

Development of Lignin Modified Tapioca Starch for Biodegradable Film

By

Hannan binti Rozman

Dissertation submitted in partial fulfilment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

MAY 2011

Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATE OF APPROVAL

Development of Lignin Modified Tapioca Starch for Biodegradable Film

By

Hannan binti Rozman

A project dissertation submitted in to the

Chemical Engineering Programme

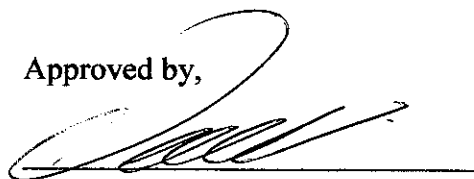
Universiti Teknologi PETRONAS

Partial fulfilment of the requirements for the

BACHELOR OF ENGINEERING (Hons)

(CHEMICAL ENGINEERING)

Approved by,



(AP DR ZAKARIA BIN MAN)

Assoc. Prof. Dr. Zakaria Man
Chemical Engineering Department
Universiti Teknologi PETRONAS

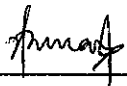
UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

September 2011

CERTIFICATE OF ORIGINALITY

This avowal is to certify that I am responsible for the work submitted in this project, that the work done is of my own unless specified in the references and acknowledgements, and the original work contained herein have not been undertaken or done by unspecified sources or persons.



(HANNAN BINTI ROZMAN)

ACKNOWLEDGEMENT

The author would like to take the opportunity to thank everyone involved in making this Final Year Project a successful educational session. Highest praise is to Allah the Almighty, for the blessing of knowledge, endurance and perseverance in completing this Final Year Project within the prescribed timeline. Deepest gratitude goes to AP. Dr. Zakaria bin Man; Final Year Project supervisor for the continuous and relentless support and guidance throughout the project. The author would also like to thank the following individuals for their professionalism and contribution to the research:

- Ms. Ariyanti, co-supervisor under AP. Dr. Zakaria bin Man
- Ms. Nik Fauziah and Mr. Zulhilmi, fellow researcher
- Mr. Fazli and Mr. Asnizam, Chemical Engineering laboratory Technicians
- Mechanical Engineering laboratory technicians

Also, the author would like to express heartfelt appreciation to beloved parents, family and friends for continuous moral support and advices throughout the project completion, and to anyone who has directly or indirectly contributed towards the success of the project.

Thank you.

ABSTRACT

The objective of the present investigation is to synthesize starch/lignin film, a new starch based polymer and to evaluate its application in the design of controlled release fertilizer. The properties of the film were compared with different ratio of lignin content. Starch/lignin polymer was synthesized by gelatinization of starch in the presence of urea, borax and lignin. Thermal Gravitational Analyzer (TGA), Scanning Electron Microscopy (SEM), X-ray Diffusion (XRD), and Universal Testing Machine (UTM) are used to evaluate the influence of lignin content on the film mechanical and thermal properties. The film was prepared by using solution casting method composed of tapioca starch mixed with lignin. Other tests such as biodegradability test and water absorption test have been performed and it is shown that lignin actually reduced the water affinity of the films. The results prove that the water-uptake of these blends could be reduced and that simultaneously stiffer materials with a less pronounced degradation rate can be obtained.

TABLE OF CONTENTS

CHAPTER 1.....	1
INTRODUCTION.....	1
1.1 Background of Study.....	1
1.2 Problem Statement.....	3
1.3 Objectives of Study.....	3
1.4 Scope of Study.....	4
CHAPTER 2.....	5
LITERATURE REVIEW.....	5
2.1 Introduction.....	5
2.2 Controlled Release Fertilizer (CRF).....	6
2.3 Starch.....	7
2.4 Lignin.....	8
2.5 Critical Analysis 1: controlled release of urea encapsulated by starch-g-poly (L-lactide).....	9
2.6 Critical Analysis 2: Controlled-release fertilizer encapsulated by starch/PVA coating.....	10
2.7 Critical Analysis 3: Use of Kraft lignin as filler for starch films.....	10
2.8 Conclusion.....	11
CHAPTER 3.....	12
METHODOLOGY.....	12
3.1 Project Workflow.....	12
3.2 Experimental.....	12
3.3 Preparation of Starch/lignin Film.....	13
3.4 Mechanical Properties Measurement.....	13
3.5 Thermal Analysis.....	13
3.6 Microscopic Analysis.....	14
3.7 X-ray Diffraction.....	14
3.8 Swellability Test.....	14
3.9 Moisture Absorption.....	14
3.10 Kinetic Moisture Absorption.....	14
3.11 Biodegradability.....	15

CHAPTER 4.....	16
RESULT AND DISCUSSION.....	16
4.1 FTIR.....	16
4.2 Mechanical Analysis.....	17
4.3 Thermal Analysis.....	18
4.4 Microscopic Analysis.....	21
4.5 XRD.....	23
4.6 Water Affinity.....	24
4.6.1 Swellability Test.....	24
4.6.2 Moisture Absorption.....	25
4.6.3 Kinetic Moisture absorption.....	25
4.6.4 Biodegradability.....	26
CHAPTER 5 - CONCLUSION.....	27
REFERENCES.....	28

LIST OF FIGURES

Figure 1 : Starch molecular structure.....	7
Figure 2: Lignin molecular structure.....	9
Figure 3: Project workflow.....	12
Figure 4: Experimental work.....	12
Figure 5: FTIR spectra of starch–borate–lignin and pure starch film.....	16
Figure 6: Stress for modified films.....	17
Figure 7: Strain for modified films.....	17
Figure 8: TGA curve for 0% lignin.....	18
Figure 9: TGA curve for 10% lignin.....	19
Figure 10 : TGA curve for 20% lignin.....	19
Figure 11: Weight residue (%) at 500 ^o C for modified films.....	20
Figure 12 : SEM images for modified films at 1000 and 5000 magnification.....	21
Figure 13 : XRD for modified films.....	23
Figure 14: Percentage swelling of modified films.....	24
Figure 15: Moisture absorption (wt%) for modified films.....	25
Figure 16: Moisture absorption rate for modified films.....	25

Figure 17: Biodegradability (days) for modified films	26
Figure 18: TGA curve for 0% lignin film	32
Figure 19: TGA curve for 5% lignin film	32
Figure 20: TGA curve for 10% lignin film	33
Figure 21: TGA Curve for 15% lignin film	33
Figure 22: TGA curve for 20% lignin film	34

CHAPTER 1

INTRODUCTION

3.1 Background of Study

Synthetic polymers have provided undeniable benefits for the development of the society. However, non-biodegradable petroleum-based plastics have become a threat to the environment and the diminishing petrochemical resources. Therefore, an increasing attention has been paid on the development of environmentally friendly materials, which is a solution not only to the growing environmental threats but also to the uncertainty of petroleum supply.

Starch based polymer can be effectively used as an encapsulating matrix in the controlled released for agrochemicals after derivation and cross-linking (Tarvainen et al., 2004; Tuovinen et. al., 2003). Research has shown that slow or controlled release technology could effectively avoid the loss of fertilizers and serious environmental pollutions.

Starch is an abundant biopolymer in the nature. The potential advantages are, apart from its environmental gains, it is also low cost, not depending on petroleum sources, available from renewable resources, and enabling to replace some synthetic polymers. However, the industrial development of starch polymer is hindered by its disadvantages such as the relatively low tensile property and high water absorbency (Wu R.L. et. al., 2008). Therefore, one way to improve starch properties which is the water affinity and maintaining its biodegradability is to blend starch with hydrophobic compounds such as lignin.

In this study, biodegradable starch/lignin blend films are to be prepared for urea fertilizer coating. This project is also to investigate the films' structure, the influences of the blending ratio of starch and lignin to the film's properties.

3.2 Problem Statement

General

In recent years, the research has been ongoing to find a suitable alternative and film-forming membrane material that can be safely used in agroindustries in order to improve the utilization of fertilizer nutrient. The most widely used fertilizer is urea because of its high nitrogen content and comparatively low cost of production (Chen et. al., 2005). However, due to surface runoff, leaching, and vaporization, the utilization efficiency of urea is generally below 50%. About 40-70% of nitrogen escapes to the environment and cannot be absorbed by crops, which causes not only large economic losses but also very serious environmental pollution (Guo et. al., 2007).

Specific

Starch is the cheapest biodegradable polymer available in large amounts from renewable plant resources and it is a prospective replacement for synthetic plastics which can be a solution to the growing environmental threats and the uncertainty of petroleum supply. However, natural starch polymer contains many hydroxyl groups that make the starch matrix hydrophilic and capable of absorbing water and swelling dramatically in moist environment. By cross-linking and blending starch with lignin, it is anticipated that the properties of the film will be improved.

3.3 Objectives of Study

The main objectives of this study are:-

- i. To develop a starch/lignin polymer film
- ii. To investigate the film's structure, the influences of the blending ratio of starch and lignin to the film's properties.

3.4 Scope of Study

This study is conducted to develop a new approach for preparing a new type of slow release fertilizer coating using natural and biodegradable polymer. The scope of work for this project is confined to the study of starch/lignin blends for urea fertilizer release only. The timeframe for this study is 1 year and will be done in two phase:

1. In the first phase, the project will be more on studying and reviewing information on the journals and experiments report available in the net and library.
2. As for the second phase, by using all information and data gained from the first phase, a proper experiment will be done to achieve the objectives stated earlier. The project will be in the form of laboratory experiments. It composes of two stages which are experiment and data analyzing stage.

CHAPTER 2

LITERATURE REVIEW

3.5 Introduction

Fertilizers are one of the most important products of the agrochemical industry. They are added to the soil to release nutrients necessary for plant growth. However, the potential hazards of fertilizers to the environment have results in stringent limitation to their use. About half of the applied fertilizers, depending on the method of application and soil condition, are lost to the environment, which results in the contamination of water (O.A.Salman, 1989). Use of conventional fertilizers may lead to concentration levels that are too high for effective action. A high concentration may produce undesirable side effects either in the target area, which could lead to crop damage, or in the surrounding environment (K. El Rafaie et. al., 1996).

One method of reducing nutrient losses involves the use of controlled-release fertilizers (CRF). The CRF can be physically prepared from the granules of the soluble fertilizers by coating them with materials, which reduce their dissolution rate. CRF demonstrate many advantages over the conventional type, such as decreased rate of removal of the fertilizers from the soil by rain or irrigation water, sustained supply of minerals for a prolonged time, increased efficiency of the fertilizer, lower frequency of application in accordance with normal crop requirement, minimized potential negative effects associated with over dosage, and reduced toxicity (K. Byung Su et. al., 1996).

