PREPARATION AND MODIFICATION OF THERMOPLASTIC STRCH COMPOSITES PREPARED FROM RICE AND GLUTINOUS RICE STARCH BLEND BY USING COTTON FIBERS AS REINFORCEMENT

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Abstract

This research studied on the preparation of thermoplastic starch prepared from rice and glutinous rice starch. The thermoplastic starch was modified using cotton fibers as reinforcing filler. Different ratios of rice starch to glutinous rice starch, i.e. 100:0 50:50 0:100, were studied. In addition, different the lengths of cotton fibers (2 mm and 5 mm), and contents of cotton fibers (0%wt, 5%wt, 10%wt, 15%wt) were also examined. Then, the thermoplastic starch sample were tested for mechanical, morphology, thermal, physical and biodegradable properties. The results showed that the incorporation of cotton fiber into the TPS matrix caused the considerable improvement of tensile strength and Young's modulus. Moreover, water absorption of the TPS samples was clearly reduced by the cotton fiber . For morphology, obtained from Scaning Electron Microscope (SEM), the results illustrated good phase compatibility and dispersion of cotton fiber inside TPS matrix. In addition, thermal stability and biodegradability were improved by using cotton fiber.

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Chapter 1

Introduction

Non-biodegradable plastics has caused the environmental problems due to their disposal. Although recycling is an environmentally attractive solution, the small percentage of plastics are actually recycled and most end-up municipal landfill sites. As a result, there has been increased the opportunities for the production of biodegradable polymers which based on natural renewable resources.

Biodegradable polymers can be degraded by living organisms. They offers a possible alternative to traditional non-biodegradable polymers. Accordingly, the researchers has focused on the development of biodegradable products on the basis of agricultural raw materials.

Thailand is an agricultural country, especially a rice exporter. Due to rice which is the main food of Thai people, Asian people also consume. In addition, the glutinous rice are widely popular in the consumer and the main food of Thai people in the Northeast and North regions of Thailand is also used as a raw material in local food well as ingredients in foods and snacks.

Food industries that use glutinous rice flour as raw materials grow very quickly. Because of the food made of the glutinous rice is soft, ready to eat and easy to prepare. Therefore, rice flour and glutinous rice flour are products of the primary products derived from rice.

Since Thailand is a rice export is No. 7 in the world by the year 2007/2008 with output 29.642 million tons and increased to 32.099 million tons in 2008/2009 [1].

Starch is an agro-polymer which is potentially useful material for biodegradable plastic because of its natural abundance and low cost. Starch is the major carbohydrate in plant tube and seed endosperm, where is found as granule. The granule mainly contains amylose and amylopectin molecules. The largest source of starch is corn, wheat, potato and rice.

Thermoplastic starch (TPS) is the one of low cost biodegradable polymers use for many non-food items such as paper, cardboard etc. TPS is not really a thermoplastic, but under high shear and temperature, it can melt and flow as a thermoplastic material. However, TPS shows poor mechanical properties and high water absorption.

Generally, natural fibers are widely used to improve material functional properties. The advantages of natural fibers are their low price, low density, non-abrasive behavior during processing and biodegradability. Natural fibers are mainly composed of cellulose, lignin and hemicellulose.

One useful technique to improve mechanical properties and reduce water uptake of TPS is to add natural fibers into TPS matrix. K. Chompoorat and B. Chansuprom [2] reported that the use of either rice starch or glutinous rice starch to prepare TPS caused poorer mechanical properties than those of the use of rice and glutinous rice starch blend. Therefore, this research concerned with property improvement of TPS prepared from rice and glutinous rice starch blend by using cotton fibers as reinforcement. Physical, mechanical, morphological, thermal and biodegradable properties were then investigated.

1.1 Objectives

1.1.1 To prepare TPS from rice and glutinous rice starch blend.

1.1.2 To improve properties of the TPS using cotton fibers as reinforcing filler.

1.2 Scope of this work

1.2.1 To produce TPS from rice and glutinous rice starch blend reinforced by cotton fibers.

1.2.2 To study the effect of cotton fiber contents and lengths on the properties of TPS.

1.2.3 To examine physical, mechanical, morphological, thermal and biodegradable properties of the TPS.

1.3 Expected results

1.3.1 To produce biodegradable TPS prepared from rice and glutinous rice starch blend using cotton fibers as reinforcement.

1.3.2 To increase economic values of rice and glutinous rice starches.

Chapter 2

Theory and Literature Reviews

2.1 Thermoplastic Starch [3]

The term " destructurized starch" refer to a form of thermoplastic starch described as molecularly dispersed in water. Destructurization of starch is defined as melting and disordering of the molecular structure of the starch granules and as a molecular dispersion. The molecular structure of the starch granules is molten and consequently the granular structure disappears. This is achieved by heating the starch above the glass transition and melting temperature of its components until they undergo endothermic transitions. In the melt stage both the crystalline and the granular structure of the starch are destroyed and the starch-water system forms a single phase in which no structure is discernible microscopically. The disappearance of the molecular structure of the starch granule may be determined using conventional light microscopy techniques.

If starch is heated above the glass transition and melting temperatures in presence of plasticizers the endothermic transition can be replaced by an exothermic transition. Destructurized starch, in simple terms, is a form of thermoplastic starch suitable for applications in the sector of plastics, with minimized defects tired to granular of native starch.

Thermoplastic starch alone can be processed as a traditional plastic; its sensitivity to humidity, however, makes it unsuitable for most of the applications. Starch can be also made thermoplastic at water contents lower than 10%, in the presence of high boiling point plasticizers, to avoid expansion phenomena at die.

Another term "Thermoplastically Processable Starch" is defined as a thermoplastic starch substantially water free. Thermoplastically Processable Starch is a modified native

starch which is obtained without water, since instead of water use is made of a plasticizer or additive. The starch is thermoplastically processed together with the additive and the thermal transition taking place here is exothermic.

2.2 Starch Compositions and Structures of Components [4]

Starch granules are composed of two types of alpha-glucan, amylose and amylopectin, which represent approximately 98-99% of the dry weight. The ratio of the two polysaccharides varies according to the botanical origin of the starch. The 'waxy' starches contain less than 15% amylose, 'normal' 20-35% and 'high' (amylo-) amylose starches greater than about 40%. The structure of the alpha-glucans is discussed below in more detail. The moisture content of air-equilibrated starches ranges from about 10-12% (cereal) to about 14-18% (some roots and tubers).

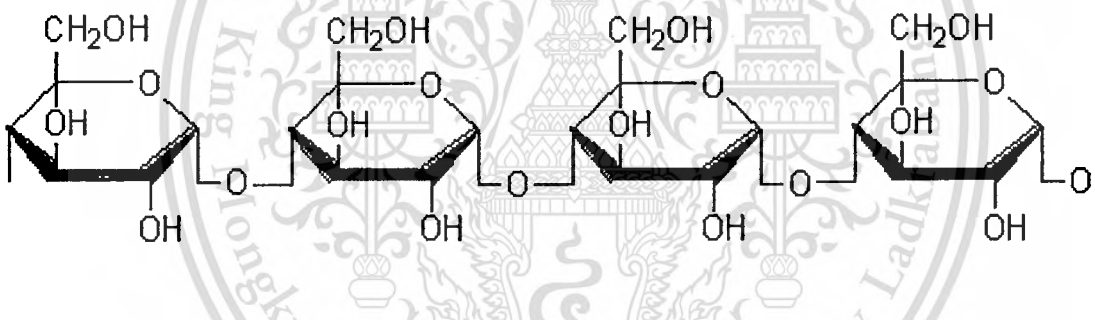
2.2.1 Amylose and Amylopectin Fine Structure

Amylose and amylopectin have different structures and properties. Amylose is a relatively long linear a-glucan containing around 99% (1→4)- α -and (1→6)- α -linkages and differs in size and structure depending on botanical origin. Each chain contains approximately 200-700 glucose residues equivalent to a molecular weight of 32,400-113,400.

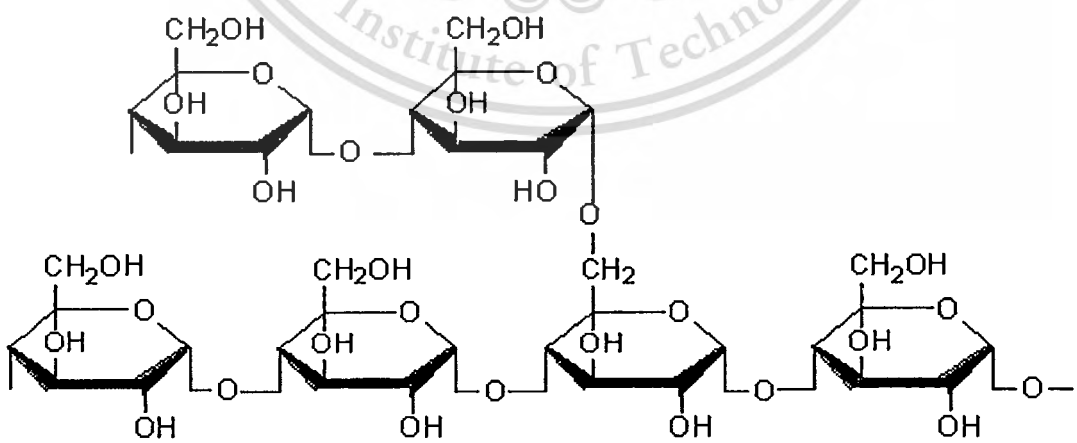
Amylopectin is a much larger molecule than amylase with a molecular weight of $1x10^7$ - $1x10^9$ and a heavily branched structure built from about 95% (1→4)- α – and 5% (1→6)- α – linkages. In common with amylose, the molecular size, shape, structure and polydispersity of the molecule varies with botanical origin. Unlike amylose, however, there is great additional variation with respect to the unit chain lengths and branching patterns. Amylopectin unit chains are relatively short compared to amylose molecules with a broad

distribution profile. They are typically, 18-25 units long on average although the range is extended if high-amylose starches are also included.

The individual chains can be specifically classified in terms of their lengths (chain length, CL) and consequently position within starch granules. The A and B_1 chains are the most external and form double helices within the native granules. Their CL is typically ~ 12-24 depending on genetic origin and starches with 'A-type' crystallinity, having shorter chain lengths on average than 'B-type' starches. With the exterior chains of amylopectin comprising a range from CL 12-24, the A-type chains are typically CL 12-16 and B_1 CL 20-24. Amylopectin molecules from high amylose starches contain relatively high proportions of very long chains.



(a). Amylose



(b). Amylopectin

Figure 2.1 Structure of (a) amylose and (b) amylopectin [5]

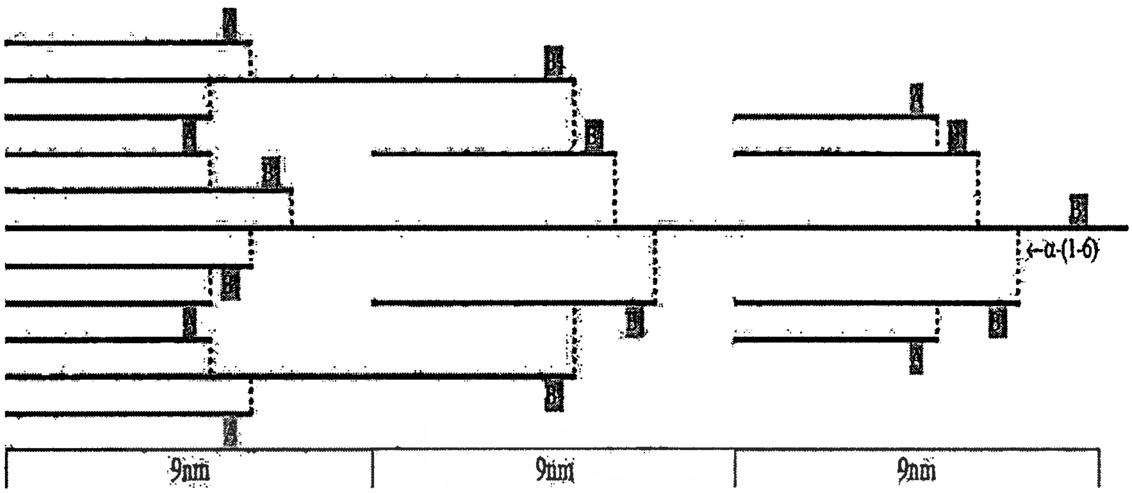


Figure 2.2 Schematic representation of a section of amylopectin indicating the branching pattern of unit (1→4)- α –chains (A, B_1-B_3) joined together by (1→6)-α-linkages. [6]

2.3 Lignocellulosic Fibers / Natural Fibers [6]

Natural fibers are subdivided based on their origins, coming from plants, animals or minerals. All plant fibers are composed of cellulose while animal fibers consist of proteins (hair, silk, and wool). Plant fibers include bast (or stem or soft sclerenchyma) fibers, leaf or hard fibers, seed, fruit, wood, cereal straw, and other grass fibers. Over the last few years, a number of researchers have been involved in investigating the exploitation of natural fibers as load bearing constituents in composite materials. The use of such materials in composites has increased due to their relative cheapness, their ability to recycle and for the fact that they can compete well in terms of strength per weight of material. Natural fibers can be considered as naturally occurring composites consisting mainly of cellulose fibrils embedded in lignin matrix. The cellulose fibrils are aligned along the length of the fiber, which render maximum tensile and flexural strengths, in addition to providing rigidity. The reinforcing efficiency of natural fiber is related to the nature of cellulose and its

crystallinity. The main components of natural fibers are cellulose (a-cellu-lose), hemicelluloses, lignin, pectins, and waxes.

Cellulose is a natural polymer consisting of D-anhydro- glucose ($C_6H_{10}O_5$) repeating units joined by 1,4-β-D-glyco- sidic linkages at C_1 and C_4 position. The degree of polymerization (DP) is around 10,000. Each repeating unit contains three hydroxyl groups. These hydroxyl groups and their ability to hydrogen bond play a major role in directing the crystalline packing and also govern the physical properties of cellulose. Solid cellulose forms a microcrystalline structure with regions of high order i.e. crystalline regions and regions of low order i.e. amorphous regions. Cellulose is also formed of slender rod like crystalline microfibrils. The crystal nature (monoclinic sphenodic) of naturally occurring cellulose is known as cellulose I. Cellulose is resistant to strong alkali (17.5 wt%) but is easily hydrolyzed by acid to water-soluble sugars. Cellulose is relatively resistant to oxidizing agents. Hemicelluloses is not a form of cellulose and the name is a misnomer. They comprise a group of polysaccharides composed of a combination of 5- and 6-carbon ring sugars. Hemicelluloses differs from cellulose in three aspects. Firstly, they contain several different sugar units whereas cellulose contains only 1,4-β-D-glucopyranose units. Secondly, they exhibit a considerable degree of chain branching containing pendant side groups giving rise to its non crystalline nature, whereas cellulose is a linear polymer. Thirdly, the degree of polymerization of native cellulose is 10-100 times higher than that of hemicelluloses. The degree of polymerization (DP) of hemicelluloses is around 50-300. Hemicelluloses form the supportive matrix for cellulose microfibrils. Hemicellulose is very hydrophilic, soluble in alkali and easily hydrolyzed in acids. Lignin is a complex hydrocarbon polymer with both aliphatic and aromatic constituents. They are totally insoluble in most solvents and cannot be broken down to monomeric units. Lignin is totally amorphous and hydrophobic in nature. It is the

compound that gives rigidity to the plants. It is thought to be a complex, three-dimensional copolymer of aliphatic and aromatic constituents with very high molecular weight. Hydroxyl, methoxyl and carbonyl groups have been identified.

Lignin has been found to contain five hydroxyl and five methoxyl groups per building unit. It is believed that the structural units of lignin molecule are derivatives of 4-hydroxy-3-methoxy phenylpropane. The main difficulty in lignin chemistry is that no method has been established by which it is possible to isolate lignin in its native state from the fiber. Lignin is considered to be a thermoplastic polymer exhibiting a glass transition temperature of around 90 °C and melting temperature of around 170 °C. It is not hydrolyzed by acids, but soluble in hot alkali, readily oxidized, and easily condensable with phenol.

