4.2 shows the tensile modulus of the PLA/JSP based composites with different loading of NC. The pure PLA has the highest value of tensile modulus with 5737.7MPa. For PLA with 3% loading of NC, the result shows a reduction of 35.2% and

45.5% for the composites without and with thymol respectively. This reduction might be due to the poor adhesion between the polymer matrix which is caused by the agglomeration.

For the PLA/JSP composites without thymol, the value of tensile modulus increased as the loading of NC increased. The percentage of increment of the tensile modulus is 19.8% and 25.8% for the loading of NC of 3% and 5% respectively. With 10% of thymol content, the percentage of increment of the tensile modulus is 17.9% for 3% of NC and 7.9% for 5% of NC content. Previous studies conducted by Sung et al (2017), Janoobi et al. (2010) and Haafiz et al. (2013) also show similar results of the improvement in tensile modulus as the loading of NC increased. Hafiz et al. (2013) stated that the improvement in the tensile modulus when the loading of NC increased is because of the higher crystallinity and the stiffening effect of the filler.

The tensile modulus of the PLA/JSP composites without thymol has demonstrated higher value than the composites containing 10% thymol content. The reduction percentage for each of the composites was 55%, 55.7% and 61.4% for the PLA/JSP composite with the loading of NC of 0%, 3% and 5% respectively. A similar trend of reduction can be observed at a study conducted by Marzuki (2018) where there is a reduction of tensile modulus when thymol is added into the composites of PLA containing 30% loading of JSP. P. Persico and co-worker (2009) also observed a similar reduction of tensile modulus as carvacrol, an isomer of thymol, was added into Low Density Polyethylene (LDPE) matrix. They found that the reduction was due to the carvacrol that acts as a plasticizer which decreased the stiffness of the polymer.

4.1.3 Elongation at Break of PLA/JSP Composites

Figure 4.3 shows the elongation at break of PLA/JSP composites containing thymol at different loading of NC. Low value of elongation at break for pure PLA shows that it is a brittle material. As expected, the presence of NC and/or JSP in the PLA matrix did not contribute to the flexibility of PLA. With the addition of NC into the PLA/JSP based composites, the elongation at break decreased as the loading of the NC increased. There are 5.9% and 13.1% reduction percentage for 3% and 5% loading of NC without thymol content.

Interestingly, regardless of the loading of filler in the PLA/JSP composites, the composites containing thymol at 10% loading demonstrated high flexibility up to 7% than PLA/JSP without thymol. The flexibility of the composites is due to the increase in the mobility of the polymeric chain due to the thymol that exhibit the plasticizer effect (Sungsanit et al. 2012).

With 10% thymol content, the reduction percentage is 13.7% and 16.2% for 3% and 5% loading of NC respectively. This trend is common for thermoplastic composites as it occurs as the fiber concentration inside the polymer increased (Mathew, Oksman & Sain, 2005). Other previous study that had been conducted by Pei et al. (2010) who incorporated NC into poly(l-lactide) (PLLA) also stated that the reason the decreased elongation at break is due to the stiffening effect of the filler which prevents the strain to fail.