Many systems based on natural polymers have already been investigated, such as PCL/starch (Ikeo et al., 2006), PHB/lignin (Kai et al., 2004), PCL/cellulose (Sanchez-García et al., 2008), etc. However, these synthetic biodegradable polymers are expensive and/or rely on the petroleum resources. In addition, because of the poor compatibility between hydrophobic polymers and natural polymers, reactive compatibilizers or coupling agents are often used to improve interfacial interactions of

these composites. Recently, many attentions had been paid on preparing the totally biodegradable blends with the natural polymers and their derivatives, such as cellulose diacetate/starch (Lee et al., 2006), starch acetate/native starch (Guan and Hanna, 2004), cationic starch/cellulose (Bratskaya et al., 2006) and chitosan/cellulose acetate (Liu and Bai, 2005), etc. These blends present good compatibility and retain biodegradability. However, compared with the preparation of environmental friendly materials based on pure natural polymers, using their derivatives will increase the cost and complicacy.

In this literature review, past researches in recent years are analyzed to study the available systems in natural and biodegradable polymer as fertilizer coating and also to study the feasibility of the new proposed system which is using starch and lignin. It is hypothesized that lignin modified starch will increase the strength of normal starch polymer and also reduce the swelling in moist environment.

3.6 Controlled Release Fertilizer (CRF)

Measured nutrient uptake by plants from fertilizers can be achieved through modification of fertilizer products - either chemically to reduce their solubility or physically, for example, by coating encapsulation. Controlled release fertilizers (CRFs) have been used for many years, beginning with the sulfur coated urea (Jacobs, D.F, 2003). The early sulfur coated materials did not always give a uniform response, because either the coating sometimes might have cracked or the coating would have been of uneven thickness, allowing the fertilizer granules to break down at different times.

However, newer generation of CRFs have resin coats that better control the release of the fertilizer. CRFs could match the fertilizer application more closely with the amount actually needed for plant growth. Coated CRFs use a polymer or sulfur coating to encapsulate water-soluble nutrients. The coating thickness and media temperature primarily control the rate of nutrient release. The uncoated nitrogen reaction products

are relatively insoluble in water and nutrient release is generally controlled by water availability and/or microbial decomposition.

3.7 Starch

Polysaccharides, and specially starch and its derivatives, have been studied extensively to this end. Starch is a natural polymer available in large amounts from several renewable plant sources, and it is produced in abundance beyond available markets. It is the cheapest biopolymer and it is entirely biodegradable. Starch is a polymer of glycosidic units linked by α -(1-4) bonds. It is composed of two polymers, amylose and amylopectin (Coulate, 1996).

Starch is formed in granules, which exhibit molecular ordering and a crystalline X-ray diffraction pattern. When heated in suitable conditions, the granules lose their shape and develop an amorphous phase. When plasticizers are added to this amorphous phase, thermoplastic starch is produced (TPS) (Wiedmann, & Strobel, 1991). Under these conditions, a great variety of composites and blends can be produced.

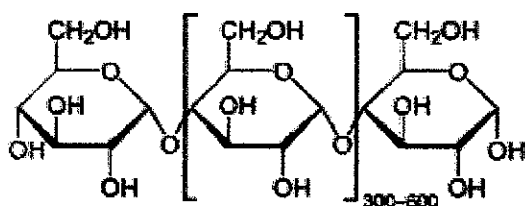


Figure 1 : Starch molecular structure

In order to improve starch properties, starch is graft-copolymerized with various monomers. Through the variation of grafting monomers, different changes in properties can be achieved as studied by Arvanitoyannis et. al. (1999) and Zhu & Zhuo (2001).

3.8 Lignin

Lignin or lignen is a complex chemical compound most commonly derived from wood, and an integral part of the secondary cell walls of plants. It is one of the most abundant organic polymers on earth, exceeded only by cellulose, employing 30% of non-fossil organic carbon and constituting from a quarter to a third of the dry mass of wood. As a biopolymer, lignin is unusual because of its heterogeneity and lack of a defined primary structure. Its most commonly noted function is the support through strengthening of wood (xylem cells) in trees.

Lignin, as a major by-product in the papermaking industry, is generally discharged into rivers rather than recycled and reused because of the lack of and inefficiency of alkali recycling. Every year up to 5×10^7 ton lignin are produced and disposed of as waste. It not only wastes resources but also brings up serious aquatic environmental contamination (Zhang and Chuang, 2001). This shows that lignin is an enormous and inexpensive raw natural material. Its natural macromolecule structure is composed of phenol units, connected by various types of linkages, thus forming a branched structure owning diverse functional groups (Carsten *et al.*, 2000). In regards to this finding, it has been reported that lignin possess extensive cross-linking and strong intermolecular interactions which can improve the strength of starch polymers. Its hydrophobic properties also can reduce the water affinity of starch polymers.

Furthermore, it has been reported in the study by Carsten *et al.* (2000), that lignin can increase the plasticity of starch matrix due to its lower molecular weight fraction and can form a cementing material for cellulose fibrils, which can improve the mechanical properties of the composite material of lignin/cellulose. Therefore, lignin can be used as a plasticizer of starch, a reinforcing agent of cellulose and a compatibilizer of cellulose and starch, to prepare natural biopolymer composites composed of cellulose, starch and lignin.

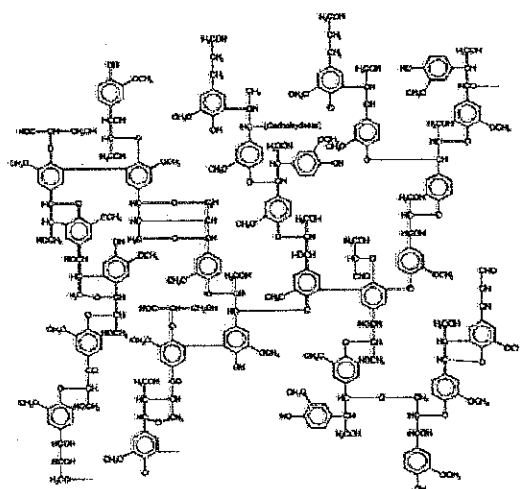


Figure 2: Lignin molecular structure

3.9 Critical Analysis 1: controlled release of urea encapsulated by starch-g-poly (L-lactide)

First review is on the research done by Chen et. al. (2008) with the title controlled release of urea encapsulated by starch-g-poly (L-lactide). The objective of the study was to develop a new approach for preparing a new type of slow release membrane encapsulated urea fertilizer using starch-g-PLLA. The method used in this study is solution casting and the urea is individually encapsulated with starch polymer modified by L-lactide through in-situ graft copolymerization. The results shown that introduction of hydrophobic PLLA reduced the swellability of starch matrix and decrease the release rate of urea.

The approach used in the research has shown positive result using hydrophobic material such as PLLA, therefore the use of lignin which is also hydrophobic is anticipated to give significant improvements to the film. The water tolerance of the matrix could improve the capability of controlling urea release. This study also used solution casting method which is more excellent in the thickness uniformity than the melt extrusion method. Furthermore, in the solution casting method, the produced film contains foreign materials less than in the melt extrusion method. Therefore, the solution casting method is preferable in the film production.

3.10 Critical Analysis 2: Controlled-release fertilizer encapsulated by starch/PVA coating

Second review is on the research done by Han et. al.(2008), where the title is controlled-release fertilizer encapsulated by starch/polyvinyl alcohol coating. The objective of the research was to develop a new approach for preparing a new type of slow release membrane encapsulated urea fertilizer using starch/PVA blend film. In the research, the method used was blending starch with PVA and cross-linked with formaldehyde. The structure was then observed using X-ray diffraction (XRD), Fourier transform infrared absorption spectra (FTIR) and atomic force microscopy (AFM). The results shown that crystal structure of PVA was changed after being blended with starch, water absorbency increased along PVA content but decreased along formaldehyde content due to the cross-linking reaction.

For this research, the use of PVA is less preferable due to the high content of –OH in PVA which increases the water absorbency of the polymer. However, cross-linking starch/PVA with formaldehyde reduced the hydrophilicity of the starch. This is due to the intermolecular and intramolecular linkage between of –OH between starch and PVA molecules. (Han et.al., 2008) This chemical binding using formaldehyde has shown great effect on the compatibility of the starch/PVA blend.

3.11 Critical Analysis 3: Use of Kraft lignin as filler for starch films

Third review is on the research done by Baumberger S. et. al. (1997), Use of Kraft lignin as filler for starch films. The objective was to evaluate the influence of lignin content on the film mechanical properties. The film was prepared by using melt extrusion method followed by thermal molding, composed of commercial Kraft lignin mixed with wheat starch. Then, the mechanical properties were evaluated by stress strain tests at different ambient relative humidity levels. In the dissolution tests and water absorption tests that have been performed, results shown that lignin actually reduced the overall affinity of the films. As the percentage of lignin increased, the film resistance to elongation significantly decreased, compared to the control starch film.

These results are consistent with the hypothesis of a two phase material consisting of a hydrophilic starch matrix filled with hydrophobic lignin aggregates, as confirmed by microscopic observations. The experiment showed that the lower molecular weight fraction of lignin may be responsible for improvement of starch polymer. However, in the melt extrusion method, the polymer is heated to melt, and then the melt polymer is extruded to form a film. The melt extrusion method has merits in that the productivity is high and the cost for equipments is relatively low. Therefore, it is difficult to adjust the film thickness accurately.

3.12 Conclusion

Taken together, the results of these past researches indicate that polymer blend gives better mechanical properties and phase morphology (Chen et. al., 2008, Han et. al., 2008, Baumberger S. et. al., 1997). It can be assumed from these literature reviews that the presence of highly cross-linked aromatic skeletons of lignin will give significant effect to the starch blend. Therefore, the modified starch products could be expected to have widely potential in agriculture industry as the controlled release fertilizer coating.