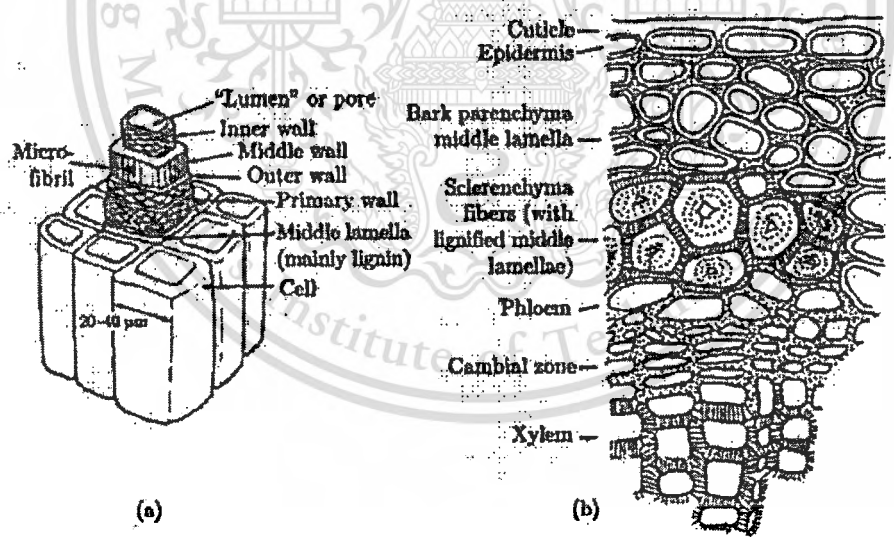


Figure 2.3 Schematic representations of (a) a natural fiber, (b) different types of cells and their arrangement in flax fiber. [7]

2.4 Cellulose Fiber Composites [6]

The exhaustive use of petroleum based resources has initiated the efforts to develop biodegradable plastics. This is based on renewable biobased plant and agricultural products that can compete in the markets currently dominated by petroleum based products. The production of 100% biobased materials as substitute for petroleum based products is not an economical solution.

A more viable solution would be to combine petroleum and biobased resources to develop a cost-effective product having immense applications. Biopolymers or synthetic polymers reinforced with natural or bio fibers (termed as iocomposites) are a viable alternative to glass fiber composites. Scientists are looking at the various possibilities of combining biofibres such as sisal, flax, hemp, jute, banana, wood and various grasses with polymer matrices from non-renewable and renewable resources to form composite materials to make the biocomposite revolution a reality.

Broadly defined, biocomposites are composite materials made from natural/bio fiber and petroleum derived nonbiodegradable polymers (PP, PE) or biodegradable polymers (PLA, PHA). The latter category i.e. biocomposites derived from plant derived fiber (natural/biofiber) and crop/bioderived plastic (biopolymer/bioplastic) are likely to be more eco-friendly and such composites are termed as green composites.

The best known renewable resources capable of making biodegradable plastics are starch and cellulose. Starch is one of the least expensive biodegradable materials available in the world market today. It is a versatile polymer with immense potential for use in non-food industries. Cellulose from trees and cotton plants is a substitute for petroleum feed stocks to make cellulose plastics.

Another aspect that has gained global attention is the development of biodegradable plastics from vegetable oils like soybean oil, peanut oil, walnut oil, sesame oil and sunflower

oil.Green composites from soy protein based bioplastics and natural fibers show potential for rigid packing and housing and transportation applications. Fish oil based polymers have also attracted the attention of researchers due to their high degree of unsaturation. Fish oil based polymers also possess unique good damping and shape memory properties

2.5 Biodegradable Polymers: Past, Present, and Future [8]

There are a seemingly limitless number of areas where biodegradable polymer materials may find use. The sectors of agriculture, automotives, medicine, and packaging all require environmentally friendly polymers. Because the level of biodegradation may be tailored to specific needs, each industry is able to create its own ideal material. The various modes of biodegradation are also a key advantage of such materials, because disposal methods may be tailored to industry specifications.

Environmental responsibility is constantly increasing in importance to both consumers and industry. For those who produce biodegradable plastic materials, this is a key advantage. Biopolymers limit carbon dioxide emissions during creation, and degrade to organic matter after disposal. Although synthetic plastics are a more economically feasible choice than biodegradable ones, an increased availability of biodegradable plastics will allow many consumers to choose them on the basis of their environmentally responsible disposal.

The processes which hold the most promise for further development of biopolymer materials are those which employ renewable resource feedstocks. Biodegradable plastics containing starch and/or cellulose fibers appear to be the most likely to experience continual growth in usage. Microbially grown plastics are scientifically sound, and a novel idea, but the infrastructure needed to commercially expand their use is still costly, and inconvenient to develop. Time is of the essence for biodegradable polymer development, as society's current

views on environmental responsibility make this an ideal time for further growth of biopolymers.

2.6 Biodegradable Polymer [9]

Biodegradation is a natural process by which organic chemicals in the environment are converted to simplier compounds, mineralized and redistributed through elemental cycles such as the carbon, nitrogen and sulphur cycles. Biodegradation can only occur within the biosphere as microorganisms play a central role in the biodegradation process. A number of standards authorities have sought to produce definitions for biodegradable plastics and some of these are provided below:

ISO 472: 1988—A plastic designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the plastics and application in a period of time that determines its classification. The change in chemical structure results from the action of naturally occurring microorganisms.

ASTM sub-committee D20.96 proposal—Degradable plastics are plastic materials that undergo bond scission in the backbone of a polymer through chemical, biological and/or physical forces in the environment at a rate which leads to fragmentation or disintegration of the plastics.

DIN 103.2 working group on biodegradable polymers—Biodegradation of a plastic material is a process leading to naturally occurring metabolic end products.

General definition of biodegradation—It is a process whereby bacteria, fungi, yeasts and their enzymes consume a substance as a food source so that its original form disappears. Under appropriate conditions of moisture, temperature and oxygen availability, bio-degradation is a relatively rapid process. Biodegradation for limited periods is a reason- able

target for the complete assimilation and disappearance of an article leaving no toxic or environmentally harmful residue.

2.6.1 Natural Biodegradable Polymer

Biopolymers are polymers formed in nature during the growth cycles of all organisms; hence, they are also referred to as natural polymers. Their synthesis generally involves enzyme-catalyzed, chain growth polymerization reactions of activated monomers, which are typically formed within cells by complex metabolic processes.

2.6.1.1 Polysaccharide [9]

For materials applications, the principal polysaccharides of interest are cellulose and starch, but increasing attention is being given to the more complex carbohydrate polymers produced by bacteria and fungi, especially to polysaccharides such as xanthan, curdlan, pullulan and hyaluronic acid. These latter polymers generally contain more than one type of carbohydrate unit, and in many cases these polymers have regularly arranged branched structures.

Starch, for example, is a physical combination of branched and linear polymers (amylopectin and amylose, respectively), but it contains only a single type of carbohydrate, glucose.

Both cellulose and starch are composed of hundreds or thousands of D-glucopyranoside repeating units. These units are linked together by acetal bonds formed between the hemi-acetal carbon atom, C_1, of the cyclic glucose structure in one unit and a hydroxyl group at either the C_3 (for cellulose and amylose) or the C_6 (for the branch units in amylopectin) atoms in the adjacent unit. This type of structure occurs because in aqueous solution, glucose can exist in either the acyclic aldehyde or cyclic

hemiacetal form, and the latter form is the structure that become incorporated into the polysaccharide. Also, the cyclic form can exist as one of two isomers, the α-isomer with an axial OH group on the ring or the β-isomer with an equatorial OH group. In starch the glucopyranoside ring is present in the α-form while in cellulose the repeating units exist in the β-form. Because of this difference, enzymes that catalyze acetal hydrolysis reactions during the biodegradation of each of these two polysaccharides are different and are not interchangeable.

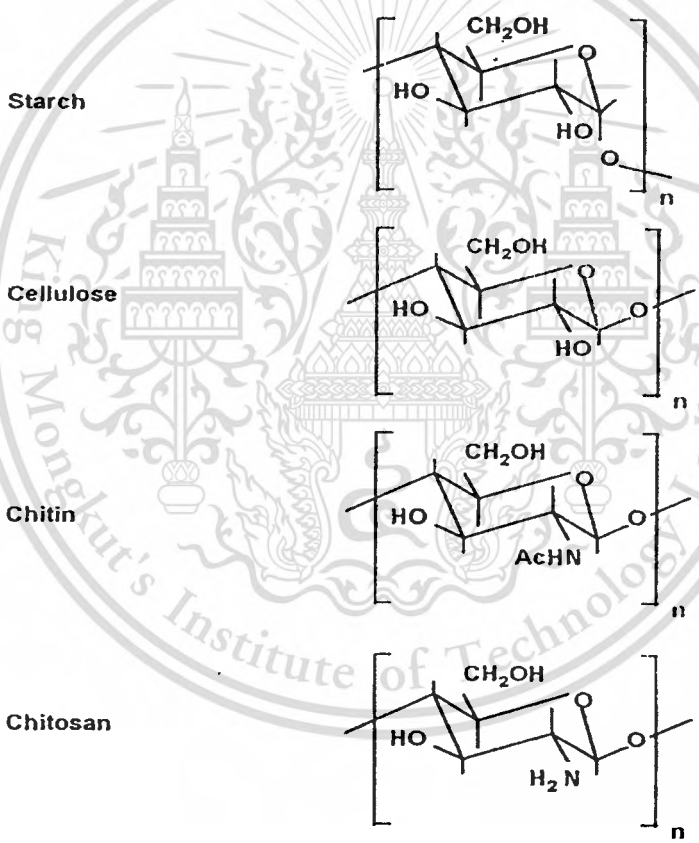


Figure 2.4 Structure of polysaccharides [9]

2.6.1.2 Polypeptides of Natural Origin

The proteins that have found applications as materials are, for the part, neither soluble nor fusible without degradation, so they are used in the form in which they are found in nature. This description is especially true for the fibrous proteins wool, silk and collagen. All proteins are specific copolymers with regular arrangements of different types of α-amino acids, so the biosynthesis of proteins is an extremely complex process involving many different types of enzymes. In contrast, the enzymatic degradation of proteins, with general purpose proteases, is a relatively straightforward, amide hydrolysis reaction.

2.6.1.3 Bacterial Polyesters

The natural polyesters, which are produced by a wide variety of bacteria as intracellular reserve materials, are receiving increased attention for possible applications as biodegradable, melt processable polymers which can be produced from renewable resources. The members of this family of thermoplastic biopolymers, which have the general structure given plastics with good impact properties to strong tough elastomers, depending on the size of the pendant alkyl group, R, and the composition of the polymer.

2.6.2 Factors Affecting Biodegradation [9]

2.6.2.1 Effect of Polymer Structure

Natural macromolecules, e.g. protein, cellulose, and starch are generally degraded in biological systems by hydrolysis followed by oxidation. It is not surprising, then, that most of the reported synthetic biodegradable polymers contain hydrolyzable linkages along the polymer chain; for example, amide enamine, ester, urea, and urethane linkages are susceptible to biodegradation by microorganisms and hydrolytic

enzymes. Since many proteolytic enzymes specifically catalyze the hydrolysis of peptide linkages adjacent to substituent in proteins, substituted polymers containing substituent such as benzyl, hydroxy, carboxy, methyl, and phenyl groups have been prepared in the hope that an introduction of these substituent might increase biodegradability.

Among benzylated polymers, mixed results have been obtained for polyamides. The achiral poly(hexamethylene-α-benzylmalonamide) is hydrolyzed readily by chymotrypsin, an enzyme known to catalyze the hydrolysis of peptide linkages adjacent to the benzyl group of the phenylalanine residues in proteins specifically. On the other hand, poly(alkylene-d,l-α-benzyladipamide)s have very low biodegradabilities.

Apparently, the chiral specificity of enzymes are maintained here. In an investigation designed to study the effects of stereochemistry on the biodegradation of polymers, monomeric and polymeric esterureas were synthesized from d-, l-, and d,l-phenylalanines. When subjected to enzyme-catalyzed degradation, the pure l-isomer was degraded much faster than the d,l-isomers. Chymotrypsin was also effective in degrading benzyl-substituted poly(ester-urea)s derived from phenylalanine, but not in degrading the unsubstituted poly(ester-urea)s derived from glycine. This agreed with the well-known substituent specificity of chymotrypsin. Since most enzyme-catalyzed reactions occur in aqueous media, the hydrophilic-hydro-phobic character of synthetic polymers greatly affects their biodegradabilities. A polymer containing both hydrophobic and hydrophilic segments seems to have a higher biodegrad-ability than those polymers containing either hydrophobic or hydrophilic structures only. A series of poly(alkylene tartrate)s was found to be readily assimilated by *Aspergillus niger*. However, the polymers derived from C_6 and C_8 alkane diols were more degradable than the more hydrophilic polymers derived from C_2 and C_4 alkane diols or the more hydrophobic polymers derived from the C_{10} and C_{12} alkane diols. Among the degradable poly(α-

amino acid-*co*-ε-caproic acid)s, the hydrophilic copolyamide derived from serine was more suscep-tible than those containing only hydrophobic segments. In order for a synthetic polymer to be degradable by enzyme catalysis, the polymer chain must be flexible enough to fit into the active site of the enzyme. This most likely accounts for the fact that, whereas the flexible aliphatic polyesters are readily degraded by biological systems, the more rigid aromatic poly(ethylene terephthalate) is generally considered to be bioinert.

2.6.2.2 Effect of Polymer Morphology

One of the principal differences between proteins and synthetic polymers is that proteins do not have equivalent repeating units along the polypeptide chains. This irregularity results in protein chains being less likely to crystallize. It is quite probable that this property contributes to the ready biodegradability of proteins. Synthetic polymers, on the other hand, generally have short repeating units, and this regularity enhances crystallization, making the hydrolyzable groups inaccessible to enzymes. It was reasoned that synthetic polymers with long repeating units would be less likely to crystallize and thus might be biodegradable; indeed, a series of poly(amide-urethane)s were found to be readily degraded by subtilisin.

Selective chemical degradation of semicrystalline polymer samples shows certain characteristic changes. During degradation, the crystallinity of the sample increases rapidly at first, then levels off to a much slower rate as the crystallinity approaches 100%. This is attributed to the eventual disappearance of the amorphous portions of the sample. The effect of morphology on the microbial and enzymatic degradation of PCL, a known biodegradable polymer with a number of potential applications, has been studied. Scanning electron microscopy (SEM) has shown that the degradation of a partially crystalline polycaprolactone film by filamentous fungi proceeds in a selective manner, with the amorphous regions being

degraded prior to the degradation of the crystalline region. The microorganisms produce extracellular enzymes responsible for the selective degradation. This selectivity can be attributed to the less-ordered packing of amorphous regions, which permits easier access for the enzyme to the polymer chains. The size, shape and number of the crystallites all have a pronounced effect on the chain mobility of the amorphous regions and thus affect the rate of the degradation. This has been demonstrated by studying the effects of changing orientation via stretching on the degradation.

Biodegradation proceeds differently from chemical degradation. Studies on the degradation by solutions of 40% aqueous methylamine have shown a difference in morphology and molecular weight changes and in the ability of the degrading agents to diffuse into the substrate. Also, it was found that the differences in degradation rates between amorphous and crystalline regions are not same. The enzyme is able to degrade the crystalline regions faster than can methylamine. Quantitative GPC (gel permeation chromatography) analysis shows that methylamines degrade the crystalline regions, forming single and double transverse length products. The enzyme system, on other hand, shows no intermediate molecular weight material and much smaller weight shift with degradation. This indicates that although degradation is selective, the crystalline portions are degraded shortly after the chain ends are made available to the exoenzyme. The lateral size of the crystallites has a strong effect on the rate of degradation because the edge of the crystal is where degradation of the crystalline material takes place, due to the crystal packing. A smaller lateral crystallite size yields a higher crystallite edge surface in the bulk polymer. Prior to the saturation of the enzyme active sites, the rate is dependent on available substrate; therefore, a smaller lateral crystallite size results in a higher rate of degradation. The degradation rate of a PCL film is zero order with respect to the total polymer, but is not zero order with respect to the concentrations of the crystallite edge

material. The drawing of PCL films causes an increase in the rate of degradation, whereas annealing of the PCL causes a decrease in the rate of degradation. This is probably due to opposite changes in lateral crystallite sizes.

2.6.2.3 Effect of Radiation and Chemical Treatments

Photolysis with UV light and the γ-ray irradiation of polymers generate radicals and/or ions that often lead to cleavage and crosslinking. Oxidation also occurs, complicating the situation, since exposure to light is seldom in the absence of oxygen. Generally this changes the material's susceptibility to biodegradation. Initially, one expects the observed rate of degradation to increase unit most of the fragmented polymer is consumed and a slower rate of degradation should follow for the crosslinked portion of the polymer. A study of the effects of UV irradiation on hydrolysable polymers confirmed this. Similarly, photooxidation of polyalkenes promotes the biodegradation. The formation of carbonyl and ester groups is responsible for this change.

2.6.2.4 Effect of Molecular Weight

There have been many studies on the effects of molecular weight on biodegradation processes. Most of the observed differences can be attributed to the limit of detecting the changes during degradation, or, even more often, the differences in morphology and hydrophilicity-hydrophobicity of polymer samples of varying molecular weight. Microorganisms produce both exoenzymes [degrading polymers from terminal groups (inwards)] and endoenzymes (degrading polymers randomly along the chain). One might expect a large molecular effect on the rate of degradation in the ease of exoenzymes and a relatively small molecular weight effect in the case of endoenzymes. Plastics remain relatively immune to microbial attack as long as their molecular weight

remains high. Many plastics, such as PE, PP and PS do not support microbial growth. Low molecular weight hydrocarbons, however, can be degraded by microbes. They are taken in by microbial cells, 'activated' by attachment to coenzyme-A, and converted to cellular metabolites within the microbial cell. However, these processes do not function well (if at all) in an extracellular environment, and the plastic molecules are too large to enter the cell. This problem does not arise with natural molecules, such as starch and cellulose, because conversions to low molecular weight components by enzyme reactions occur outside the microbial cell. Photodegradation or chemical degradation may decrease molecular weight to the point that microbial attack can

proceed, however.