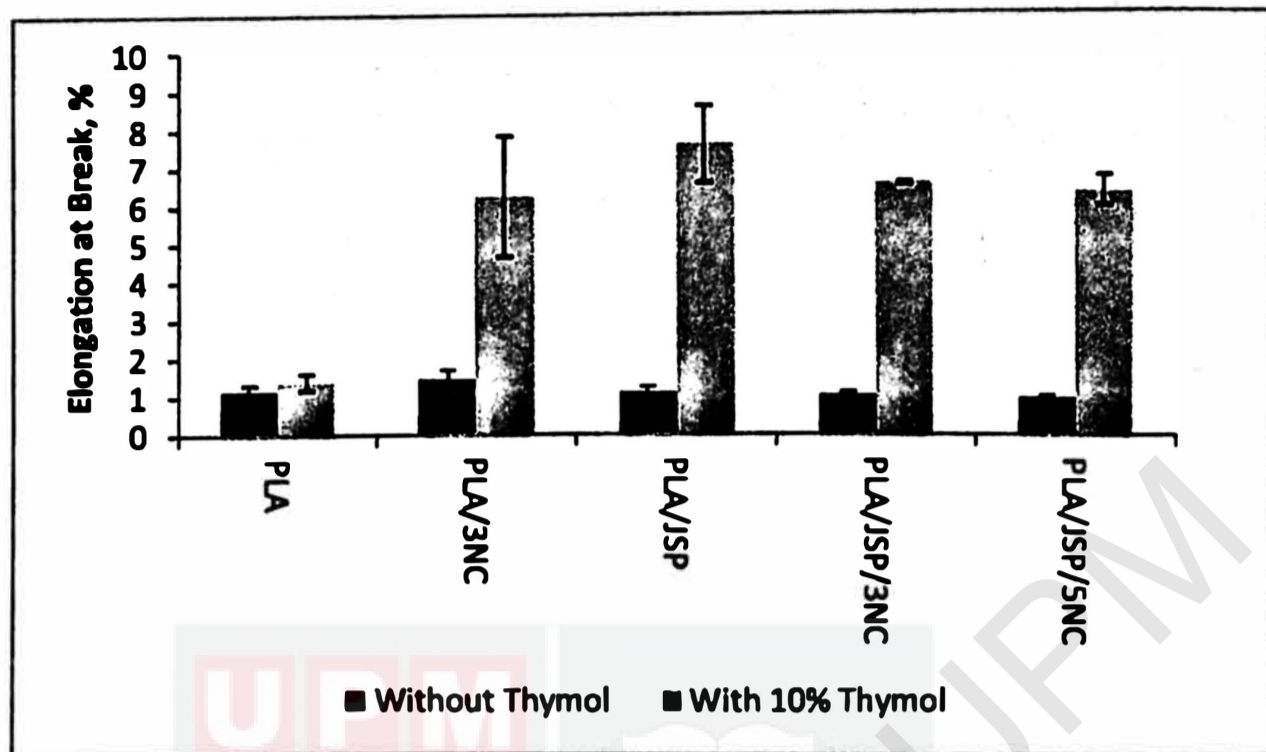


Figure 4.3: Elongation at break of PLA/JSP composite containing thymol at different loadings of NC

The PLA/JSP composites without thymol have lower elongation at break than the ones with 10% thymol content. With the addition of the 10% thymol content, the improvement in elongation at break is 85.4%, 84.1% and 84.8% for the 0%, 3% and 5% of NC loading. These improvements suggest that thymol increased the elasticity of the composites as it acts as a plasticizer mentioned previously by P. Persico et al. (2009).