CHAPTER 3

METHODOLOGY

3.13 Project workflow

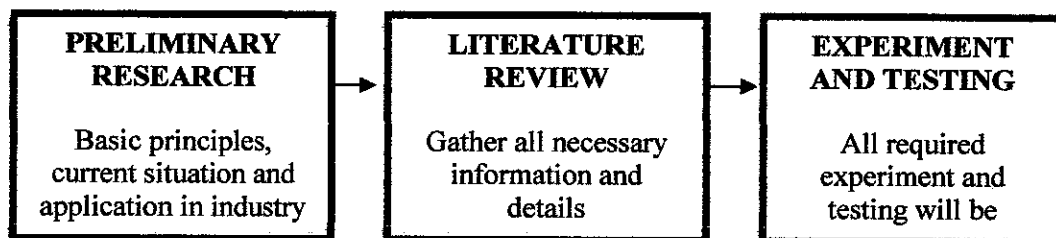


Figure 3: Project workflow

3.14 Experimental

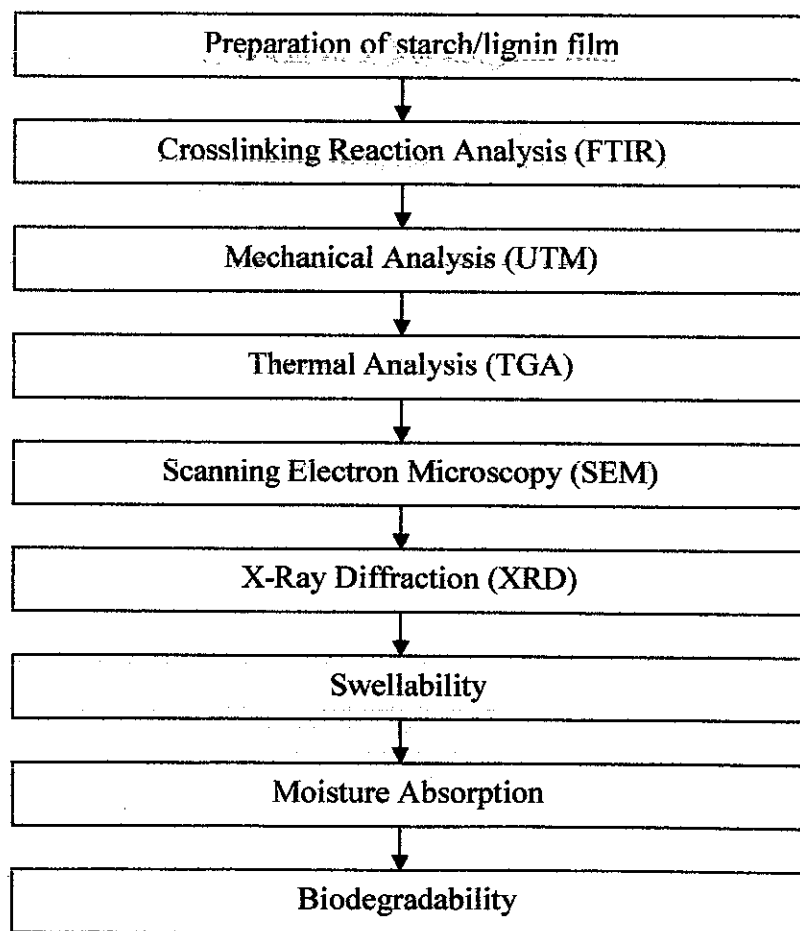


Figure 4: Experimental work

3.15 Preparation of Starch/lignin Film

Tapioca starch (5g) is dispersed in 95 ml of purified water to form starch slurry. The starch slurry is heated in a water bath of an 80⁰C for 30 minutes and stirred until it gelatinize and become viscous. Borax (0.25g) and urea (2.5g) are weighed in a separate beaker and mixed to the viscous starch solution. Lignin is added to the solution with different ratio of 0%, 5%, 10%, 15% and 20% under continuous heating and stirring for 3 hours. The mixture is removed from the heat, the foam is skimmed off, and the solution is distributed into a leveled plastic mold. After drying the solution at room temperature, the films are allowed to dry in a hot-air oven at 50⁰C for 8 hours and dried starch/lignin films are removed from the mold.

3.16 Mechanical Properties Measurement

In the mechanical testing of the film a tensile test is carried out using Universal Testing Machine (UTM 50kN) where a film sample is stretched at a constant rate until it breaks. The samples were stored under controlled temperature and moisture conditions until testing, and at least six specimens per sample were used. The films are cut into 10cm x 1.5cm with an average thickness of 0.2mm. The standard used for this test is ASTM D882-02 - Standard test method for tensile properties of thin plastic sheeting. The stress-strain curves obtained are used to determine the tensile strength and elongation at break.

3.17 Thermal Analysis

Thermogravimetric analysis is carried out using a SDT Q600 (TA Co., USA) under nitrogen atmosphere. Samples (about 10 mg) were heated from room temperature to 800⁰C at a heating rate of 10⁰C/min.

3.18 Microscopic Analysis

Film samples were examined for surface characteristics using a JEOL JSM-5800 LV scanning electron microscope (SEM) (JOEL Ltd., Tokyo, Japan). Five samples were mounted on a bronze stub and sputter-coated (Sputter coater SPI-Module, PA, USA) with a layer of gold prior to imaging, allowing surface visualization. The surfaces of the films are observed at magnification of 1000 and 5000.

3.19 X-ray Diffraction

The X-ray diffraction patterns with Cu Ka radiation at 40 kV and 30 mA were recorded in the range of 2 Theta with an X-ray diffractometer (X0 pert, Philips). The composite films were cut into powder for the measurement of X-ray diffraction.

3.20 Swellability Test

Exactly weighed blend films were immersed in distilled water for 24 h until sufficiently swollen. The excess water is removed and the swollen films are reweighed to calculate the absorbency, which is the ratio of the weight of the swollen film to the dried film.

3.21 Moisture Absorption

Films are cut into small squares 2cm x 2cm. Each specimen is dried in the oven at 80°C for 24 hours. The dried films are weighed for initial weight and are put in the relative humidity box with a RH of 55% for 24 hours. Swollen films are reweighed for final weight and moisture uptake is calculated.

3.22 Kinetic Moisture Absorption

Films are cut into small squares 2cm x 2cm. Each specimen is dried in the oven at 80°C for 24 hours. The dried films are weighed for initial weight and then immersed in distilled water. The immersed films are then reweighed every one hour until the weights become constant. Graph of water uptake against time is plotted for each sample.

3.23 Biodegradability

Films are cut into small squares 2cm x 2cm. Each specimen is weighed and placed in plates containing distilled water. The plates are exposed to ambient conditions for 30 days. Variations in film morphology and disintegration time are recorded.

CHAPTER 4

RESULT AND DISCUSSION

4.1 FTIR

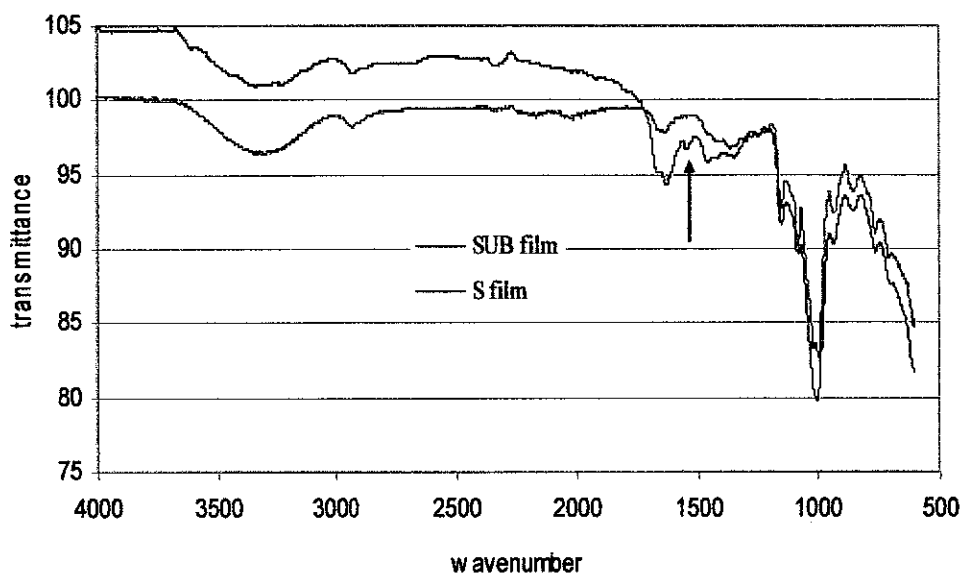


Figure 5: FTIR spectra of starch-borate-lignin and pure starch film

In the preparation of the samples, the lignin modified starch film was crosslinked together with urea and borate. The crosslinking reaction between starch-urea-borate was first characterized by comparing the FTIR spectra of reacted and non- reacted samples which is pure starch. From Figure 5, it can be observed that new bond is formed which the secondary amine bond. Thus, the crosslinking reaction between starch-urea-borate is proved.

The effect of lignin to the film can be investigated by keeping a constant amount of urea and borate throughout the experiment.