The upper limits of molecular weight, beyond which uptake and intracellular degradation do not occur, have not been established for all alkane-derived materials. Very slow degradation of paraffins, PE glycols, and linear alkyl benzene sulphonates occurs when the length of the polymer chain exceeds 24-30 carbon atoms. It could be concluded from these amply documented results that alkane-based plastics with molecular weights exceeding 400-500 daltons (i.e. greater than 30 carbon atoms) must be degraded into smaller molecules by photodegradation, chemical or other biological means before biodegradation. LDPE with a molecular weight average of M_W= 150 000 contains about 11 000 carbon atoms. Decreasing molecules of this size to biologically acceptable dimensions requires extensive destruction of the PE matrix. This destruction can be partly accomplished in blends of PE and biodegradable natural polymers by the action of organisms, such as arthropods, millipedes, crickets, and snails.

Insertion of carbon monoxide into the chain permits chain scission by a Norrish-type reaction in a photochemical process. It was found that E/CO polymers with 2.5% CO linkages lost about 98% of their original elongation after 40 h of sunlamp

exposure. However, after 650 h of exposure, the samples that originally had M_w= 618 700 and M_n= 45 000 had photolytic products with M_w= 15 000 and M_n= 7300.

2.7 Modes of Biodegradation [9]

The biological environment, i.e. the biological surroundings in which polymers are present, includes the biological agents responsible for the deterioration of polymeric substances. Biological agents such as bacteria, fungi and their enzymes consume a substance as a food source so that its original form disappears. Under appropriate conditions of moisture, temperature, and oxygen availability, biodegradation is a relatively rapid process.

2.7.1 Microorganisms

Two types of microorganism are of particular interest in the biodegradation of natural and synthetic polymers.

2.7.1.1 Fungi

Eumycetes, or true fungi, are microorganisms of particular importance in causing the degradation of materials. Fungi are nucleated, spore-forming, nonchlorophyllous organisms, which reproduce both sexually and asexually; most of them possess filamentous, somatic structure, and cell walls of chitin and/or cellulose.

True fungi are present everywhere. Their importance as deteriorative agents is a result of the production of enzymes which break down nonliving substrates in order to supply nutrient materials present in polymer compositions. Certain environmental conditions are essential for optimum growth and degradative activity. These include an optimal ambient temperature, the presence of nutrient materials, and high humidity.

The group of test fungi that evolved for assay purposes in the field of natural polymers and that were further selected for their utility in assay procedures on synthetic polymers are taxonomically a very heterogeneous group, exhibiting no marked taxonomic similarities among them (for example based on morphology). Many of them were selected primarily because their reproduction spores are produced asexually and the variation associated with spores resulting from the fusion of sexual element is minimized. The test organisms cited are also, for the most part, the selected organisms from a large number of isolations which have proved their capability for yielding reproducible results repetitively, over long periods of time, under laboratory conditions, and in synthetic or highly controlled and specific culture media.

2.7.1.2 Bacteria

Schizomycetes, a bacteria, have played an undetermined role in relation to fungi in polymer deterioration. Bacteria can be single-cell rods, cocci, or spirilla; others are chain-like or filamentous. Bacteria can either be aerobic or anaerobic; in contrast, fungi are necessarily aerobic. Some bacteria are motile; bacteria are predominantly nonchlorophyllous. Their degradative action is also chiefly a result of enzyme production and resultant break-down of the nonliving substrate in order to obtain nutrient materials.

Bacteria present in soil are important agents for material degradation. Particularly affected are cellulosic plant life, wood products, and textiles subject to cellulytic degradation.

2.7.2 Enzymes

Enzymes are essentially biological catalysts, with the same action as chemical catalysts. By lowering the activation energy they can induce an increase in reaction rates in an

environment otherwise unfavourable for chemical reactions. In the presence of enzymes, a rise in reaction rate of 10^8 - 10^{20} can often be observed. The vast majority of enzymes are proteins having a polypeptide chain with a complex three-dimensional structure. Enzyme activity is closely related to conformational structure.

The three-dimensional structure of enzymes with folds and pockets creates certain regions on the surface with characteristic primary structures (i.e. specific amino acid sequences) which form an active site. At the active site the interaction between the enzyme and substrate takes place leading to a chemical reaction, giving a particular product.

2.7.2.1 Physical Factors Affecting the Activity of Enzymes

All enzymes are adjusted to a specific environment in which their activity and three-dimensional structure are optimal for a specific purpose. For human enzymes or enzymes isolated from human cells, this environment is a water solution at pH 6-8, an ion strength of 0.15 molar (as is normal physiological saline at 0.9% NaCl) and a temperature of 35-408 °C. An extremely small change one of these parameters may render the enzyme totally inactive and sometimes can even destroy it irreversibly. Other solvents than water, especially organic solvents, are also lethal to many enzymes but, on other hand, there are enzymes that are active in extreme environments, e.g. in hot water springs or salty environments.

2.7.2.2 Enzyme Mechanisms

Different enzymes have different actions, some enzyme change the substrate through a free radical mechanism while others follow alternative chemical routes. Typical examples are biological oxidation and biological hydrolysis.

(1). Biological Oxidation

Several enzymes can react directly with oxygen, the classical example being cytochromoxidase which is active in the respiratory chain. Oxygen has a special role in the metabolism of aerobic organisms. In many cases oxygen is directly incorporated into the substrate. The enzyme can be hydroxylases (eq. 1) or oxygenases (eq. 2).

Hydroxylases are sometimes called monooxynases and catalyze the insertion of a single atom of oxygen in the substrate A as part of a hydroxyl group. The monooxynases require a second reduced substrate BH_2 which simultaneously undergoes oxidation (i.e. dehydrogenation). Usually this second substrate is NADH (NADPH).

Oxygenases, also called dioxygenases, catalyze the insertion of a whole oxygen molecule into the substrate, sometimes the product is a dihydroxy derivative but more often the oxygen atoms are incorporated as a part of a carbonyl (-CO) or a carboxyl (-COO-) grouping.

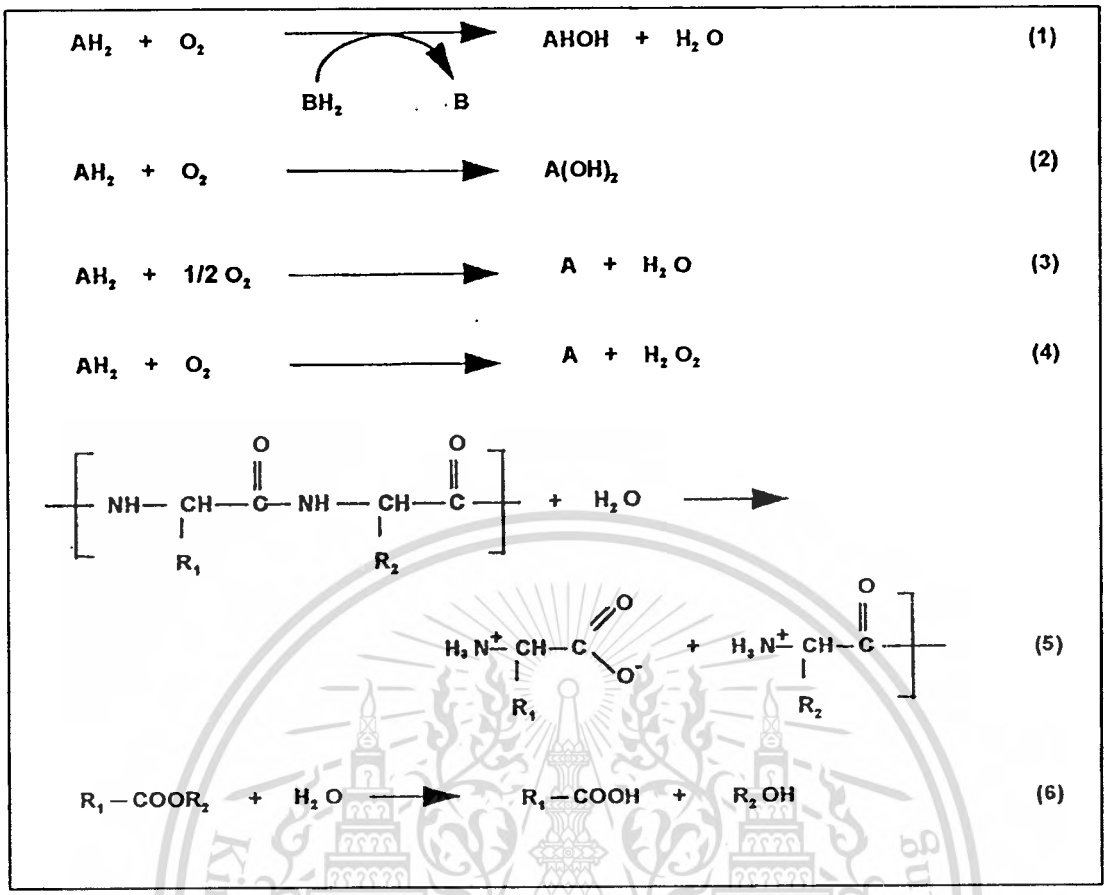


Figure 2.5 Biological oxidation and hydrolysis by enzymes [8]

Yet another type of biological oxidation exists, namely the process where the oxygen molecule is not actually incorporated into the substrate, but rather it functions as a hydrogen acceptor (i.e. electron acceptor). Enzymes of this type are called oxidases and one type produces H_2O (eq. 3) while another produces H_2O_2 (eq. 4).

One example of an oxygenase enzyme is that capable of catalyzing the splitting of aromatic structures producing (-C=O) groups instead of the (-HC=CH-) group.

(2). Biological Hydrolysis

Several different hydrolysis reactions occur in biological organisms. Proteolytic enzymes (proteases) catalyze the hydrolysis of peptide bonds (eq. 5) and also the related hydrolysis of an ester bond (eq. 6).

2.8 Classification of Composites

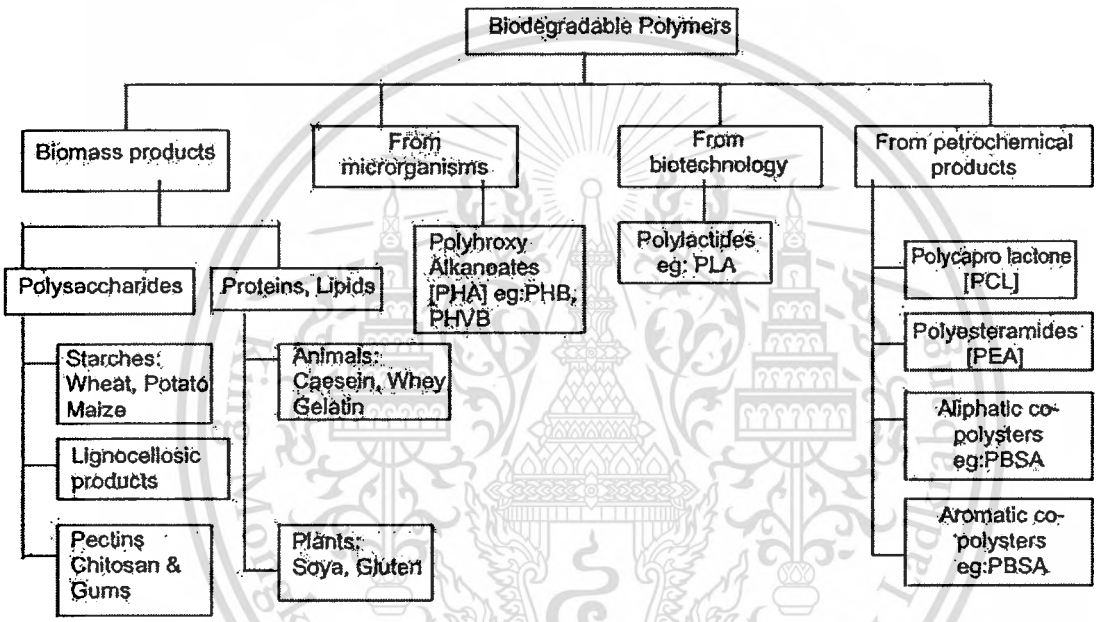


Figure 2.6 Classification of biodegradable polymer [9]

The first family is agro-polymers (e.g. polysaccharides) obtained from biomass by fractionation. The second and third families are polyesters, obtained, respecotively by fermentation from biomass or from genetically modified plants (e.g. PHA, polyhydroxyalkanoate) and by synthesis from monomers obtained from biomass (e.g. PLA, polylactic acid). The fourth family are polyesters, totally synthesized by the petrochemical process (e.g. PCL, polycaprolactone; PEA, polyesteramide; aliphatic or aromatic copolyesters). A large number of these biodegradable polymers (biopolymers) are

commercially available. They show a large range of properties and they can compete with non-biodegradable polymers in diferent industrial fields (e.g. packaging).

Another important biocomposites category is based on agro-polymers matrixes, mainly focussed on starchy materials. Plasticized starch, the so-called 'thermoplastic starch' (TPS) is obtained after disruption and plasticization of native starch, with water and plasticizer (e.g. polyol) by applying thermomechanical energy in a continuous extrusion process. Unfortunately, TPS shows some drawbacks such as a strong hydrophilic character (water sensitive), rather poor mechanical properties compared to conventional polymers and an important postprocessing variation of the properties. TPS properties reach equilibrium only after several weeks. To improve these material weaknesses, TPS is usually associated with other compounds.

2.9 Test Methods [10]

2.9.1 Moisture Absorption Experiments

Moisture absorption measurements were performed under 0, 33, 50, 75, and 100% RH (relative humidity) at 30±2 °C. all dimensions of 30 mm by 10 mm were cut from composite sheets. Prior to the absorption experiments, all specimens were thoroughly washed and then vacuum dried until a constant weight was attained. At predetermined intervals, specimens were taken out from the chambers and weighed using a ASTM E104 for determination.

2.9.2 Soil Burial Degradation Experiments

Soil burial degradation experiments were carried out at ambient temperature under moisture controlled conditions. Triplicate specimens of each composite were placed in a series of perforated boxes containing moisturized soil. The specimens (20x50 mm) were buried 10 cm beneath the surface of soil which was regularly moistened with distilled water. The samples were removed at predetermined time points, carefully washed with distilled water several times in order to ensure the stop of the degradation, dried at room temperature to a constant weight and then were stored in darkness until testing. The specimens were weighed to determine the average weight loss:

$$\text{Weight loss} = \frac{W_0 - W_t}{W_0} \cdot 100$$

where W_0 is the initial mass and W_t is the remaining mass at any given time, t. All results are the average of three replicates.

2.9.3 SEM observations

Tensile facture surfaces were examined by scanning electron microscopy (SEM). Prior to SEM observation, all samples were sputter coated with a thin layer of gold to avoid electrical charging.

2.9.4 DSC and TGA Analysis [11]

Thermogravimetry (TGA) and differential scanning calorimetry (DSC); STA 625 thermogravimetric analyzer. Investigation were made while heating the samples from 20-600 °C at the rate of 20 °C/min in the air or in nitrogen. Mass of the samples was about 10 mg. simultaneous recording of thermogravimetric and DSC signals.

2.10 Literature Reviews

K. Chompoorat and B. Chansuprom (2008) [2]. This research aimed to study on the preparation and properties of thermoplastic rice and glutinous rice starch blend plasticized by glycerol in order to produce degradable polymer. Different ratio of glutinous rice starch to rice starch, i.e. 100:0, 75:25, 50:50, 25:75 and 0:100, were studied. In addition, different amounts of glycerol (25, 50, 75 and 100 phr) and different mixing temperature (140, 150, 160 and 170 °C) were examined. It was found that the optimum temperature, was 150 °C and the amount of glycerol were either 50 or 75 phr. The blended thermoplastic starch were, then, tested mechanical, morphological, thermal and degradable property. The results showed that at high ratio of glutinous rice starch, the speciments showed high elongation at break and % strain at break. On the other hand, high ratios of rice starch caused high load, tensile strength, Young's modulus and hardness. For morphology, obtained from Scaning Electron Microscope (SEM), the results illustrated good phase compatibility. Beside, the samples with high content of glutinous rice starch were easily degraded than those of rice starch. Furthermore, onset degradation temperatures were not affected by mixing temperature, glycerol content and rice ratio.

L. Avérous et al. (2001) [12]. This paper was focused on the interactions between leafwood cellulose fibers and a plasticized wheat starch matrix. Different plasticized starch (TPS)-based composites were elaborated. LDPE-based composites were analysed. Mechanical properties, thermo-mechanical properties (DMTA) and morphology (SEM) were evaluated. DMTA analysis showed for TPS composites a strong evalution of the main relaxation temperature, which could be linked to the existence of cellulose-starch interactions resulting in a decrease of starch chain mobility. This phenomenon was consistent with the evolution of mechanical behaviour. SEM observations correlate this hypothesis. After cryogenic fracture,

TPS composites present fibers, which were embedded in the matrix on the composites, reinforcing effects were observed according to the evolution of fiber length and fiber content.