4.2. Thermal Property

4.2.1 Thermal Analysis of PLA/JSP Composites

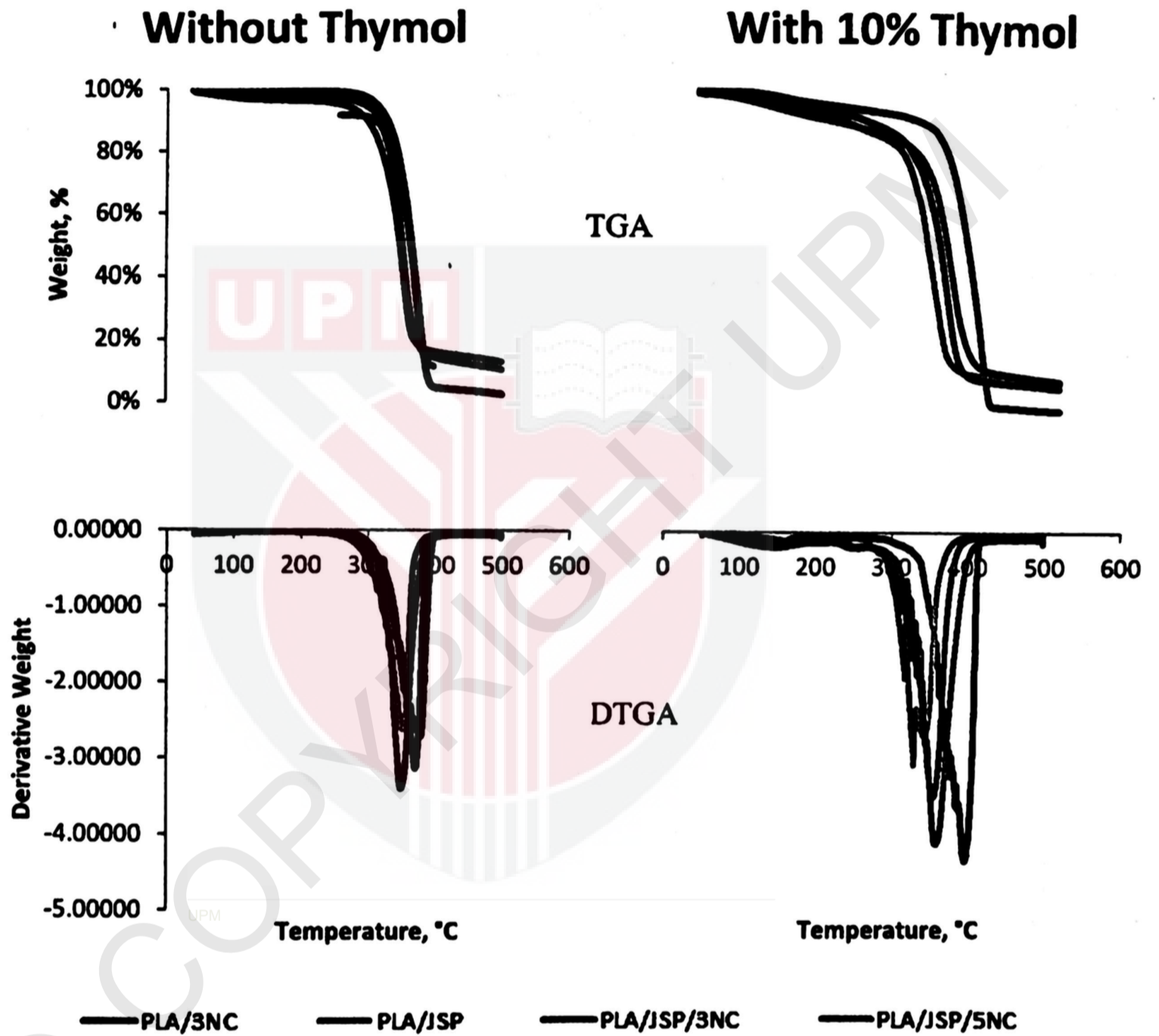


Figure 4.4: TGA and DTGA profile of PLA/JSP composites containing thymol at different loadings of NC

Figure 4.4 shows the TGA and DTGA profile of PLA/JSP composites containing thymol at different loading of NC. Based on TGA curves, there is no noticeable step that can be observed at the first region for the PLA/JSP composites without thymol content. This might be due to the drying process that had been done for all the materials before undergone mixing process which remove all the moisture content. For PLA/JSP composites containing thymol, there is a noticeable step due to presence of thymol that start to vaporise between 50°C to 300°C as there is a peak shown at the DTGA curves. Ramos and co-workers (2012) who incorporated thymol into polypropylene films suggested that the evaporation of thymol from polymer composites occurred between 100°C until 200°C. The vaporised of thymol contributed about 20% weight loss.

For the second region of weight loss, it occurred between 300°C until 400°C. This loss might be due to the structural degradation of PLA/JSP composites which contributed to a total weight loss about 80% for the PLA/JSP composites without thymol content and 60% for the PLA/JSP composites containing thymol. The incorporation of NC into the composites increased the onset of the degradation. However, the rate of the degradation of the composites shows no significant change. The final region of the weight loss occurred at temperature above 400°C where the decomposition of the carbonaceous materials occurred to produce a mixture of hydrocarbons and also carbon (Mandal and Chakrabarty, 2014).

Table 4.1 shows the degradation temperature of PLA/JSP composites containing thymol at different loadings of NC. The PLA with 10% thymol content and 3% loading of NC has the highest degradation temperature at 400°C than the pure PLA and

PLA/JSP composites. The degradation temperature for the PLA/JSP composites without thymol content are 352°C, 371°C and 350°C for the loading of NC of 0%, 3% and 5% respectively. A study conducted by Mandal and Chakrabarty (2014) who incorporated NC into PLA composites also provided a similar increment as the loading of the NC inside the composites increased. By referring to Table 4.1, the addition of 10% thymol into the PLA/JSP based composites matrix decreased the degradation temperature. Marzuki (2018) also reported a decreased in degradation temperature when thymol was added into the polymer matrix.