4.2 Mechanical Analysis

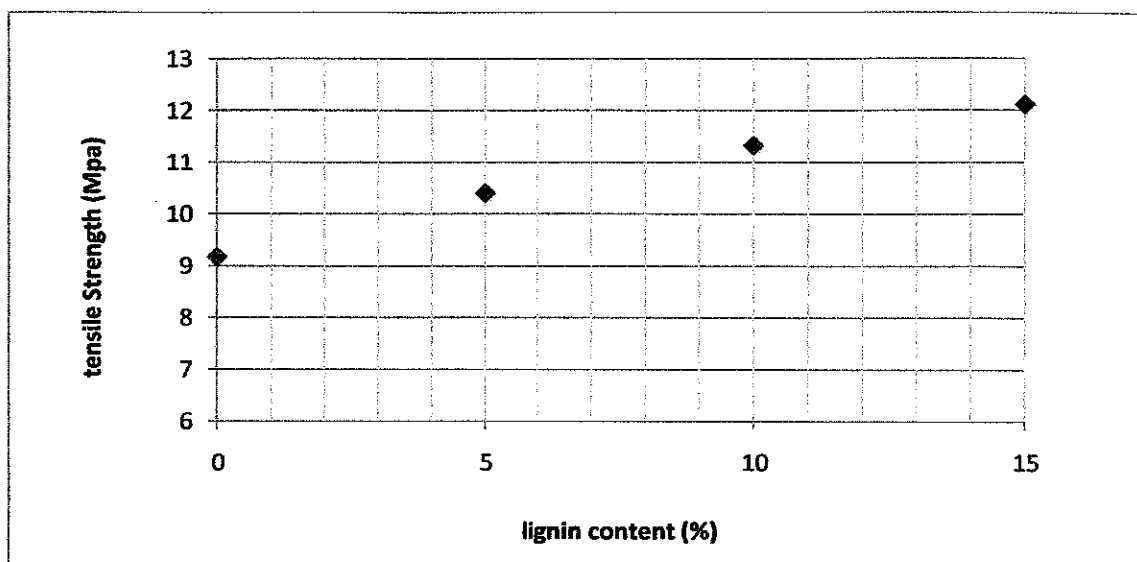


Figure 6: Stress for modified films

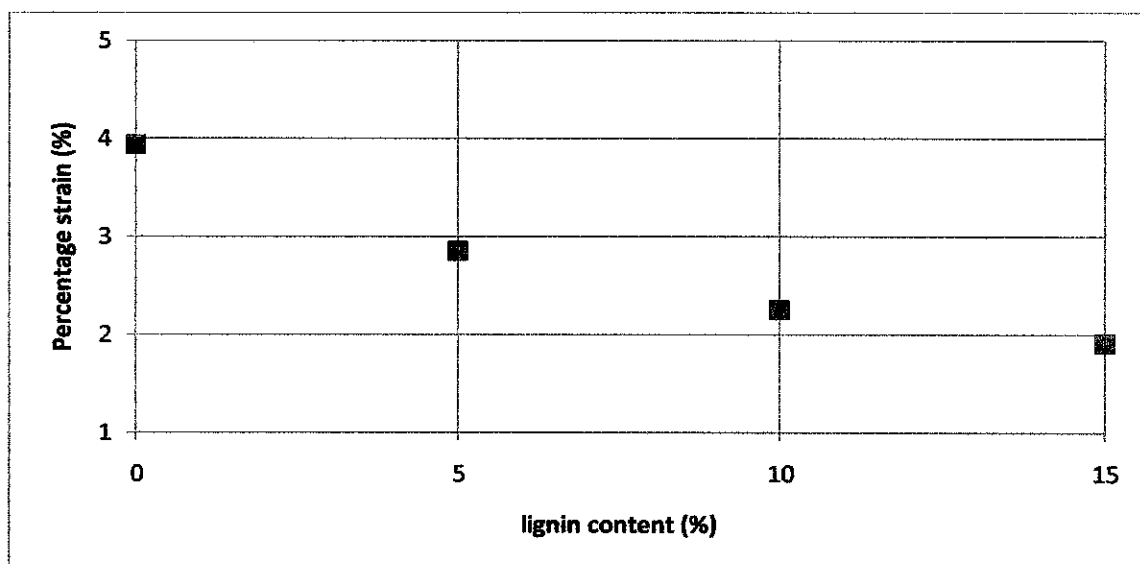


Figure 7: Strain for modified films

Tensile strength (σ_b) and elongation at break (ϵ_b) are important mechanical properties which mainly depend on components in the films. Figure 6 shows the tensile strength (MPa) for the modified films consisted of starch, lignin, urea and borate. The amount of

urea and borate are kept constant for all samples while lignin content is varied from 0%, 5%, 10% and 15%.

Based on Figure 1 above, the maximum stress at break is increasing as lignin content increases. For example, the value of stress for 0% lignin is 9.17MPa while for 15% lignin, the maximum stress is 12.11MPa. This result indicates that the tensile strength of the modified film is improved with the presence of lignin.

However, the elongation at break (eb) is decreasing along lignin content. As can be seen from Figure 7, 0% lignin content has the largest value of strain which is about 4%. This result shows that with higher lignin content in the modified film, the film become more brittle.

4.3 Thermal Analysis

The TGA curves indicate that the decomposition temperature increases with increasing lignin content. This lower rate of thermal degradation of higher lignin content film is attributed to the higher crosslink density than that of lower lignin content film. The starch-lignin polymer of tightly crosslinked structures requires more energy for the decomposition and ring structure to be formed.

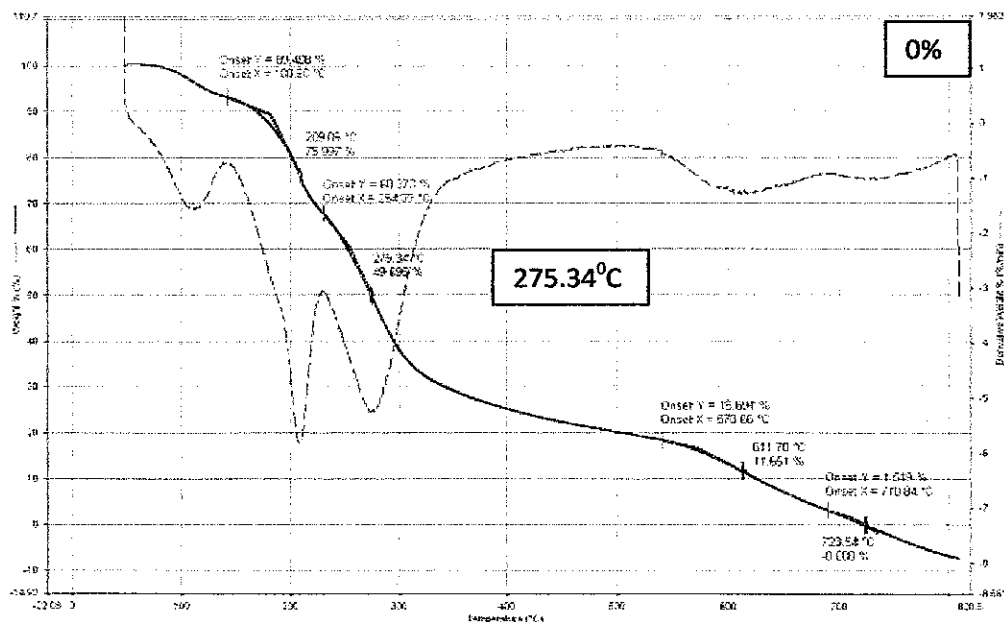


Figure 8: TGA curve for 0% lignin

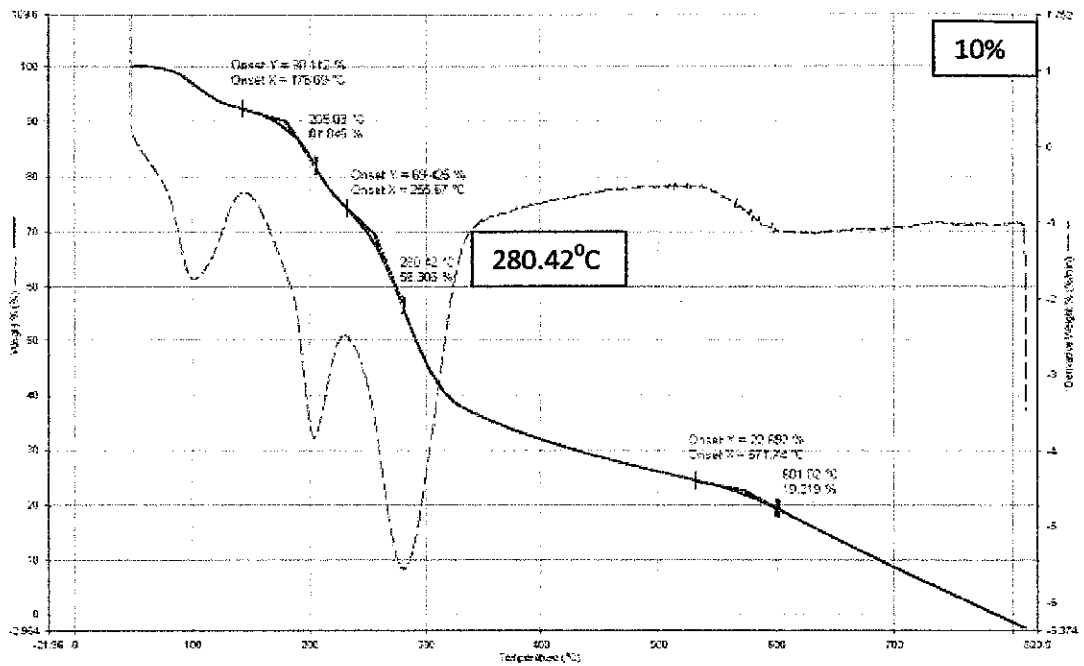


Figure 9: TGA curve for 10% lignin

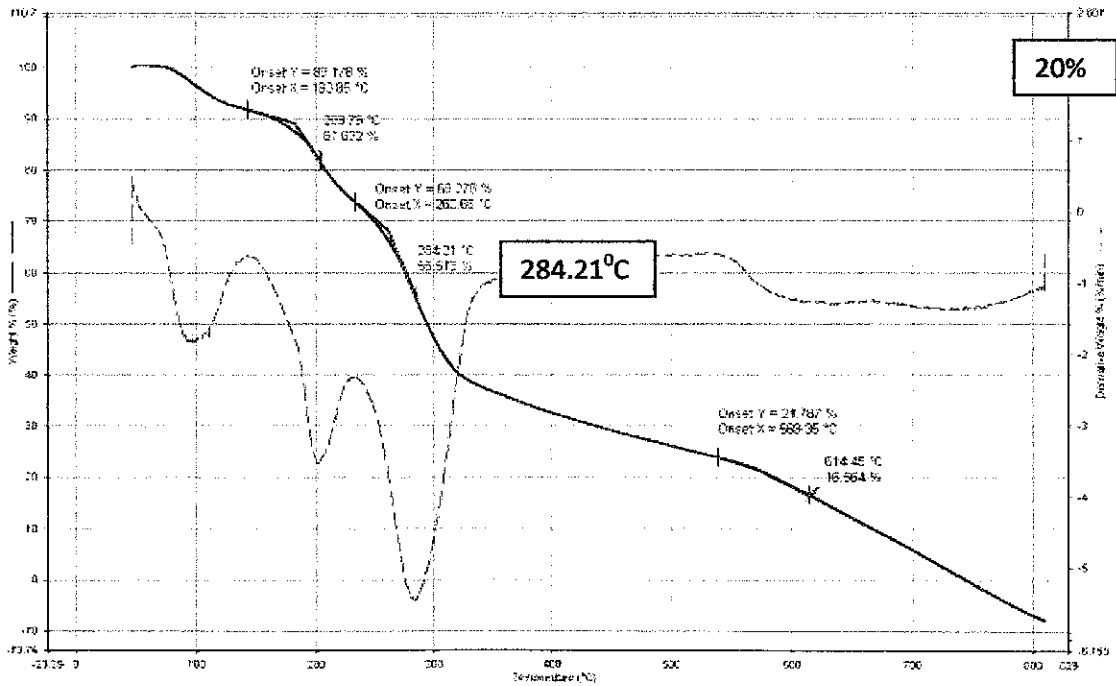


Figure 10 ; TGA curve for 20% lignin

From Figure 10, it is observed that 20% lignin content has the highest decomposition temperature which is 284.21°C at the third peak.

The higher thermal stability of lignin-starch can also be assumed by the high thermal resistance of lignin (S.Sarkar et.al.,2000), which appears due to the large number of ether linkages and aromatic groups in its chemical structure. Figure 11 also shows that the char residue at 500°C of 20% lignin is higher than that of 5% lignin content. This higher char residue of higher lignin-starch may be due to the high molecular weight of lignin char (Brauns FE, 1960).