T. Bourtoom and M. S. Chinnan (2008) [13]. Biodegradable blend films from rice starch-chitosan were developed by casting film-solution on leveled trays. The influence of the ratio of starch and chitosan (2:1, 1.5:1, 1:1, and 0.5:1) on the mechanical properties, water barrier properties, and miscibility of biodegradable blend films was investigated. The biodegradable blend film from rice starch-chitosan showed an increase in tensile strength (TS), water vapor permeability (WVP), lighter color and yellowness and a decreasing elongation at the break (E), and film solubility (FS) after incorporation of chitosan. The introduction of chitosan increased the crystalline peak structure of starch film: however, too high chitosan concentration yielded phase separation between starch and chitosan. The amino group band of chitosan molecule in the FTIR spectrum shifted from 1541.15 cm^{-1} in the chitosan film to 1621.96 cm^{-1} in the biodegradable blend films. These results pointed out that there was a molecular miscibility between these two components. The properties of rice starch-chitosan biodegradable blend film and selected biopolymer and synthetic polymer film were compared: the results demonstrated that rice starch-chitosan biodegradable blend film had mechanical properties similar to the other chitosan films. However, the water vapor permeability of rice starch-chitosan biodegradable blend film was characterized by relatively lower water vapor permeability than chitosan films but higher than polyolefin.

I. S. M. Zaidul et al. (2008) [14]. Potato starches with various contents of amylose from the Eniwa, Benimaru, and Norin No.1 cultivars were blended with wheat flour at 10 to 50% potato starch (on a weight basis), and differential scanning calorimetry (DSC) studies were then conducted to determine if there were any traces of starch at 30% wt suspension. The

amylose content of Eniwa potato starch was higher than those of the Benimaru and Norin No.1 potato starches. Eniwa potato starch also exhibited significantly hiher DSC traces than the Benimaru and Norin No. 1 potato starches. The DSC traces of the gelatinization peak temperature (T_p) of the Eniwa potato starch-wheat flour mixture remained almost identical up to 30% and then showed a tendency to decrease from 40% potato starch in the mixtures due to significant dilution of wheat four by potato starches at 40 and 50%. However, the T_p values of yhe Eniwa potato starch-wheat flour mixtures, and exhibited a trailing shoulder up to 40% Eniwa potato starch. On the other hand, on trailing shoulder was evident at 50% Enawa potato starch in the mixture or in the Benimaru and Norin No.1 potato starch-wheat flour mixtures. Such phenomena occurred due to the smaller differnces in the T_p of the control wheat flour, Benimaru and Norin No 1 potato starches. The T_p of the control wheat flour, Benimaru and Norin No. 1 potato starches. The T_p of the mixtures was slightly higher than that of the control samples due to the influences of the wheat gluten in the mixtures.

L. Averous and N. Boquillon (2004) [15]. The paper was focused on the study of the thermal and mechanical behaviour of reinforced leagwood agro-materials. Various formulations based on plasticized wheat starch matrix were carried out, varying matrix formation, filler content, fibers length and nature. Cellulose and lignocellulose fibers, which showed unequal surface tensions, were tested. After extrusion and injection moulding, the properties of these wheat starch-based biocomposites were analysed. Mechanical properties, thermo-mechanical properties (DMTA) and thermal degradation (TGA) were analysed. DMTA analysis showed important variations of main relaxation temperature, which could be linked both, to interactions resulting in a decrease of starch chain mobility and to a regular reinforcing effect. These results were consistent with the static mechanical behavior, which varied according to the filler content (up to 30 wt%), fiber natured (cellulose vs.

lignocellulose) and fiber length (from 60 μm to 1 mm). Besides, the addition of cellulose fillers improved the thermal resistance of these biocomposites.

N. Soykeabkaew et al. (2004) [16]. Tapioca starch-based composite foams (SCFs) were successfully prepared by baking starch-based batters incorporating either jute or flex fibers inside a hot mold. The effect of moisture content on the mechanical properties of SCFs was investigated. Both the flexural strength and the flexural modulus of elasticity appeared to be markedly improved with addition of 5-10% by weight of the fibers. At a fixed fiber content of 10% by weight, both the flexural strength and the flexural modulus of elasticity were found to increase with increasing aspect ratio of the fibers the improvement in the mechanical properties of SCFs was attributable to the strong interaction between fibers and the starch matrix, as evidenced by a series of scanning electron micrographs being take on SCF fracture surface. Between jute- and flax-reinforced SCFs, jute fibers had a greater reinforcing effect than flax fibers did. Orientation of fibers was shown to have a strong effect on both flexural strength and the flexural modulus of elasticity of SCFs, with the highest values being observed on specimens having fibers oriented in the longitudinal direction.

L. Famá et al. (2009) [17]. The influence of wheat bran content in biodegradable composites based on cassava starch and containing glycerol and potassium sorbate were studied. Films were produced by casting and three difference fraction of wheat bran fiber were used: 1.5 mg, 13.5 mg and 27.1 mg/g of matrix. It was observed that addition of wheat bran, which contains 40 g of water insoluble fiber per 100 g of bran, shifted the glycerol-rich phase glass transition temperature toward higher temperature, broadening and diminishing in intensity the peak associated with this relaxation. This effect suggests that the presence of fiber led to an enhancement in the glycerol dispersion. At room temperature, an increase in

fiber content did not affect density of the matrix but caused the increase of the storage modulus and the decrease of loss tangent, moisture content and water vapor permeability. Besides, the addition of fibers led to the increase of the yellow index. The improvement in water vapor barrier properties jointly with the enhancement of mechanical properties when fiber was present, lead to the idea that composite developed could be used to protect food and extend its shelf life.

C. M. O. Müller et al. (2009) [18]. Cassava starch-based films have promising application on food packaging, because of their environmental appeal., low cost, flexibility and transparency. Nevertheless, their mechanical and moisture barrier properties should be improved. The aim of this work was to enhance these properties by reinforcing the films with softwood short cellulose fibers. Besides, the influences of both the solubility coefficient of water in the films (β) and the diffusion coefficient of water vapor through the films (D^w) on the films' water vapor permeability (K^w) were investigated. Films were prepared by the so-called casting technique, from film-forming suspension of cassava starch, cellulose fibers (1.2 mm long and 0.1 mm of diameter), glycerol and water. The influence of fibers addition on K^w was determined at three relative humidity gradient ranges, ΔRH (2-33%, 33-64% and 64-90%). Films reinforced with cellulose fibers showed higher tensile strength and lower deformation capacity, and presented lower K^w than films without fibers. K^w showed strong dependency of β and D^w, presenting values up to 2-3 times greater at ΔRH = 64-90% than at ΔRH = 33-64%, depending on the film formulation. Therefore, adding cellulose fibers to starch-based films is a viable alternative to improve their mechanical and water barrier properties.

N. Cañigueral et al. (2009) [19]. Potato starch-based biopolymer was reinforced with flax strands. Composite materials at different fiber content were obtained by means of high-shearing mixing followed by injection molding processing. The evaluation of the mechanical properties gave a significant increase of the strength and stiffness of composites with the percentage of flax strands. The enhancement was analyzed in terms of compatibility and extrusion of the adhesion at fiber-matrix interface. The intrinsic mechanical properties of the reinforcement were measured and the behavior of the obtained composites was studied in terms of the modified rule of mixtures and the modified Halpin-Tsai equation.

Chapter 3

Experiment Details

3.1 Materials

Materials used in this study were described below:

1. Rice flour super quality ; Jade leaf Brand ®, from Bangkok Inter Food Co, Ltd. The components are shown in Table 3.1

Table 3.1 The components of rice starch

Detail	Result of analysis
Amylose	18-27%
Amylopectin	70-90%
Humidity	11.50-13.00%
Dryness	86.90-88.05%
Lipid	0.25%
Ash	0.23%
Protein	6.50-7.00%
Size	Less than 160 microns
pH	6.0-7.0

Remark : Data of the manufacturer [2]

2. Glutinous rice flour super quality ; Jade leaf Brand ®, Bangkok Inter Food Co,Ltd. The component shown in Table 3.2

Table 3.2 The components of glutinous rice starch

Details	Result of analysis
Amylose	5-7%
Amylopectin	95%
Humidity	11.00 - 13.00%
Dryness	86 - 87%
Lipid	0.20%
Ash	0.20%
Protein	6.50-7.00%
Carbohydrate	77.65 – 80%
Size	Less than 158 microns
pH	6.0-7.0

Remark Data of the manufacturer

3. Glycerol; Lab system CO, LTD

4. Cotton fibers; Local market

3.2 Instruments

The instruments used in this study are listed below :

1. Internal mixer; Lab Tech Engineering

2. Compression molding; Lab Tech Engineering

3. Universal Testing Machine; Lloyd Instrument, LR 5K

4. Balance machine

5. Mold ; thickness 2 mm

6. PVC transparent sheet

7. Thermogravimetric Analyzer (TGA); Perkin Elmer, Pyris 1 TGA HT

8. Scanning electron microscope (SEM);

10. Spectrophotometer; Hunter lab, Miniscan XE Plus

11. X-ray Diffraction (XRD); D8 Advance

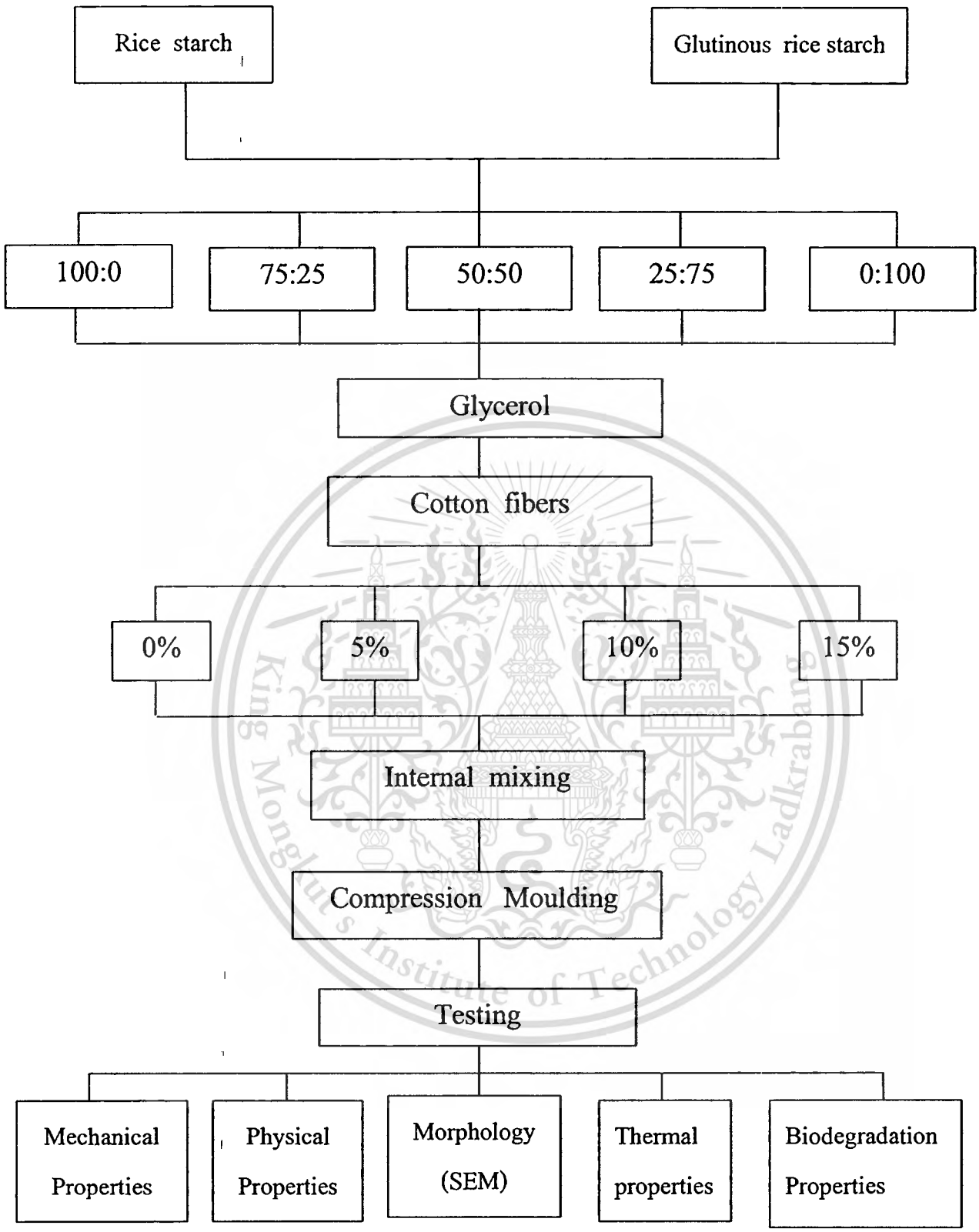


Figure 3.1 Overview of the methodology

3.3 Methodology

Part 1 : Preparation of TPS from rice and glutinous rice starch blend

1. Weigh the ingredients as shown in Table 3.3. Keep the mixture in the close container overnight.
2. Blend the mixture in the internal mixer at the temperature of 160°C using a speed of 40 rpm for 5 minutes.
3. The materials were then compressed at 160°C for 5 minutes, after that cooled down for 5 minutes.

Table 3.3 The weight ratio of rice and glutinous rice starch blend

Rice starch (g)	Glutinous rice starch (g)	Glycerol (%wt)
100	0	50
75	25	50
50	50	50
25	75	50
0	100	50

Part 2: Modification of TPS from rice and glutinous rice starch blend using cotton fibers as reinforcement

1. Cotton fibers were cut into 2mm and 5 mm in length.
2. Follow the experimental procedures as in Part 1; except for, the cotton fibers were added into the TPS matrix before blending in the internal mixer.

Note; The cotton fibers were varied in lengths; 2mm and 5 mm as well as in content. i.e. 0%, 5%, 10% and 15%

Table 3.4 The weight ratios of TPS and cotton fibers

Rice starch (g)	Glutinous rice starch (g)	Glycerol (g)	Cotton (%wt)
100	0	50	0, 5, 10, 15
50	50	50	0, 5, 10, 15
0	100	50	0, 5, 10, 15

3.4 Testing

3.4.1 Mechanical properties

Table 3.5 Standards used to test the mechanical properties of samples

Properties	Standard	Unit
Tensile strength	*ASTM D 638*	MPa
Young's Modulus	*ASTM D 638*	MPa
% elongation at break	*ASTM D 638*	%
Hardness	*ASTM D 638*	Shore A

3.4.1.1 Tensile strength, Young's modulus and % elongation

Mechanical properties of different TPS were tested using Universal Testing and were conducted by WINDAP software. The temperature and relative humidity were controlled at 23±2 °C and 60±2%, respectively.

Test conditions as follows:

Test speed: 40 mm. / min.

Gauge length: 25 mm.

Load cell: 100 N.

Tensile strength, Young's modulus and % elongation can be calculated by the following equation.

Tensile strength = F / A.

Young's modulus = $(F / A) / [(L-L_o) / L_o]$

% Elongation at break = $(L-L_o) / L_o \times 100$.

When F is the force that extended the specimens (N).

A is cross section area the specimens (mm^2).

L is the length the specimens is after it is stretched (mm).

Lo is the original length of the specimens (mm.).

3.4.2 Morphology

Scanning electron microscope was used to study morphology of TPS specimens. The specimens were immersed in liquid nitrogen before cryogenic fracture. After that a thin layer of gold was coated on the surface. The fiber distribution and interfacial boundary of different TPS samples were examined.

3.4.3 Moisture determination

Moisture content of TPS was determined according to ASTM E104. The samples were conditioned in closed containers at 30±2 °C with 50% RH, using saturated solutions of $CaCl_2$. The water absorption was given by the equation

$$W(\%) = [\,(M_t - M_o)/M_o\,] \times 100$$

where M_t is the weight at time t and M_o the initial weight.

3.4.4 X-ray diffraction analysis

X-ray diffractometer was used to obtain the X-ray spectrums using 40 kV, 30 mA and CuK_α (λ=1.542 °A). The scattering angle (2θ) range of 3-60° was performed at a rate of 1°/min.

3.4.5 Thermal properties

Thermo gravimetric analyzer was used to determine onset degradation temperature (T_d) and %weight loss at onset degradation temperature. Using the temperature range of 50-100°C with 10°C/min heating rate under nitrogen atmosphere.

3.4.6 Degradable properties (Soil Burial Test)

The TPS samples with the dimension of 20x50 mm were burial under soil surface of approximately 10 cm. The pH and temperature of soil were maintained at 7 and 32±2°C, respectively. The water content of the soil was in the range 30-40% and the weight changed was recorded for everyday. Average percentage weight change was recorded from three independently samples.

3.4.7 IR spectroscopic study

Fourier Transform Infrared spectrophotometer (Brucker IFS 28) was used to characterize the thermoplastic rice starch reinforced cotton fiber by adsorption spectra.