Table 4.1: Degradation temperature of PLA/JSP composites containing thymol at different loadings of NC

Degradation Temperature, °C			
Sample	Nano-cellulose loading, %	Without Thymol	With 10% thymol
PLA	0	372	363
	3	376	400
PLA/JSP	0	352	332
	3	371	359
	5	350	362

4.3. Bacteria Inhibition Study



Figure 4.5: Antimicrobial activity of PLA/JSP composites containing thymol at different loadings of NC against *Staphylococcus aureus*. (1A) PLA/JSP, (2A) PLA/JSP/3% NC, (3A) PLA/JSP/5% NC and (4A) PLA/3% NC

Figure 4.5 shows the inhibition zone of active PLA/JSP composites containing thymol at different loading of NC against *S. aureus*. The results show that the PLA/JSP composites containing thymol at 5% loading of NC has the biggest inhibition zone than others composites containing thymol. A small inhibition can be observed at PLA/JSP composites containing thymol at 3% loading of NC and PLA containing thymol at 3% loading of NC. These results could be explained by the diffusion of thymol from the composites, penetrated the microbial cells of the bacteria and inhibit the growth of bacteria under the disc (Bonev and Hooper, 2008). The observation suggests that the incorporation of NC increase the ability of thymol to inhibit the growth of *S. aureus*. According to Tawakkal (2017), the presence of natural fibre at higher content in the film may have increased the hydrophilicity of the film resulting in water molecules being

absorbed at the surface of the film which may contribute to the release of the thymol. Sarwar and co-worker (2018) who added silver nanoparticle as an antimicrobial agent into PVA/NC composites also state that the incorporation of NC into the polymer matrix can enhance the antimicrobial activity. They suggested that the enhancement of the antimicrobial activity might be due to the characteristic of NC which having a large surface area.



CHAPTER 5

CONCLUSION AND RECOMMEDATION

5.1. Conclusion

In this study, the mechanical, thermal and antimicrobial properties of PLA/JSP composites containing thymol and at different loadings of NC were tested. Although some contradictory data were obtained, it seems that different loading of NC had prominent effect on the properties of the composites.

In term of mechanical properties, for PLA/JSP composites, the tensile strength of the composites containing 3% loading of NC demonstrate greater tensile strength than PLA/JSP composite regardless of the thymol content. A slightly reduction of tensile strength in PLA/JSP composites with 5% loading of NC was observed which may be due to agglomeration of NC. The incorporation of NC into the composites shows increment in tensile modulus and reduction in elongation at break. The presence of fibre and NC increased the stiffness of polymers. Tensile strength and tensile modulus of composites decrease due to the presence of thymol, and elongation at break increase due to the plasticizing effect of thymol.

Thermal properties of the composite demonstrated that the incorporation of NC increases the thermal stability of the composites. The addition of thymol reduces the degradation temperature, suggests that the thymol reduces the thermal stability of PLA and PLA/JS composites.

For the antimicrobial activity, PLA/JSP composite with 5% loading of NC shows the biggest inhibition zone than others. This suggested that the presence of higher loading of NC increase the ability of thymol to inhibit the growth of *S. aureus* than the PLA/JSP composite without NC.

5.2.Recommendation

It is recommended for any further studies to be conducted on the composites containing different loadings of NC as the right amount of the loading can give advantages on the mechanical and thermal properties of the composites. Moreover, the usage of NC in the form of NC slurry could be incorporated into the polymer in order to reduce the agglomeration of the NC as well as enhance the fibre dispersion during the melt blending process. However, the type of polymer used as the matrix need to be suitable in order to avoid degradation of bio-based polymer due to the presence of water inside the NC slurry. Different types of NC including nanocrystal and metal nanoparticles can be added into the PLA/JSP to investigate the antimicrobial activity of thymol which can greatly enhance the application of active packaging.