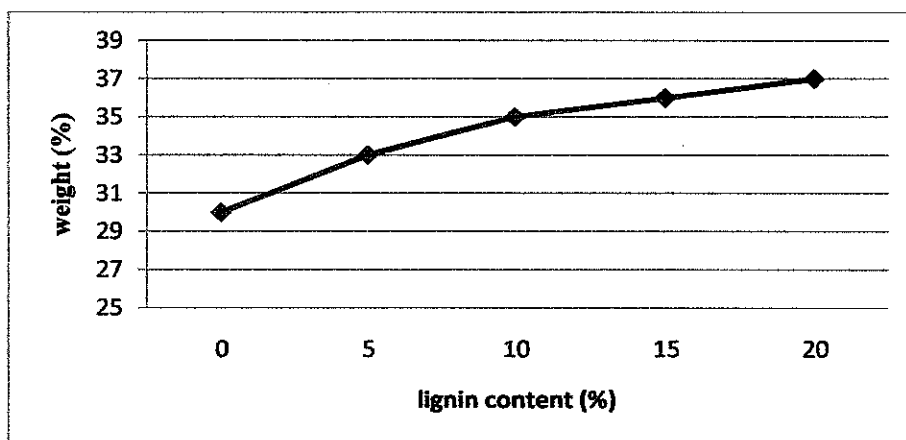


Figure 11: Weight residue (%) at 500°C for modified films

4.4 Microscopic Analysis

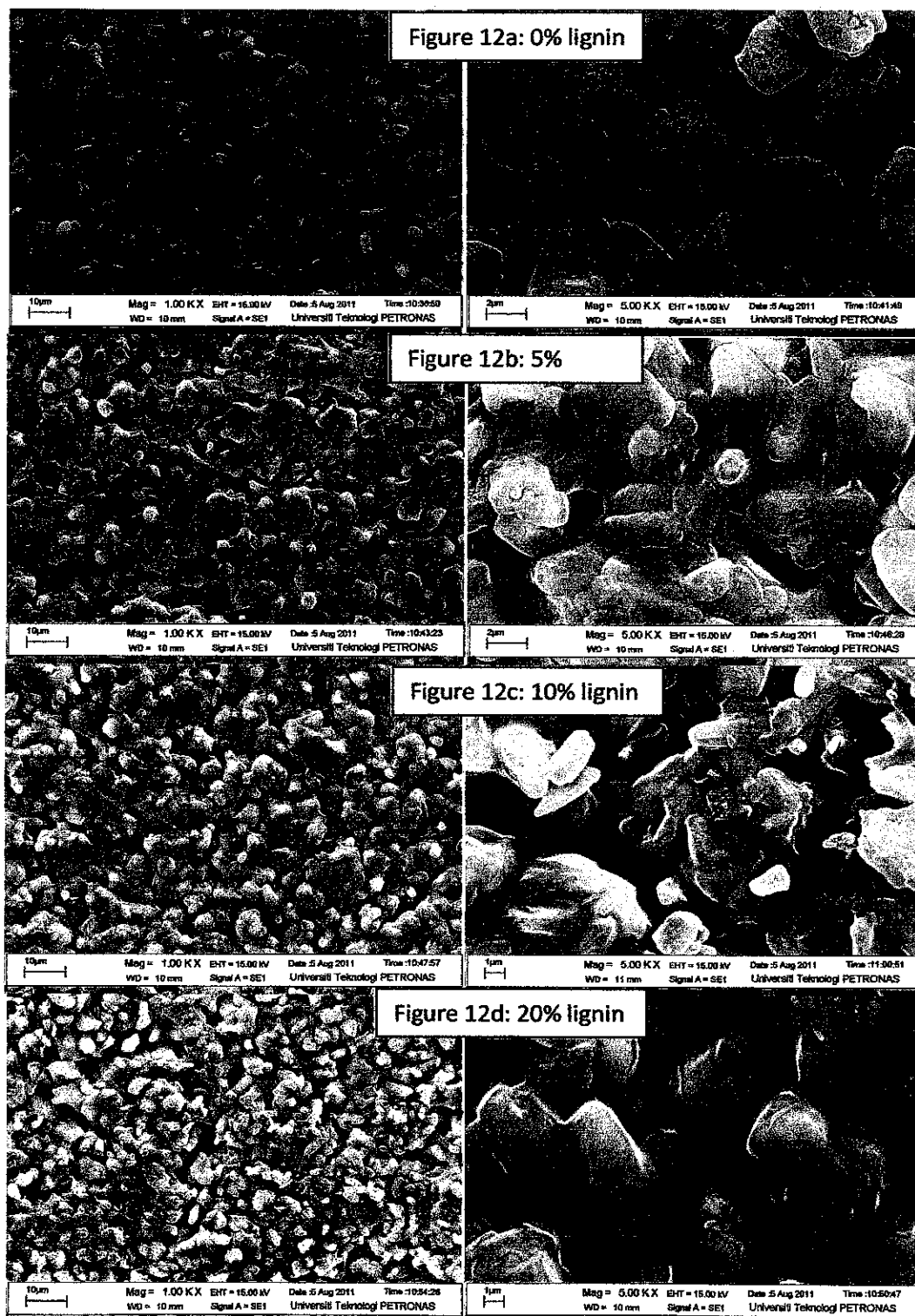


Figure 12 : SEM images for modified films at 1000 and 5000 magnification

The morphology of the lignin/starch films was identified by Scanning electron microscopy (SEM). Figure 12 shows the surface of starch films reinforced with 0 to 15% of lignin. Starch-lignin surface display the same features. The SEM images show that 20% lignin can be incorporated into starch with no major change in morphology.

However, the surfaces of the films become slightly smoother as the lignin content increases. This indicates the compatibility of lignin and starch. Figure 12a above shows the surface of starch film with 0% lignin, only crosslinked with urea and borate, which there is no smoothing effects at the edges of the particles. Figure 12d shows enlarged image of 20% lignin content where the edges become smoother. Therefore, SEM indicates that replacing 20% of the starch with lignin has no deleterious effect on overall morphology.

4.5 XRD

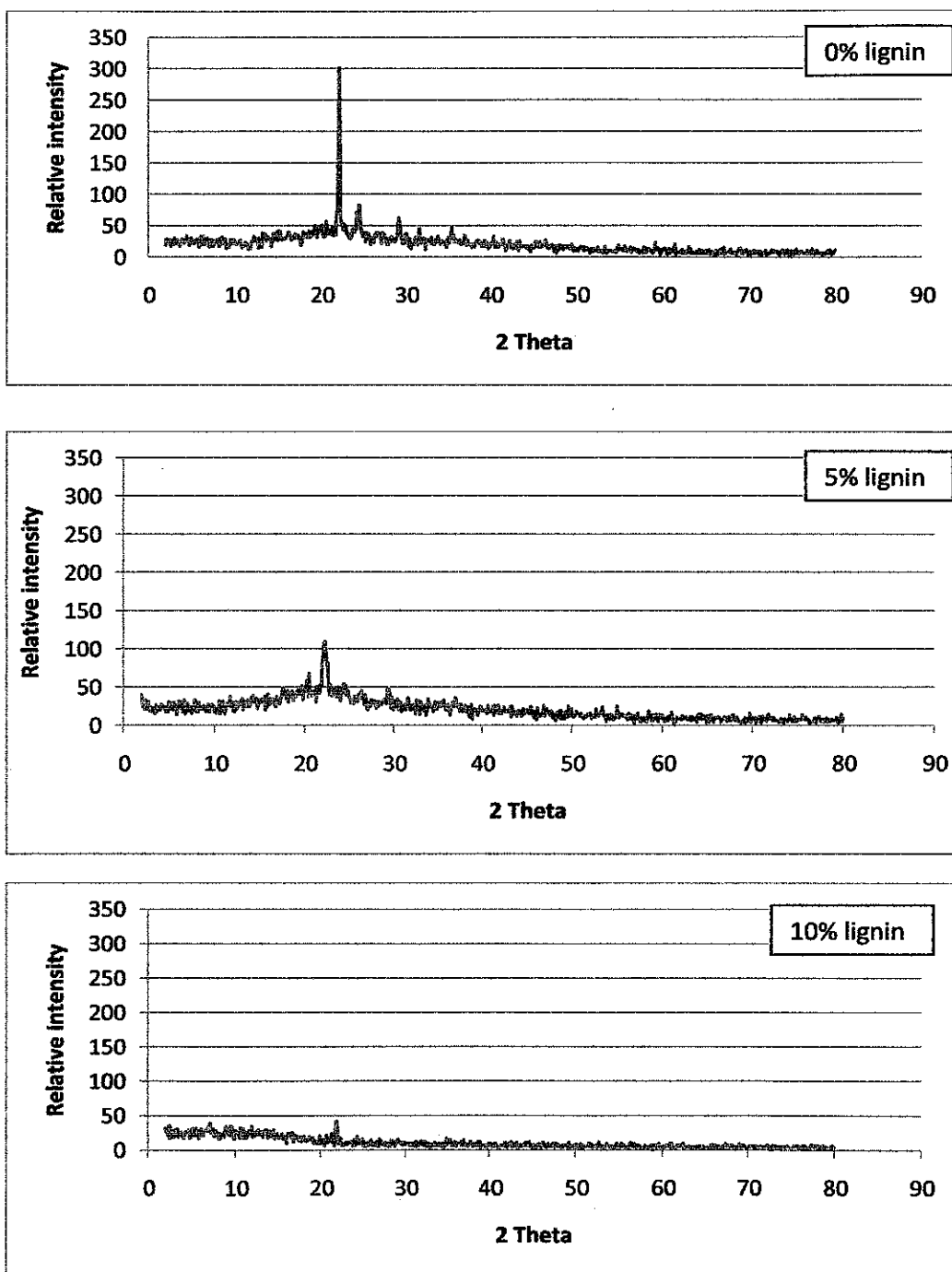


Figure 13 : XRD for modified films

X-Ray diffraction (XRD) is used to measure the nature of polymer and extent of crystallinity present in the polymer sample. Crystalline regions in the polymer seated in well-defined manner acts as diffraction grating. So the emerging diffracted pattern shows alternate dark and light bands on the screen. X-ray diffraction pattern of polymer contain both sharp as well as defused bands. Sharp bands correspond to crystalline orderly regions and defused bands correspond to amorphous regions. Crystalline structure is regular arrangement of atoms. Polymer contains both crystalline and amorphous phase within arranged randomly. When beam of X-ray passed through the polymer sample, some of the regularly arranged atoms reflect the x-ray beam constructively and produce enhanced intense pattern. Amorphous samples gives sharp arcs since the intensity of emerging rays are more, where as for crystalline samples, the incident rays get scattered. Arc length of diffraction pattern depends on orientation. If the sample is highly crystalline, smaller will be the arc length.