The samples were prepared to pellets with KBr and the IR spectrum recording in the frequency range of 4000 - 400 cm^{-1}.

Chapter 4

Results and discussions

In this research involved with the preparation of thermoplastic starch (TPS) from rice starch and glutinous rice starch and rice starch blend and the improvement of TPS properties using cotton fiber as reinforcing filler. Effect of rice ratios, cotton fiber contents and cotton fiber lengths on physical, mechanical, morphological and biodegradable properties were studied.

4.1 Physical properties

4.1.1 Fourier Transform Infrared spectroscopy (FT-IR)

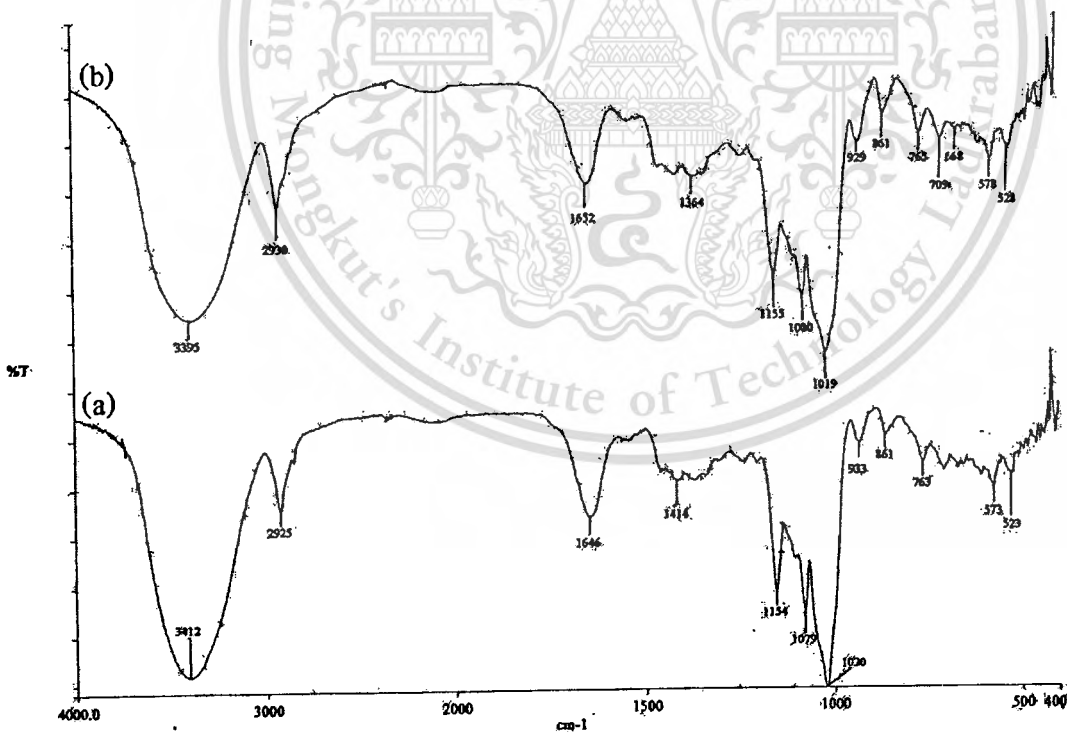


Figure 4.1 FT-IR spectra of (a) native rice starch and (b) native glutinous rice starch

FT-IR was used to study main functional groups appeared in different TPS samples prepared from rice and glutinous rice starches. FT-IR spectra of native rice starch and native glutinous rice starch (Figure 4.1) showed the broad absorption band of O-H stretching in the range of 3400-3300 cm^{-1}. The peak positions at 3000-2840, 1420-1330 and 1260-1000 cm^{-1} were assigned for C-H stretching, O-H bending and C-O stretching, respectively. The wavenumber of 1635 cm^{-1} was corresponded to bound water presented in starch [20].

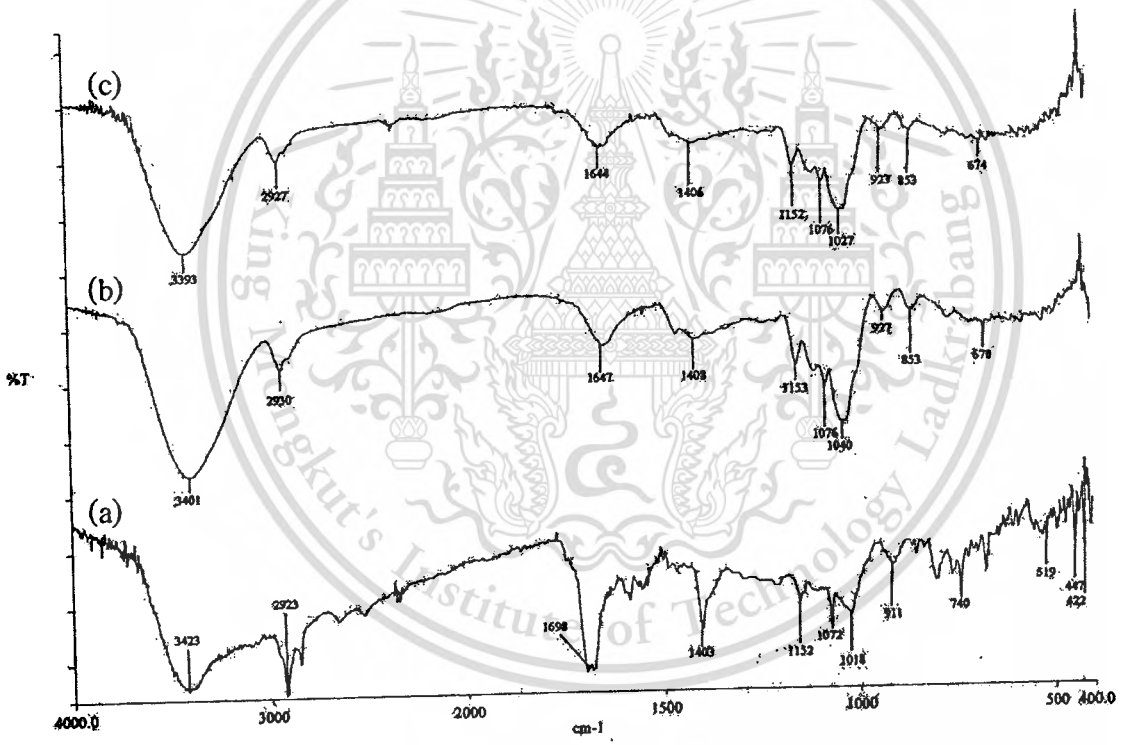


Figure 4.2 FT-IR spectra of the TPS from rice and glutinous rice starch with different rice: glutinous rice ratios (a) 100:0 , (b) 50:50 and (c) 0:100.

Figure 4.2 shows IR spectra of TPS from rice and glutinous rice starch plasticized by glycerol. It was found that similar IR spectra were obtained for the TPS prepared from rice starch, blended starch and glutinous rice starches. Comparison with IR spectra of the TPS from rice and glutinous rice starches showed the main peak positions in the range of 3400-3300 cm^{-1}, 3000-2840 cm^{-1}, 1420-1330 cm^{-1} and 1260-1000 cm^{-1}, related to O-H stretching, C-H stretching, O-H bending and C-O stretching, respectively. The difference was found in O-H stretching (Figure 4.1-4.2), i.e. 3412 cm^{-1} shifted to 3423 cm^{-1} for rice starch and 3395 cm^{-1} shifted to 3393 cm^{-1} for glutinous rice starch. The results of peak position shift indicate the increasing of intermolecular hydrogen bonding by the addition of glycerol [21].

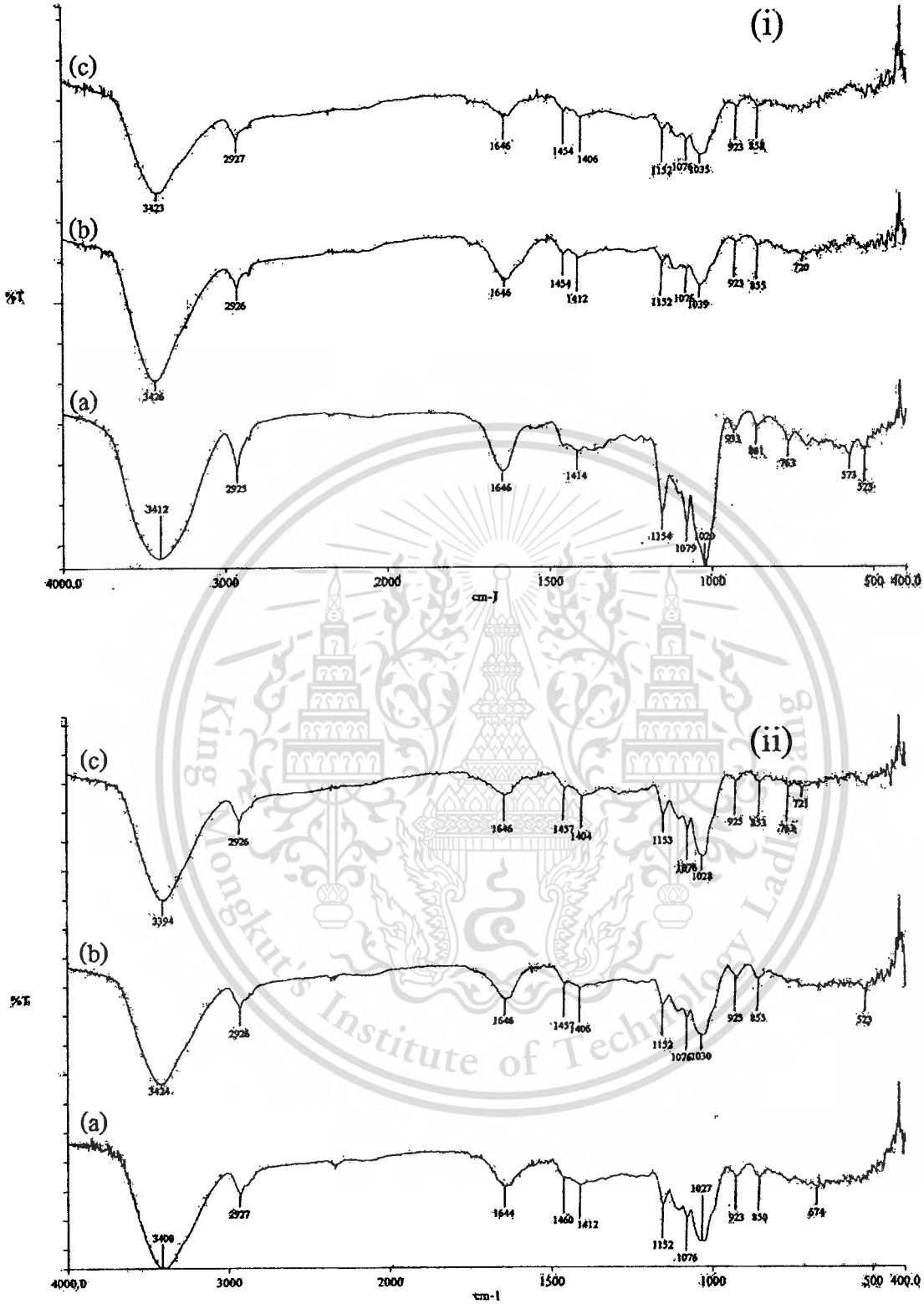


Figure 4.3 FT-IR spectra of the TPS from (i) rice starch and (ii) glutinous rice starch with different cotton contents (a) 0% (b) 5% and (c) 10%

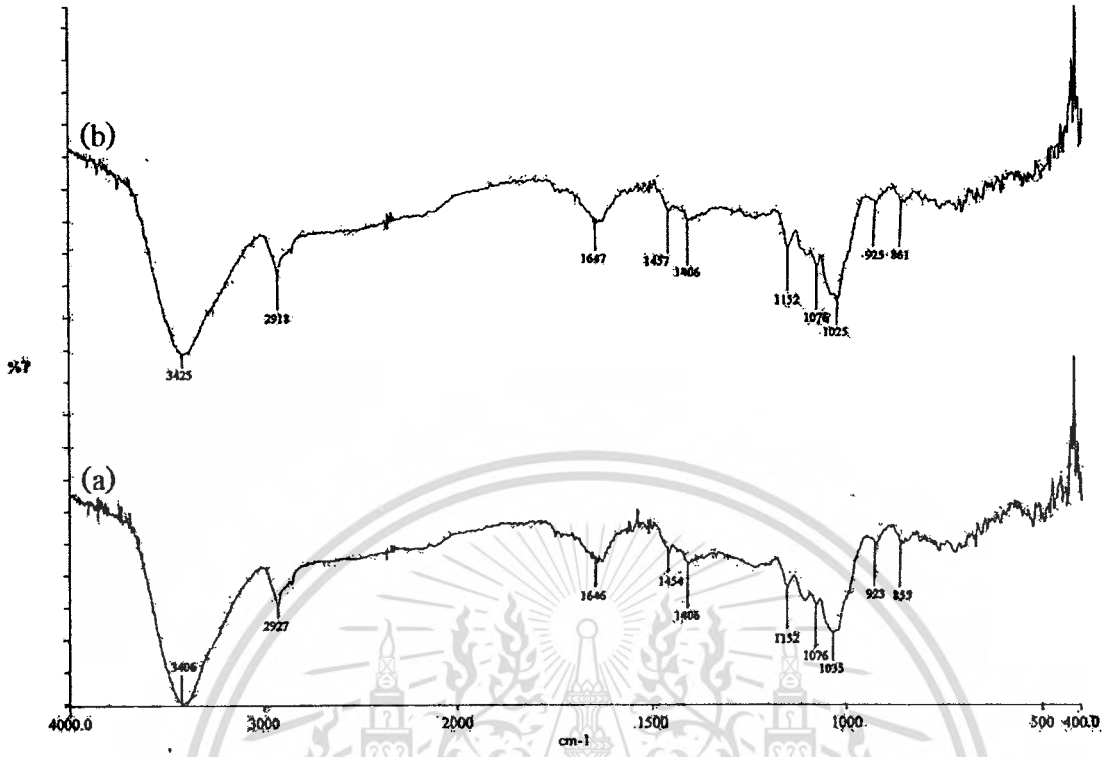


Figure 4.4 FT-IR spectra of the TPS from rice starch (100:0) with different cotton fiber lengths. (a) 2 mm and (b) 5 mm

For the TPS with the addition of cotton fibers in Figures 4.3-4.4, the IR spectra showed similar IR spectra to the TPS without cotton fibers, as expected. It should be noted that the addition of cotton fiber into the TPS caused narrow peak in the 3400-3300 cm^{-1}, indicating of a change in hydrogen bonds in the TPS/cotton fiber samples. In addition, the peak shift in the range of 3400-3300 cm^{-1} was also noticed in the TPS reinforced by different contents and lengths of cotton fibers, suggesting the change in intermolecular hydrogen bonding.

4.1.2 X-ray diffraction analysis

Crystal structure of TPS was studied by X-ray diffractometer, which was used to obtain the X-ray diffractograms using 40 kV, 30 mA and CuKα radiation (λ=1.542 A°). The scattering angle (2θ) range of 3-60° was performed at rate of 1°/min.