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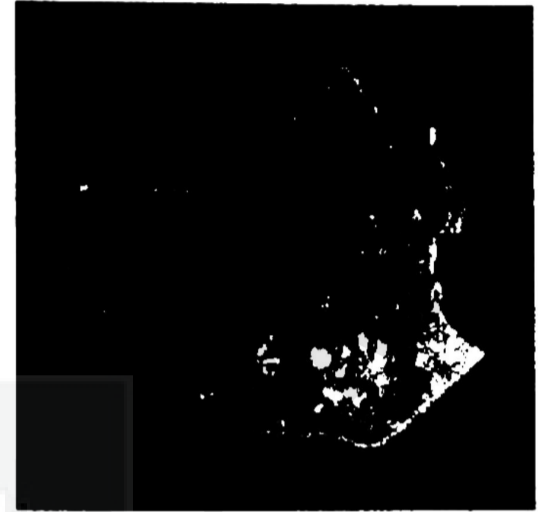
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APPENDIX: SPECIMEN

Specimen with Thymol:



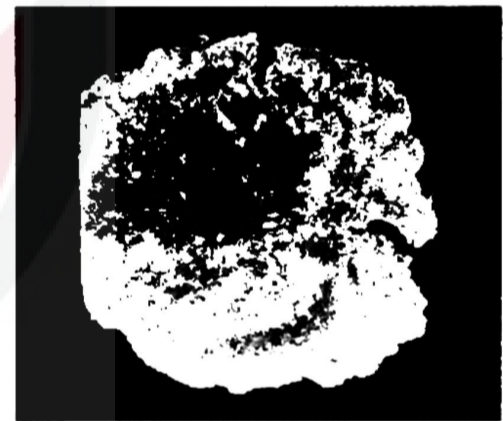
PLA/JSP/5%NF



PLA/JSP/3%NF

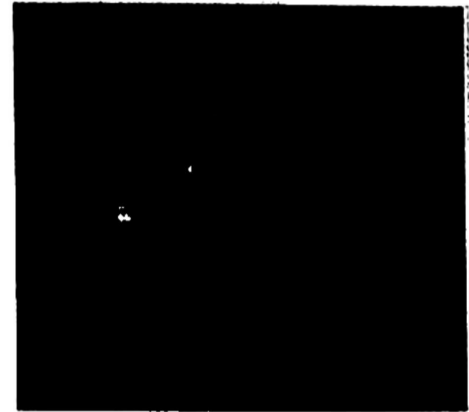
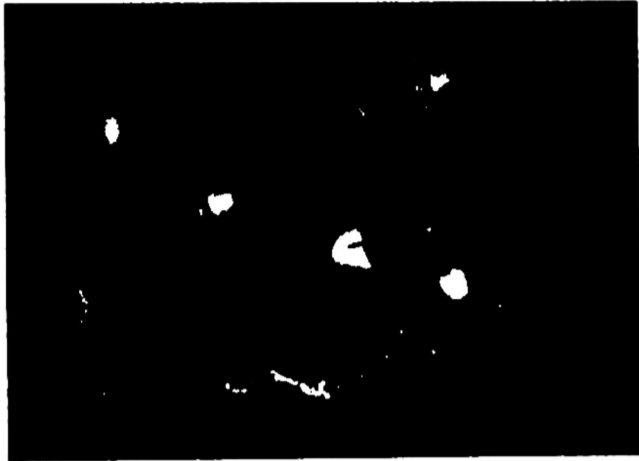