Based on Figure 13, we can see that in 10% lignin content, the arc length is smaller than that of 5% and the arc length of 5% is smaller than that of 0%. This indicates that, as the lignin content increases, the crystallinity of the film increases. The rate of crystallization of lignin-starch film is strongly enhanced by the nucleation action of lignin particles due to its highly cross-linked morphology (Rohella et al., 1996).

4.6 Water Affinity

4.6.1 Swellability Test

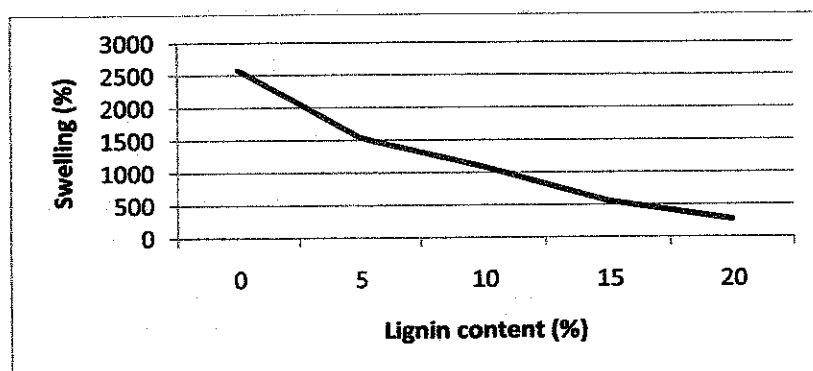


Figure 14: Percentage swelling of modified films

From the swelling test, it can be inferred that the starch-lignin films are less hydrophilic. The result shows the percent increase in weight of dry films after immersion in distilled water for 24 hours. Based on Figure 14, the water absorption of the films decrease with the increase in lignin content. For example, with 0% lignin, the weight of the film increases from 0.09g to 2.41g which is 2578% increase. For 20% lignin content, the increment decreases to only 275% of initial weight. This shows that the amount of lignin in the film affects the swelling of the film due to the hydrophobic properties of lignin. As the lignin content increases, the swelling decreases.

4.6.2 Moisture Absorption

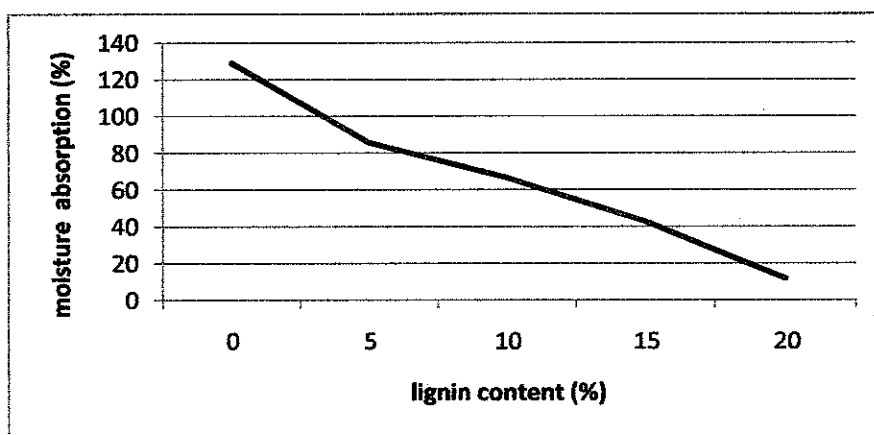


Figure 15: Moisture absorption (wt%) for modified films

4.6.3 Kinetic Moisture absorption

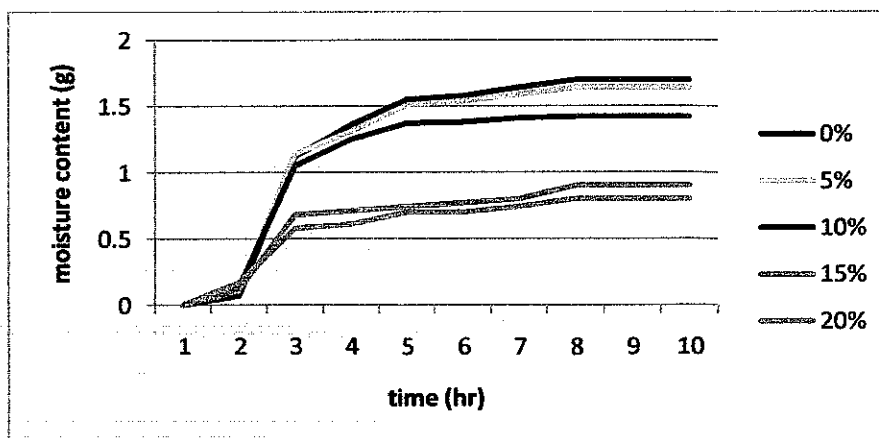


Figure 16: Moisture absorption rate for modified films

In the moisture absorption test, the film samples are brought to zero moisture content by oven-drying at 80° C for 24 hours and were put in 55% RH condition for another 24 hours. The results shows the presence of lignin slightly improves the starch water resistance as can be seen from Figure 15, the moisture absorption of modified starch film changes decreases from 129% (0% lignin) to 11.6 when 20% lignin is incorporated. As for the kinetic moisture absorption test, the films immersed in water are reweighed every 1 hour until equilibrium is reached which shows that the water uptake of the films stops after a certain time. From Figure 16, the weight of films increased and become constant after 8 hours of immersion.

4.6.4 Biodegradability

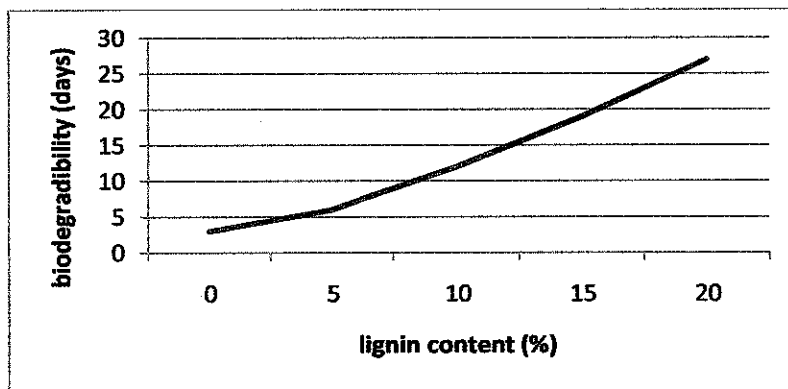


Figure 17: Biodegradability (days) for modified films

In the biodegradability test, the samples are immersed in water until the films break and dissolved in the water. Based on Figure 17, 0% lignin-starch film took only 3 days until it totally dissolved. While 20% lignin content film took 27 days to dissolve in water. The huge difference indicates that the presence of lignin prolonged the degradation rate of the starch-lignin film.

CHAPTER 5

CONCLUSION

In conclusion, the result of the experiment and analysis is coherent with the information obtained from the literature reviews previously done. The results prove that the presence of highly cross-linked aromatic skeletons of lignin improves the thermal and mechanical of the starch polymer. It also reduces the water-uptake of tapioca starch and that simultaneously stiffer materials with less pronounced degradation rate are obtained.

Therefore, the modified starch product will have better potential as a controlled release fertilizer coating in agriculture industry.

REFERENCES

- Arvanitoyannis, I. 1999. Totally-and-partially biodegradable polymer blends based on natural and synthetic macromolecules: Preparation and physical properties and potential as food packaging materials. *Journal of Macromolecular Science-Reviews in Macromolecular Chemistry and Physics C*, 39(2), 205–271
- Brauns FE, Brauns DE., 1960. The chemistry of lignin, supplement vol. New York: Academic Press.
- Bratskaya, S., Schwarz, S., Petzold, G., Liebert, T., Heinze, T., 2006. Cationic starches of high degree of functionalization: 12. *Modification of cellulose fibers toward high filler technology in papermaking*. *Ind. Eng. Chem. Res.* 45, 7374–7379.
- Carsten Mai, Oleg Milstein, Aloys Huttermann, 2000. Chemoenzymatical grafting of acrylamide onto lignin. *J Biotechnol*, 79 (2): 173–183
- Chen, L., Qiu, X., Chen, X., & Jing, X. 2005. The starch graft poly(Llactide) and the physical properties of its blending composites. *Polymer*, 46(15), 5723–5729.
- Coulter, T. P. 1996. Food—the chemistry of its components. *The Royal Society of Chemistry Paperbacks (3rd ed.)* chapter III, p.29–53.
- Guan, J.J., Hanna, M.A., 2004. Extruding foams from corn starch acetate and native corn starch. *Biomacromolecules* 5, 2329–2339.
- Guo, M., Liu, M., Zhan, F., & Wu, L. 2005. Preparation and properties of a slow-release membrane-encapsulated urea fertilizer with superabsorbent and moisture preservation. *Industrial & Engineering Chemistry Research*, 44, 4206–4211
- Ikeo, Y., Aoki, K., Kishi, H., Matsuda, S., Murakami, A., 2006. Nano clay reinforced biodegradable plastics of PCL starch blends. *Polym. Adv. Technol.* 17, 940–944
- Jacobs, D.F., Bose, R., Hasse, D.L. “Incorporating controlled release fertilizer technology into outplanting”, in *National Proceedings: Forest and*

- conservation nursery associations, L.E. Riley, R.K. Dumroese, T.D. Landis, Technical coordinators. Ogden, 2003, pp. 37-42.
- K. Byung-Su, C. Young-Sang and H. Hyun-Ku, 1996. Controlled release of urea from rosin-coated fertilizer particles, *Ind. Eng. Chem. Res.*, 35 250_257
- K. El-Refaie and Al.A. Sakran, Controlled release formulation of agrochemicals from calcium alginate, *Ind. Eng. Chem. Res.*, 35 (1996) 3726_3729
- Kai, W.H., He, Y., Asakawa, N., Inoue, Y., 2004. Effect of lignin particles as a nucleating agent on crystallization of poly(3-hydroxybutyrate). *J. Appl. Polym. Sci.* 94, 2466–2474
- Lee, S.Y., Cho, M.S., Nam, J.D., Lee, Y., 2006. Melting processing of biodegradable cellulose diacetate/starch composites. *Macromol. Symp.* 242, 126–130.
- Liu, C.X., Bai, R.B., 2005. Preparation of chitosan/cellulose acetate blend hollow fibers for adsorptive performance. *J. Membr. Sci.* 267, 68–77.
- M. Tomaszewska, A. Jarosiewicz and K. Karakulski, Physical and chemical characteristic of polymer coatings in CRF formulation, *Desalination*, 146 (2002) 319_323
- O.A. Salman, 1989. Polyethylene-coated urea. I. Improved storage and handling properties, *Ind. Eng. Chem. Res.*
- R.S. Rohella, N. Sahoo, S.C. Paul, S. Choudhury and V. Chakravorty, Thermal studies on isolated and purified lignin, *Thermochim. Acta* 287 (1996), pp. 131–138.
- Sanchez-Garcia, M.D., Gimenez, E., Lagaron, J.M., 2008. Morphology and barrier properties of solvent cast composites of thermoplastic biopolymers and purified cellulose fibers. *Carbohydr. Polym.* 71, 235–244.
- S. Sarkar and B. Adhikari J., 2000. *Adhes. Sci. Technol.* 14, p. 1719.
- Tarvainen, M., Peltonen, S., Mikkonen, H., Elovaara, M., Tuunainen, M., Paronen, P., et al. 2004. Aqueous starch acetate dispersion as a novel coating material for controlled release products. *Journal of Controlled Release*, 96, 179–191.
- Tuovinen, L., Peltonen, S., & Jarvinen, K., 2003. Drug release from starch-acetate films. *Journal of Controlled Release*, 91, 345–354.