4.1.2.1 X-ray diffraction patterns of native rice starch, native glutinous rice starch and cotton fiber

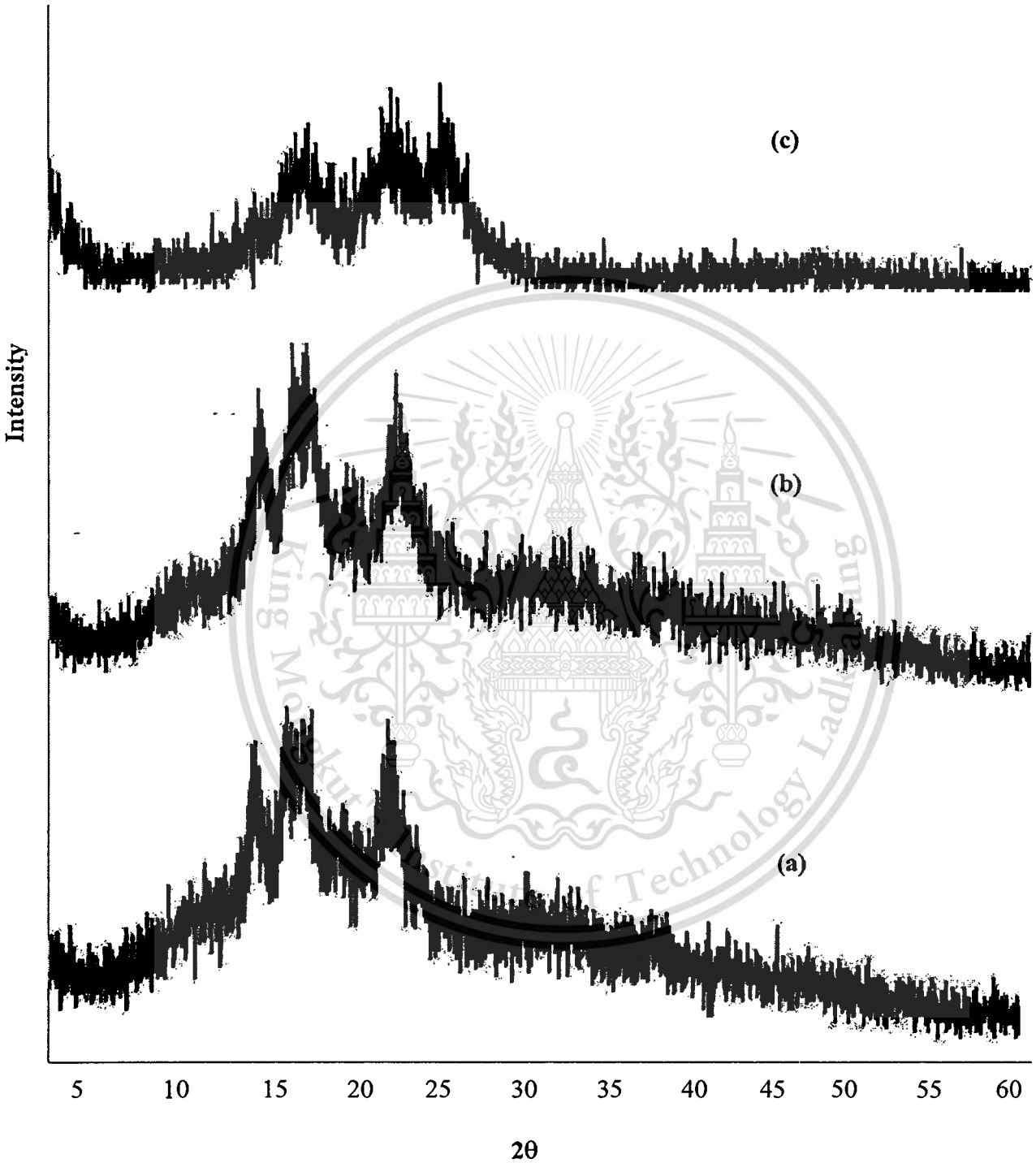


Figure 4.5 X-ray diffraction patterns of (a) native rice starch (b) native glutinous rice starch and (c) cotton fiber

The X-ray diffraction patterns of native rice starch, native glutinous rice starch and cotton fiber are shown in Figure 4.5. Native rice starch showed a typical A-type (monoclinic unit cell, a = 2.124 nm, b = 1.172 nm, c = 1.069 nm and γ = 123.5°) [22] X-ray diffraction pattern with strong peak at 2θ, 14.92°, 16.94° and 22.88°. Native glutinous rice starch also showed a typical A-type X-ray diffraction pattern with strong peaks at 2θ, 15.1°, 17.06° and 23.06° [23]. In cotton fibers, the main peaks were observed at 2θ, 17.98°, 22.52° and 25.68°, which are typical of cellulose I.

4.1.2.2 X-ray diffraction patterns of TPS from rice starch and glutinous rice starch

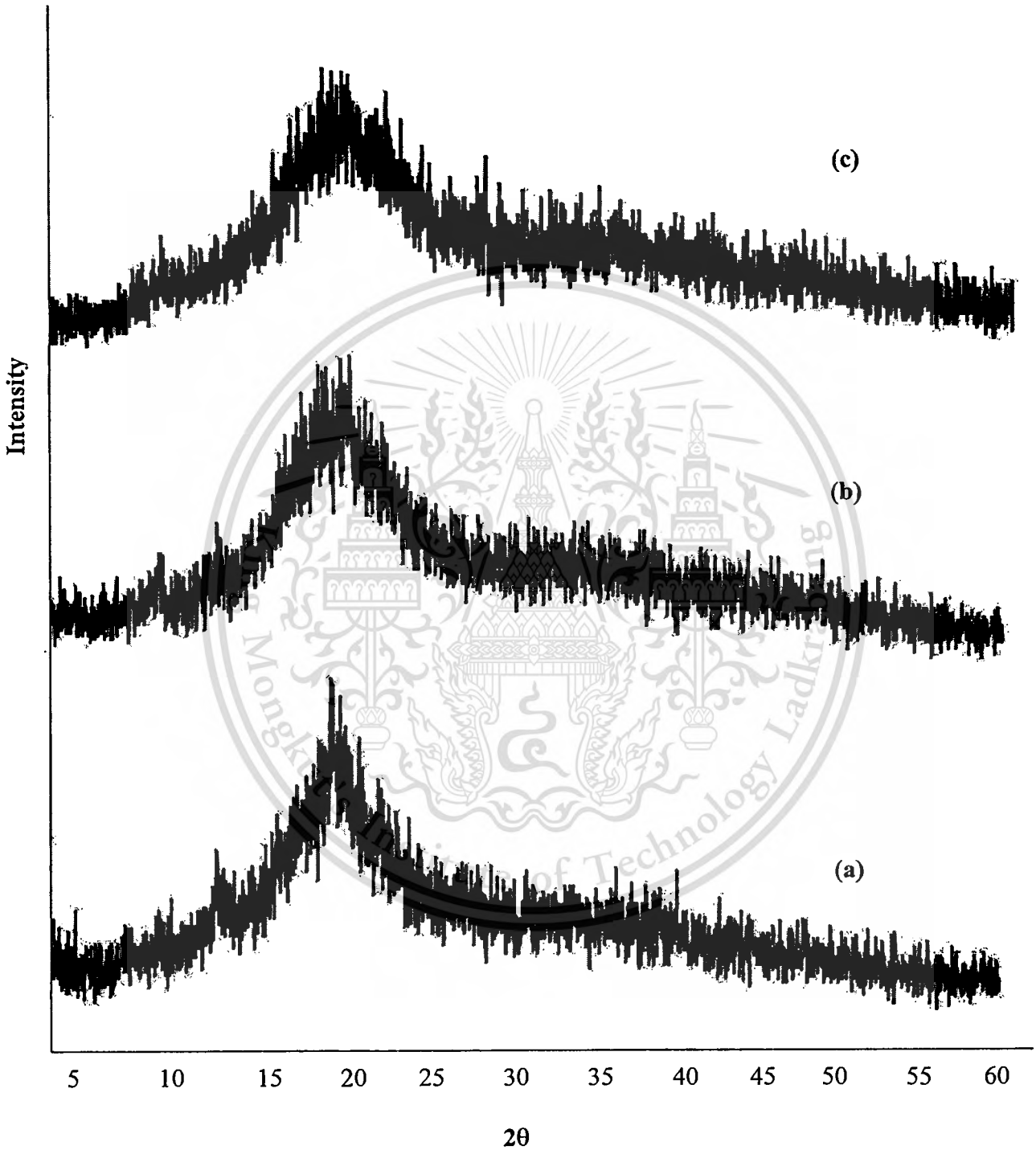


Figure 4.6 X-ray diffraction patterns of TPS from (a) rice starch (100:0) (b) blended rice starch (50:50) and (c) glutinous rice starch (0:100)

The X-ray diffraction patterns of TPS from rice starch, blended rice starch and glutinous rice starch are represented in Figure 4.6. All of the TPS samples showed V-type diffraction patterns [24], with the main peaks at 2θ, 13.1° and 19.98°, for rice starch and 19.12° for blended rice starch and glutinous rice starch. Compared to native rice starch and glutinous rice starches, crystal structures of TPS was changed due to the partially destruction inter- and intra-molecular hydrogen bonds by plasticizer [24].

4.1.2.3 Effect of cotton fiber on crystal structure of the TPS prepared from rice starch (100:0)

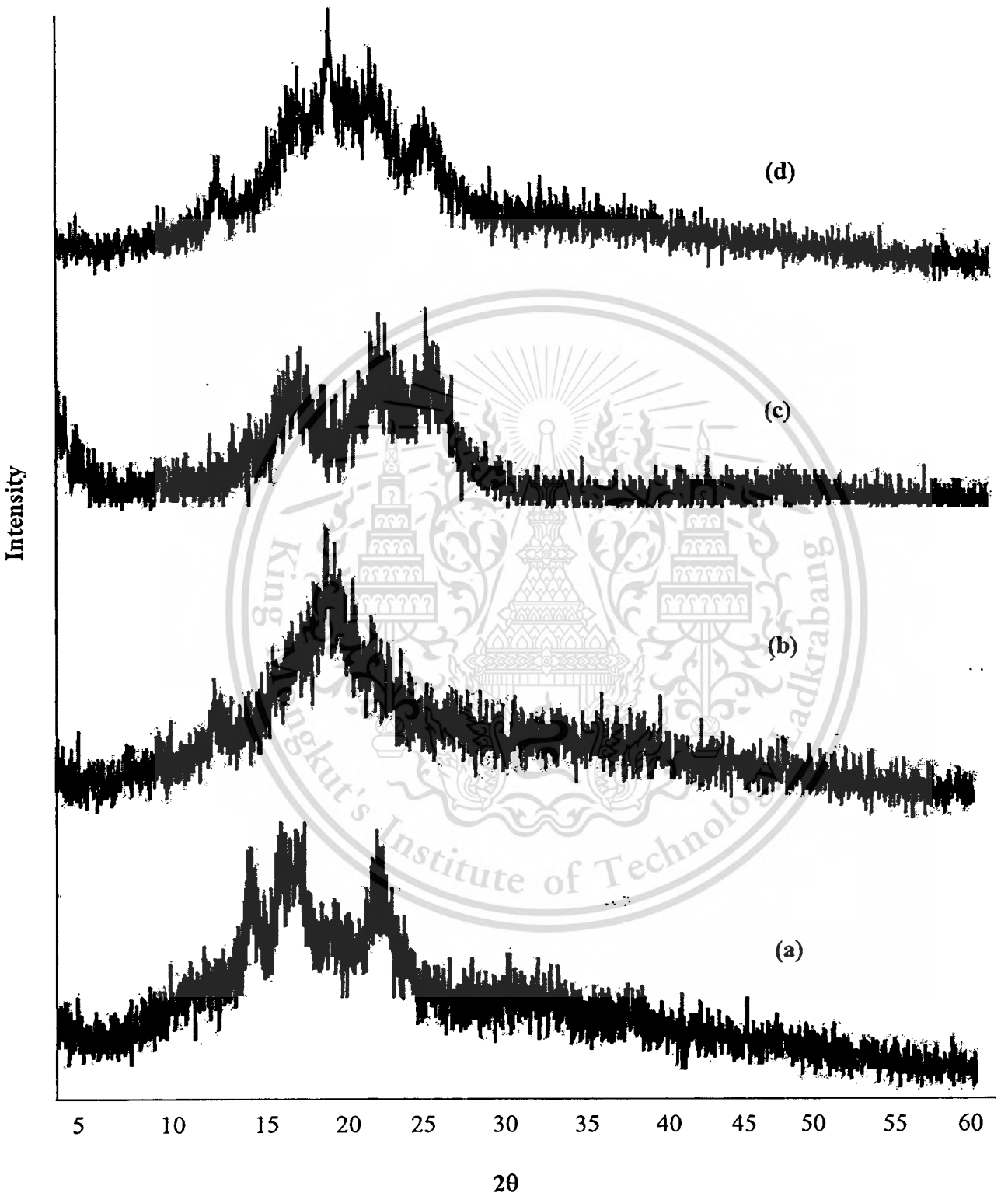


Figure 4.7 X-ray diffraction pattern of TPS (a) native rice starch (b) TPS from rice starch (c) cotton fiber and (d) TPS from rice starch reinforced by cotton fiber (10%wt at 2 mm)

4.1.2.4 Effect of cotton fiber on crystal structure of the TPS prepared from glutinous rice starch (0:100)

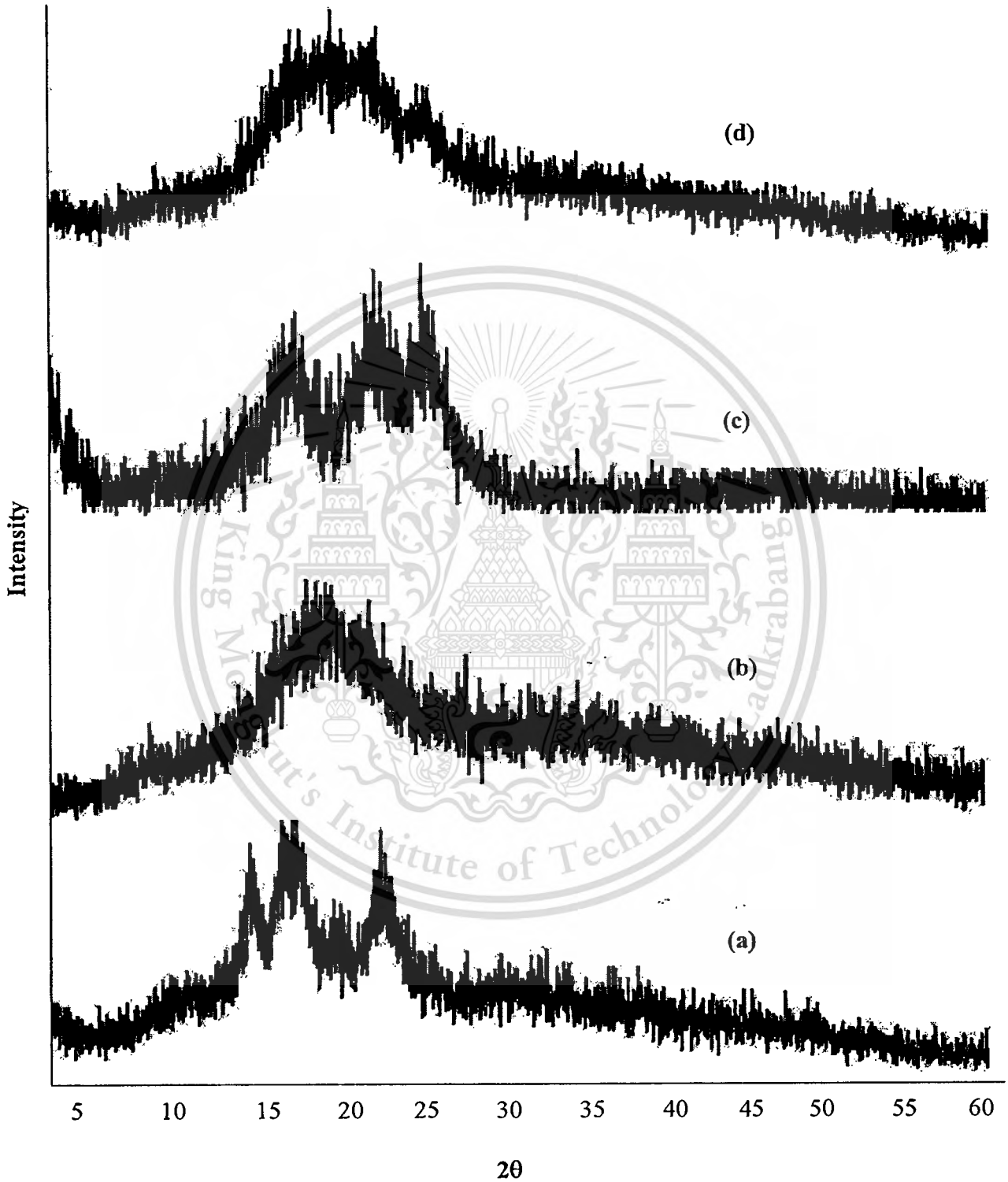


Figure 4.8 X-ray diffraction pattern of TPS (a) native glutinous rice starch (b) TPS from glutinous rice starch (c) cotton fiber and (d) TPS from glutinous rice starch reinforced by cotton fiber (10%wt at 2 mm)