PLA/JSP

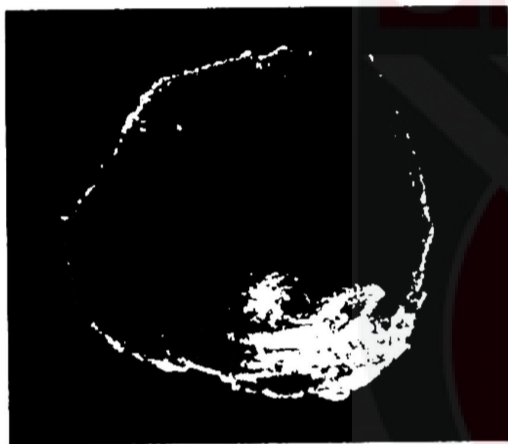


PLA/3%NF

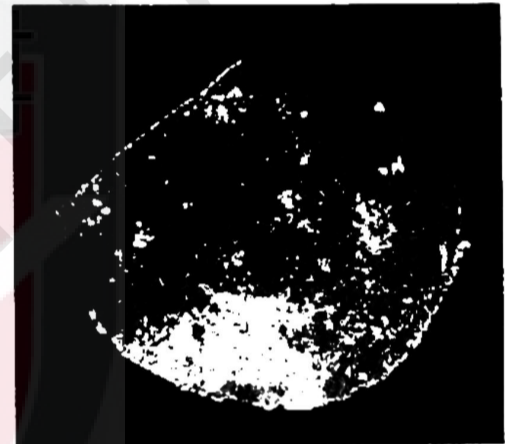
Specimen without Thymol:



PLA/JSP/5%NF



PLA/JSP/3%NF



PLA/JSP

PLA/3%NF

APPENDIX: DATA ANALYSIS

Analysis of mechanical properties

Appendix B-1: Mechanical properties of PLA/3% NC

Sample	Tensile Strength, MPa	Tensile Modulus, MPa	Elongation at Break, %
1	32.75	3696.00	1.57
2	-	3690.00	1.24
3	36.21	-	1.80
4	41.08	-	1.49
5	-	3768.00	1.21
Mean	36.68	3718.00	1.46
SD	4.18	43.41	0.24

Appendix B-2: Mechanical properties of PLA/3% NC containing thymol

Sample	Tensile Strength, MPa	Tensile Modulus, MPa	Elongation, %
1	-	-	-
2	21.31	2831.00	-
3	-	-	-
4	19.44	3248.00	5.11
5	19.89	2849.00	7.34
Mean	20.21	2976.00	6.23
SD	0.98	235.73	1.58

Appendix B-3: Mechanical properties of PLA/JSP at 0% NC

Sample	Tensile Strength, MPa	Tensile Modulus, MPa	Elongation, %
1	19.88	-	-
2	-	3500.00	-
3	-	-	-
4	18.42	4181.00	1.01
5	21.19	4248.00	1.20
Mean	19.83	3976.33	1.11
SD	1.39	413.87	0.13

Appendix B-4: Mechanical properties of PLA/JSP containing thymol at 0% NC

Sample	Tensile Strength, MPa	Tensile Modulus, MPa	Elongation, %
1	8.78	1450.00	-
2	9.26	1826.00	8.70
3	-	-	-
4	8.68	-	6.72
5	10.97	2090.00	7.27
Mean	9.42	1788.67	7.56
SD	1.06	321.63	1.02

Appendix B-5: Mechanical properties of PLA/JSP at 3% NC

Sample	Tensile Strength, MPa	Tensile Modulus, MPa	Elongation, %
1	-	4692.00	-
2	22.97	-	1.01
3	-	4708.00	1.00
4	27.27	4921.00	1.11
5	20.59	4731.00	-
Mean	23.61	4763.00	1.04
SD	3.39	106.54	0.06

Appendix B-6: Mechanical properties of PLA/JSP containing thymol at 3% NC

Sample	Tensile Strength, MPa	Tensile Modulus, MPa	Elongation, %
1	13.11	-	6.55
2	11.46	2452.00	-
3	-	2115.00	6.51
4	11.39	1738.00	-
5	10.98	2133.00	-
Mean	11.74	2109.50	6.53
SD	0.94	292.06	0.03

Appendix B-7: Mechanical properties of PLA/JSP at 5% NC

Sample	Tensile Strength, MPa	Tensile Modulus, MPa	Elongation, %
1	23.21	-	1.00
2	23.23	4988.00	1.00
3	18.52	-	0.93
4	-	4888.00	0.93
5	21.19	5127.00	0.94
Mean	21.54	5001.00	0.96
SD	2.23	120.03	0.04

Appendix B-8: Mechanical properties of PLA/JSP containing thymol at 5% NC

Sample	Tensile Strength, MPa	Tensile Modulus, MPa	Elongation, %
1	10.41	1756.00	6.05
2	6.78	-	-
3	7.85	2103.00	-
4	7.61	-	-
5	12.64	-	6.62
Mean	9.06	1929.50	6.34
SD	2.42	245.37	0.40