- Vengal J.C. & Manu Srikumar, Processing and Study of Novel Lignin-Starch and Lignin-Gelatin Biodegradable Polymeric Films Trends Biomater. Artif. Organs, Vol 18 (2), January 2005
- Wiedmann, W., & Strobel, E. 1991. Compounding of thermoplastic starch with twin-screw extruders. *Starch-Starke*, 43, 138–145.
- Wu R.L., Wang X.L., Fang Li, Hui Zhang Li, Yu-Zhong Wang, 2008. Green composite films prepared from cellulose, starch and lignin in room temperature ionic liquid.
- Zhang Q L, Chuang K T, 2001. Adsorption of organic pollutants from effluents of a Kraft pulp mill on activated carbon and polymer resin. *Adv Environ Res*, 5(3): 251–258.
- Zhu, Z., & Zhuo, R. 2001. Controlled release of carboxylic-containing herbicides by starch- g-poly(butyl acrylate). *Journal of Applied Polymer Science*, 81, 1535–1543.

Appendix I – Gantt Chart

NO	ACTIVITIES	WEEK NO													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
A	Experimental Work														
1	Methodology	■	■												
2	Preparation of film			■	■	■									
3	TGA				■	■									
4	Swellability					■	■								
5	SEM						■	■							
6	FTIR							■	■						
7	XRD								■	■					
8	UTM									■	■				
9	Biodegradability										■	■			
B	Deliverable Preparation														
1	Progress report							■	■						
2	Pre-EDX										■	■			
3	Draft Report											■	■		
4	Dissertation												■	■	
5	Technical Paper													■	■
6	Final Presentation														■