4.1.2.5 Effect of cotton fiber contents and length on crystal structure of the TPS from rice starch (100:0)

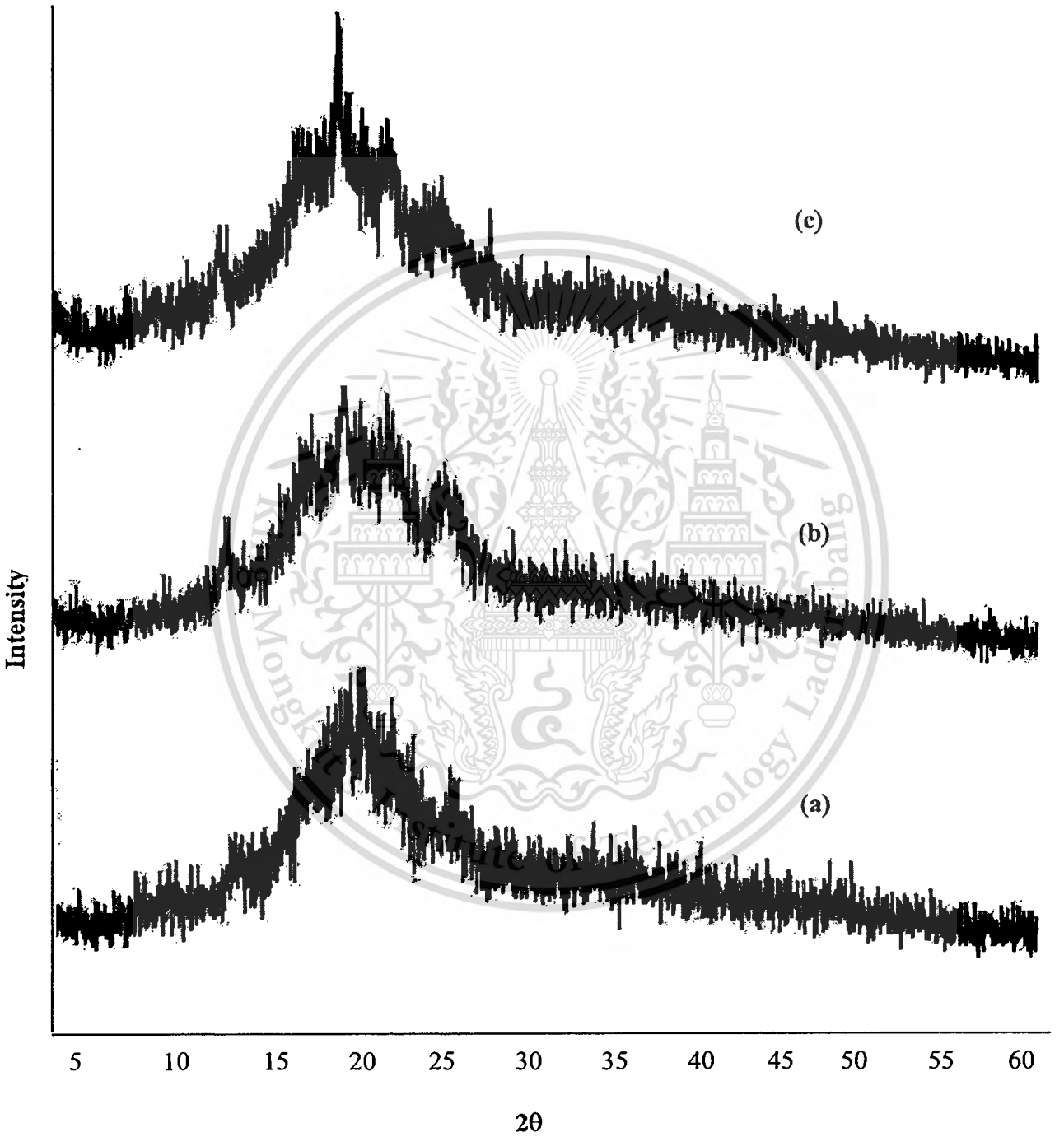


Figure 4.9 X-ray diffraction pattern of TPS from rice starch (100:0) reinforced by using cotton fiber (a) 5%wt, 2 mm (b) 10%wt, 2 mm and (c) 10%wt, 5 mm

4.1.2.6 Effect of cotton fiber contents and length on crystal structure of the TPS from glutinous rice starch (0:100)

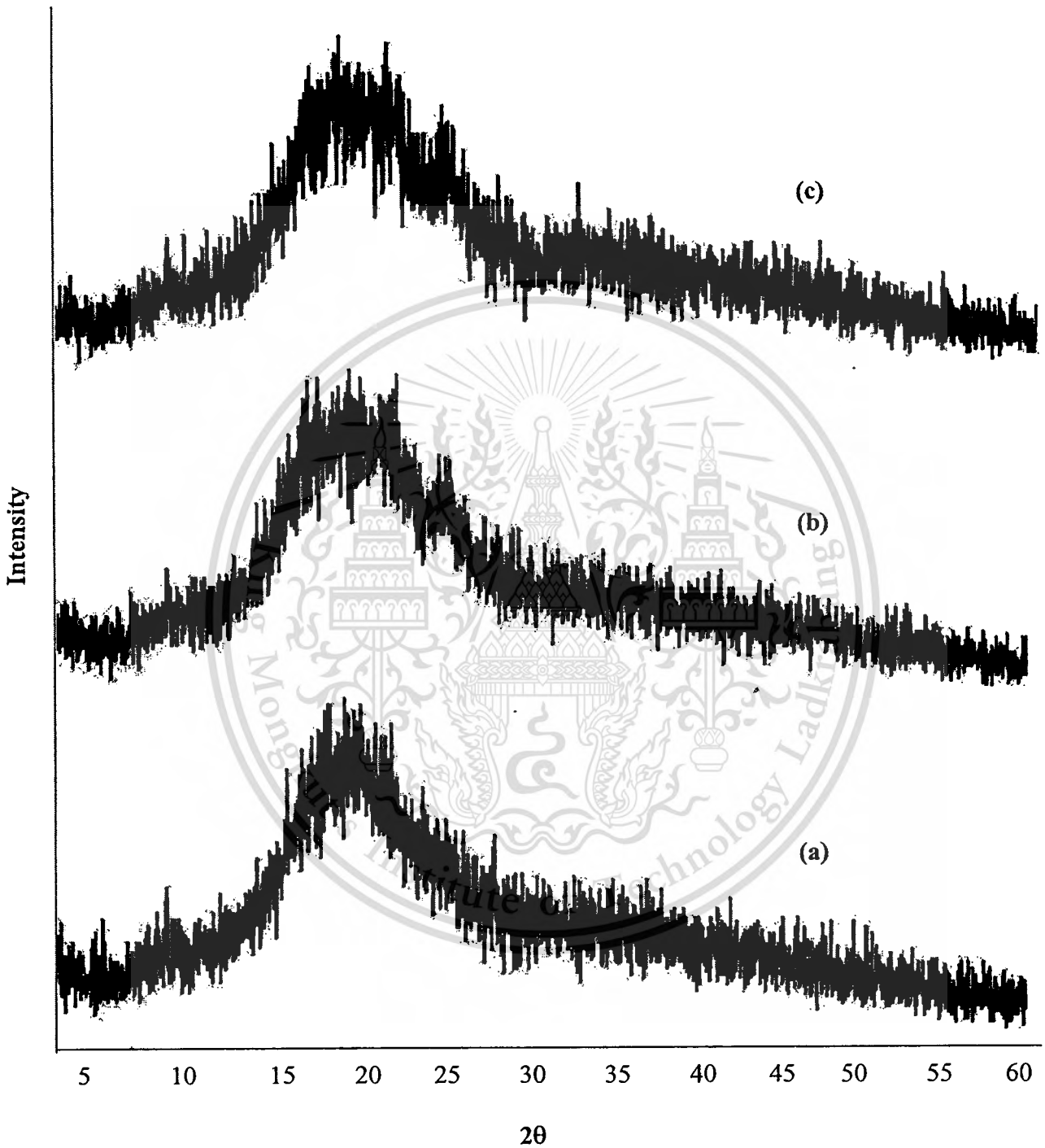


Figure 4.10 X-ray diffraction pattern of TPS from glutinous rice starch (100:0) reinforced by using cotton fiber (a) 5%wt, 2 mm (b) 10%wt, 2 mm and (c) 10%wt, 5 mm

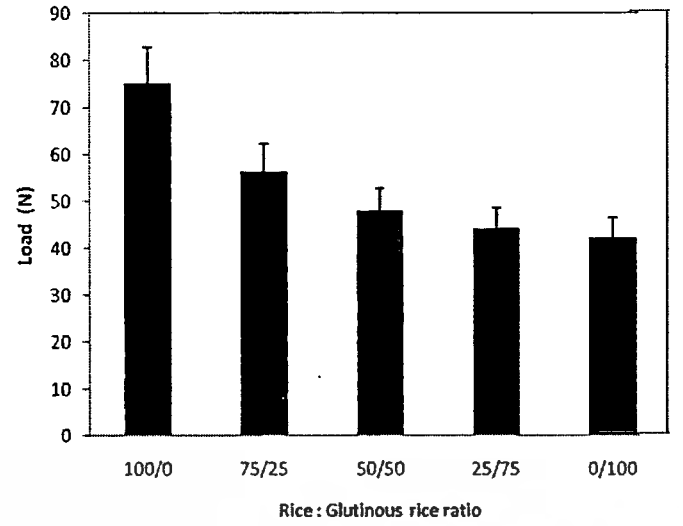
Figures 4.7 - 4.8 shows the X-ray diffraction of the TPS from rice and glutinous rice, reinforced by cotton fibers. The X-ray diffractograms of the TPS composites showed typical diffraction peaks of both TPS starch matrix and cotton fiber reinforcement. The TPS composites from rice starch (Figures 4.7 (d)) showed main peaks at 2θ, 12.95°, 17.3°, 19.82°, 22.34° and 25.68°; whereas, the TPS composites from glutinous rice starch (Figures 4.8 (d)) showed main peaks at 2θ, 20.22°, 22.98° and 25.82°.

The increase of cotton fiber contents in the TPS from rice and glutinous rice starches (Figures 4.9 – 4.10) caused the difference in the X-ray diffraction patterns. Higher content of cotton fibers showed more intense diffraction peaks for both TPS from rice and glutinous rice starches. No difference in the X-ray diffraction patterns could be observed by the effect of the cotton fiber lengths (Figures 4.9 – 4.10).

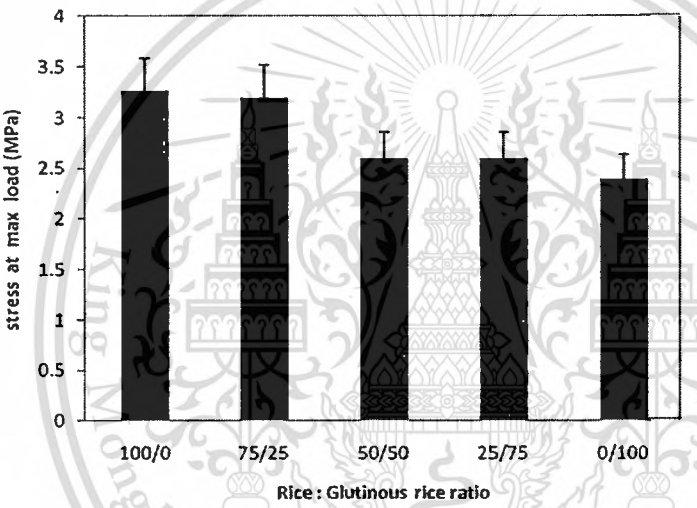
4.2 Mechanical properties

4.2.1 Effect of rice ratio (rice : glutinous rice ratio) on mechanical properties of TPS

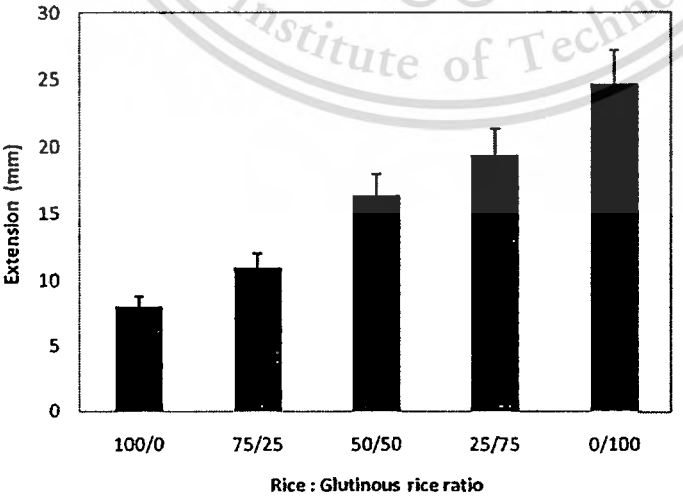
Figure 4.11 shows the mechanical properties of TPS by varying ratios of rice and glutinous rice starch i.e. 100:0, 75:25, 50:50, 25:75 and 0:100. It was found that load, stress at maximum load and Young's modulus decreased with the increased glutinous rice contents. On the other hands, elongation and %strain at maximum load increased with the increased glutinous rice contents. This is due to the different contents of amylose and amylopectin in rice and glutinous rice starch [2]. Generally, rice starch contain 21-23% amylose and 70-90% amylopectin, but glutinous rice starch contain 5-7% amylose and 95% amylopectin [2]. Glutinous rice starch contains higher contents of amylopectin, leading to flexibility and extendibility of TPS ; however, rice starch contains higher contents of amylose, leading to strength and stiffness.



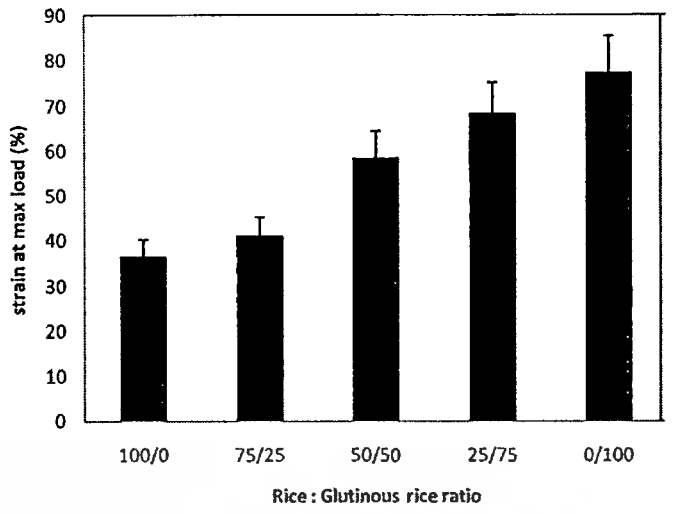
(a)



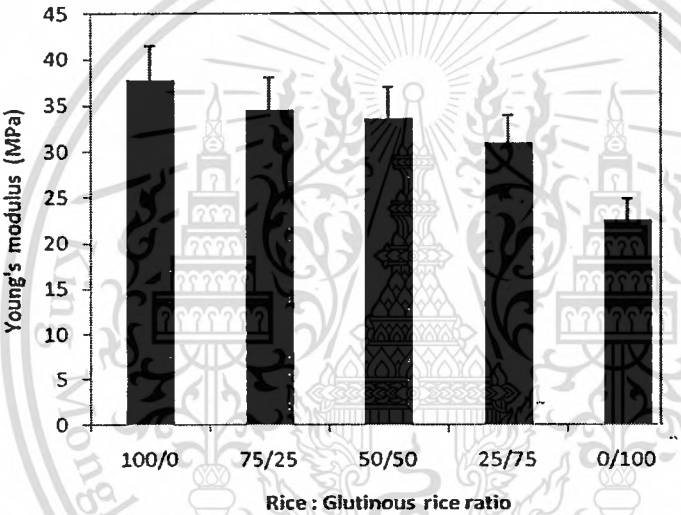
(b)



(c)



(d)



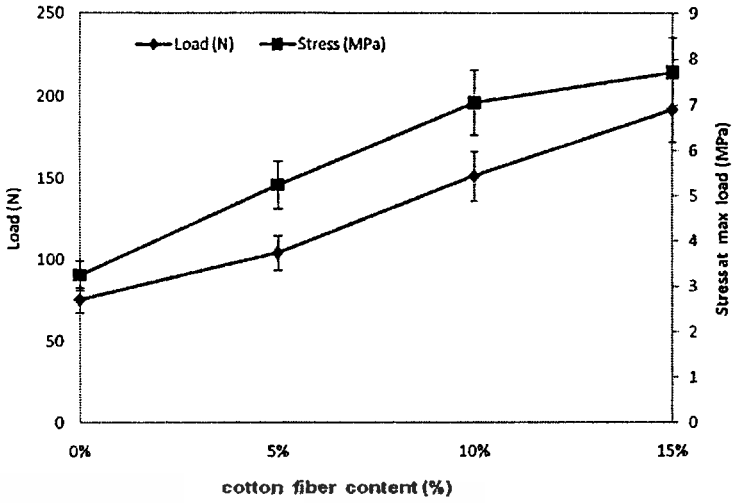
(e)

Figure 4.11 Mechanical properties of TPS with different ratio of rice and glutinous rice (a) maximum load (b) stress at maximum load (c) extension (d) strain at maximum load and (e) Young's modulus

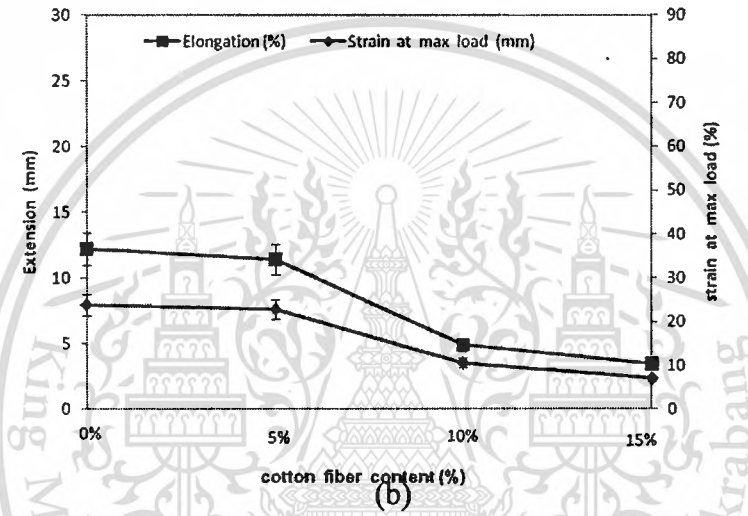
4.2.2 Effect of cotton fiber contents on mechanical properties of TPS

The addition of cotton fibers into TPS was expected to improve mechanical properties of TPS because of high aspect ratio of the fibers. Different percentages of fiber content, i.e. 0%wt, 5%wt, 10%wt and 15%wt were varied, corresponding to the aspect ratio of 1667:1 – 4167:1 (diameter= 12microns) cotton fiber. Mechanical properties of the TPS are presented in Figures 4.12 - 4.14 for different ratios of rice and glutinous rice of 100:0, 50:50 and 0:100, respectively. It was found that the maximum load and stress at maximum load increased as the fiber content increased. Young's modulus increased with the addition of the fibers in the same manner as maximum load and stress at maximum load. This is due to the reinforcement of cotton fibers [7]. Similar results was found in cassava starch reinforced by wheat bran film and potato starch reinforced by flax strands [17].