APPENDIX II – TGA Results

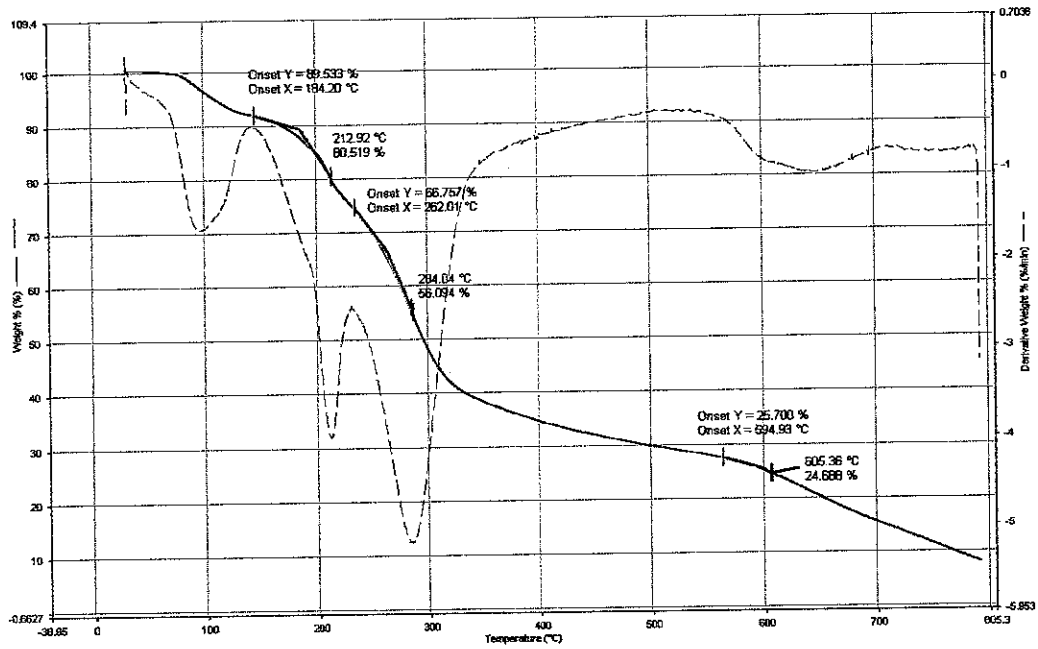


Figure 18: TGA curve for 0% lignin film

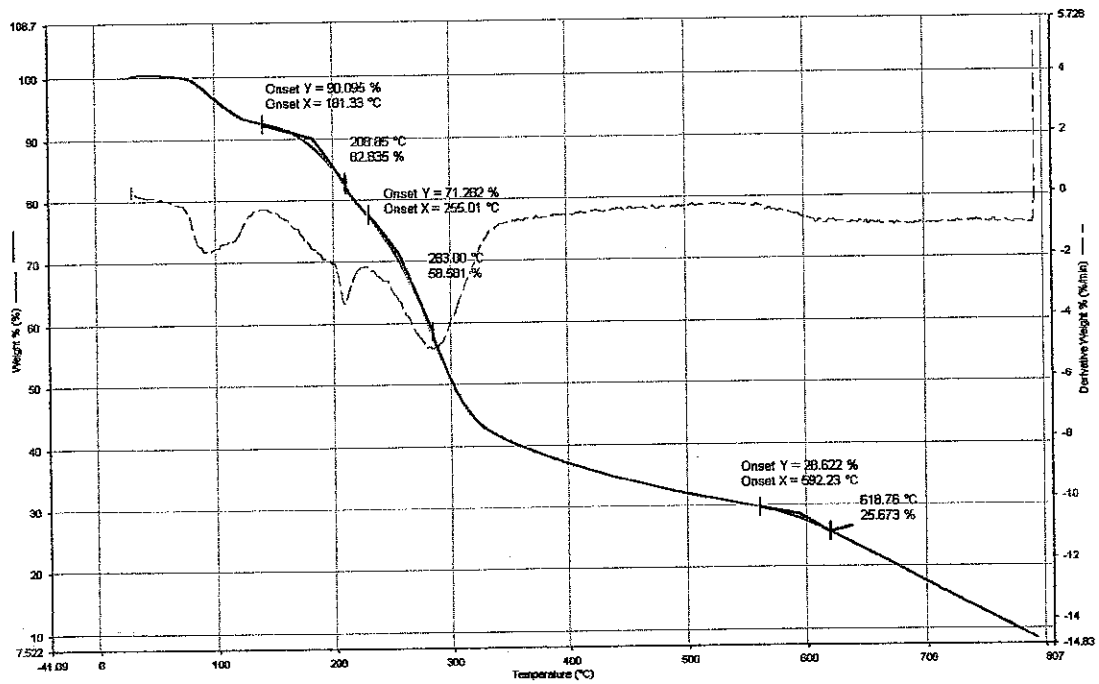


Figure 19: TGA curve for 5% lignin film

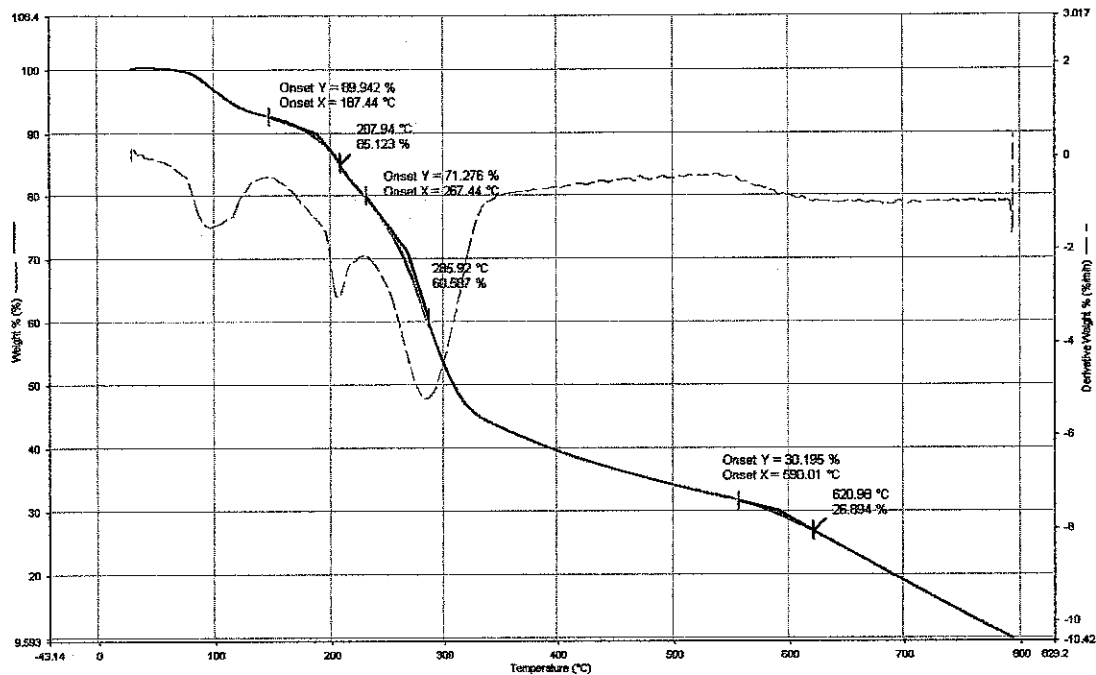


Figure 20: TGA curve for 10% lignin film

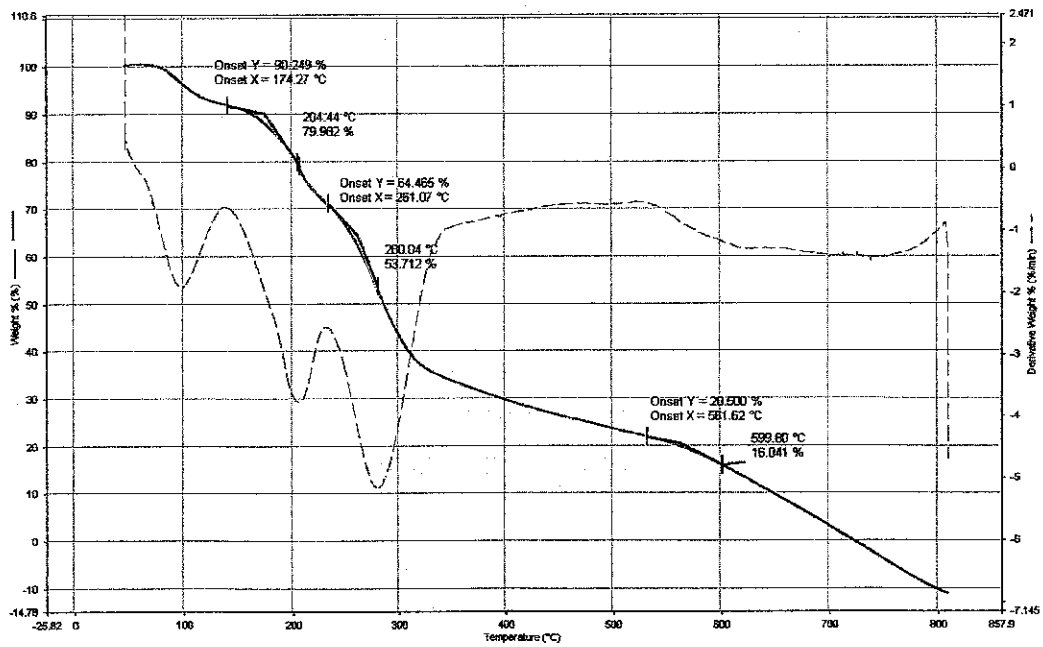


Figure 21: TGA Curve for 15% lignin film

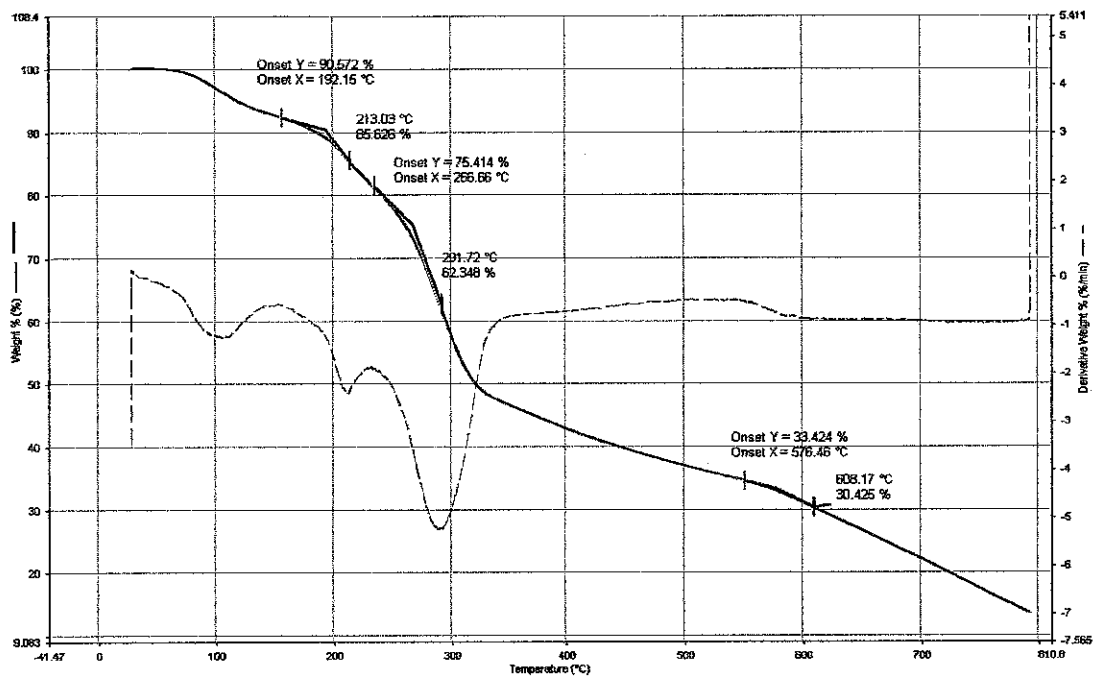
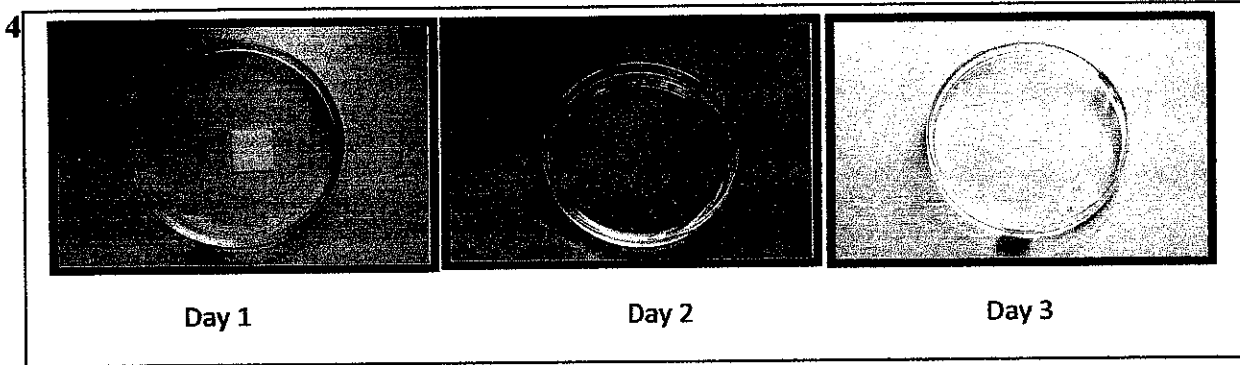


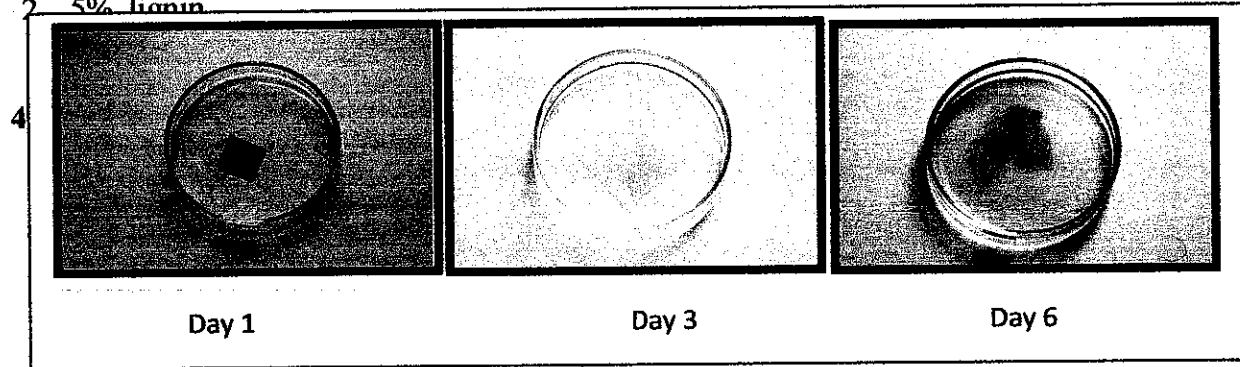
Figure 22: TGA curve for 20% lignin film

APPENDIX III – Biodegradability Test

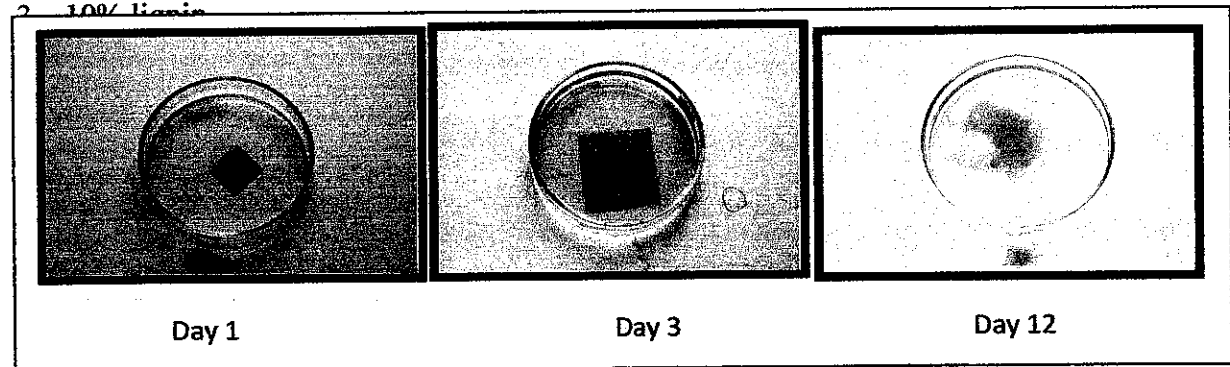
1. 0% lignin



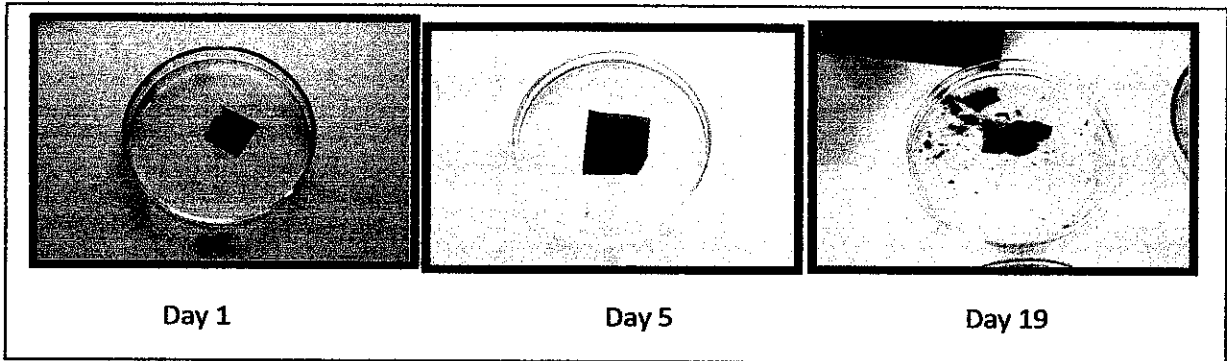
2 50% lignin



2 100% lignin



4.9 4. 15% lignin



5. 20% lignin