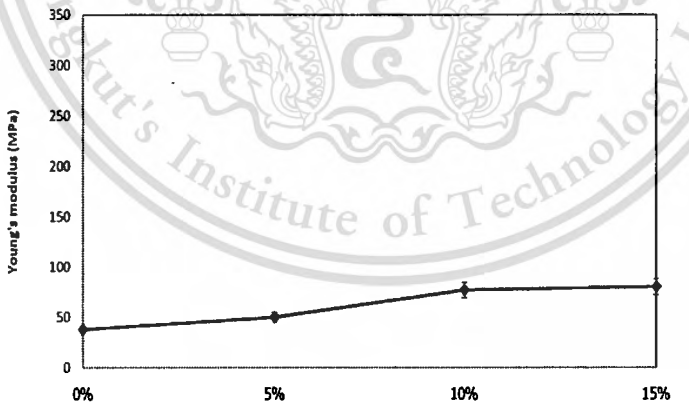
The opposite result was found in elongation testing as the extension and %strain at maximum load of the TPS decreased with increasing the fiber content. When the effect of rice : glutinous rice is considered, it is found that different ratios of the TPS with the addition of cotton fibers shows the same trends of the mechanical properties as presented in Figures 4.12 – 4.14. Moreover, the highest load, stress at maximum load and Young's modulus was obtained in the 100:0 at 10%wt of cotton fiber contents due to the stiffness of rice matrix . On the other hand, the highest extension and %strain at maximum load was obtained in 0:100 sample, as expected. This could be due to the flexibility of glutinous rice matrix.



(a)

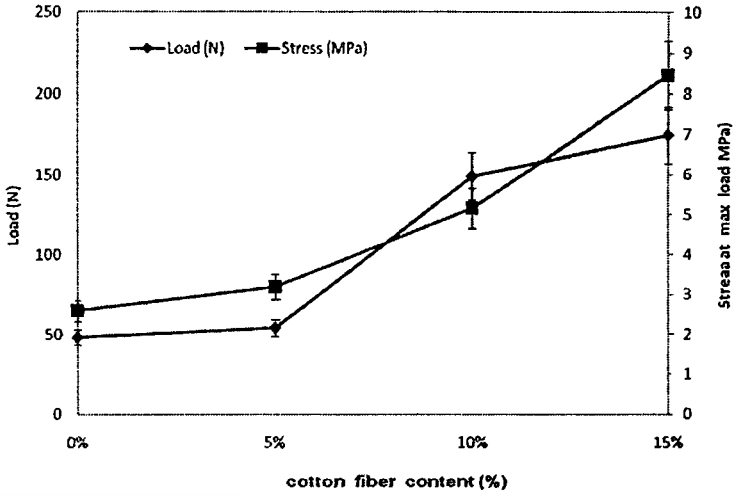


(b)

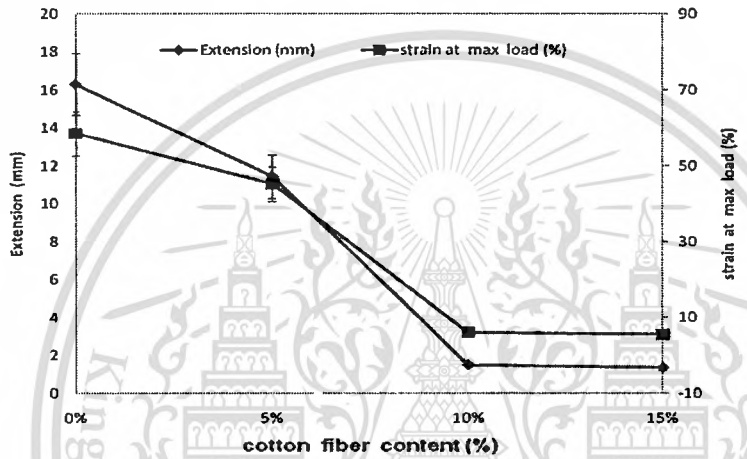


(c)

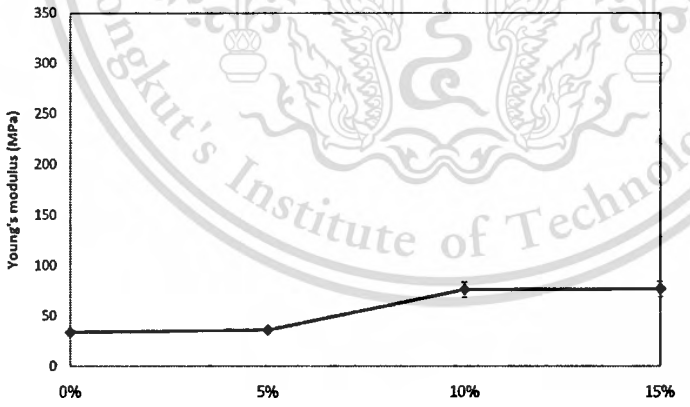
Figure 4.12 Effect of cotton fiber content on mechanical properties of the TPS at the ratio 100:0 (rice : glutinous rice) using 2 mm length of cotton fiber (a) maximum load and stress at maximum load (b) extension and strain at maximum load and (c) Young's modulus



(a)

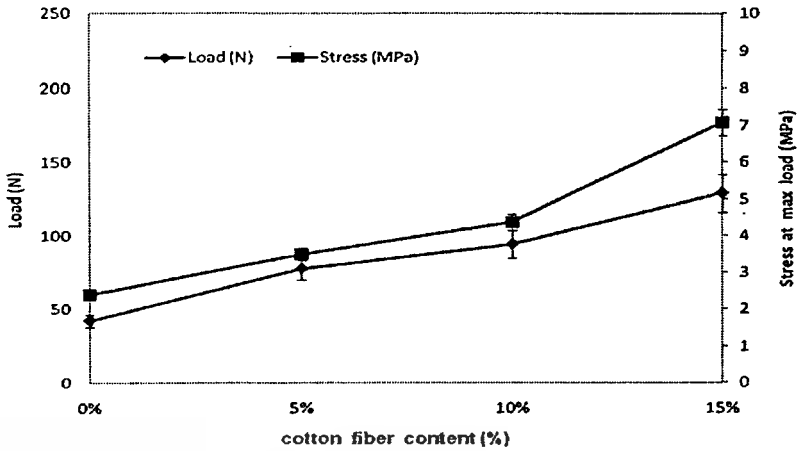


(b)

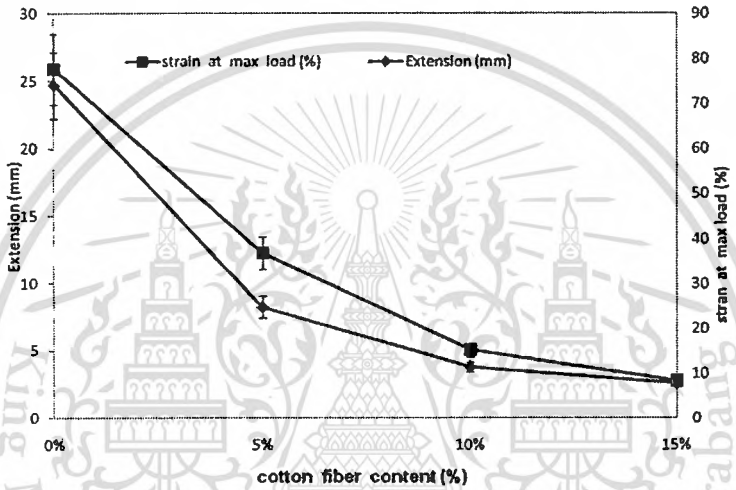


(c)

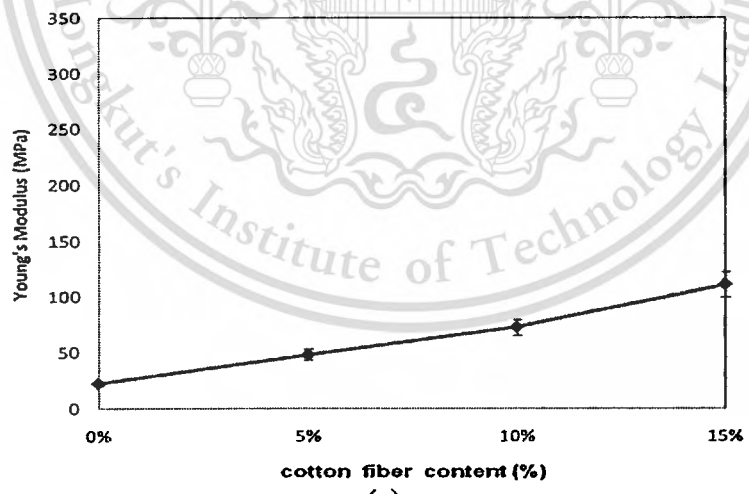
Figure 4.13 Effect of cotton fiber content on mechanical properties of the TPS at the ratio 50:50 (rice : glutinous rice) using 2 mm length of cotton fiber (a) maximum load and stress at maximum load (b) extension and strain at maximum load and (c) Young's modulus



(a)



(b)



(c)

Figure 4.14 Effect of cotton fiber content on mechanical properties of the TPS at the ratio 0:100 (rice : glutinous rice) using 2 mm length of cotton fiber (a) maximum load and stress at maximum load (b) extension and strain at maximum load and (c) Young's modulus

Figures 4.12 – 4.14 show the mechanical properties of TPS by using a fixed length of 5 mm for different ratios of rice and glutinous rice of 100:0, 50:50 and 0:100, respectively. Different percentages of fiber content were 0%wt, 5%wt, 10%wt and 15%wt. It was found that the maximum load, stress at maximum load and Young's modulus increased as the fiber content increased, which was due to the reinforcement of the cotton fibers, as found with the addition of 2 mm length cotton fibers (Figures 4.12 - 4.14). On the other hand, extension and %strain at maximum load decreased with increasing fiber content.

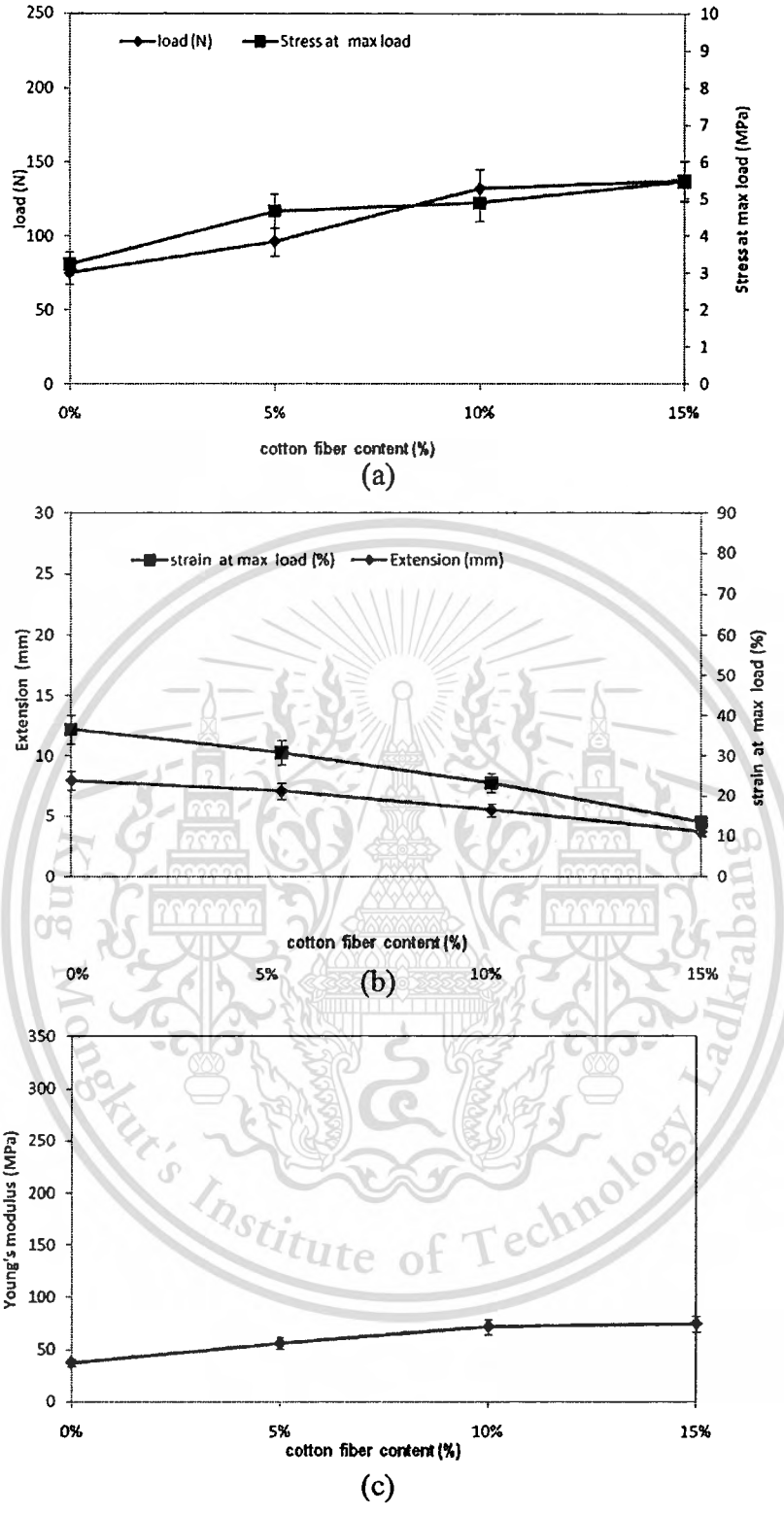
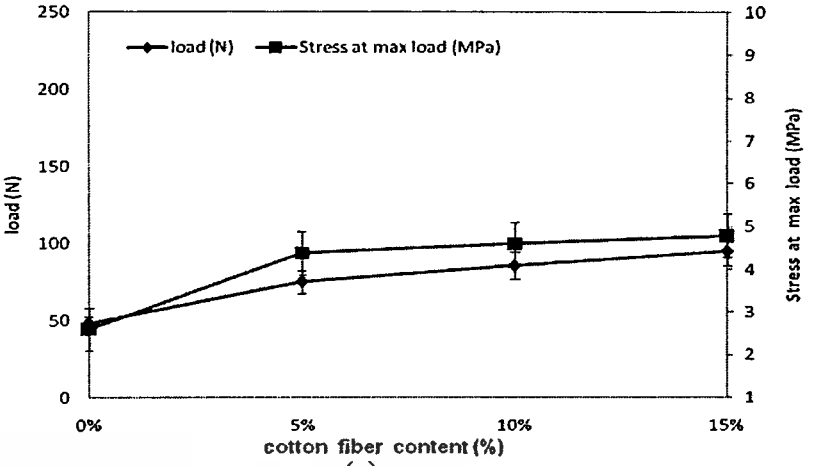
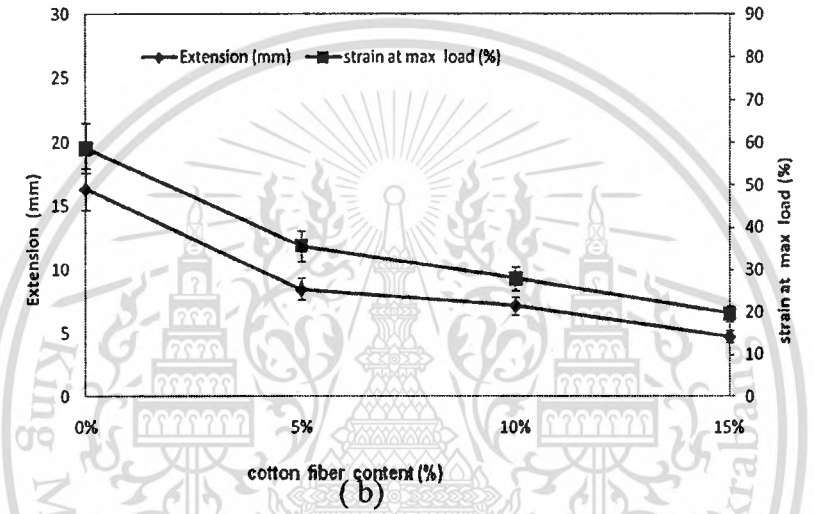


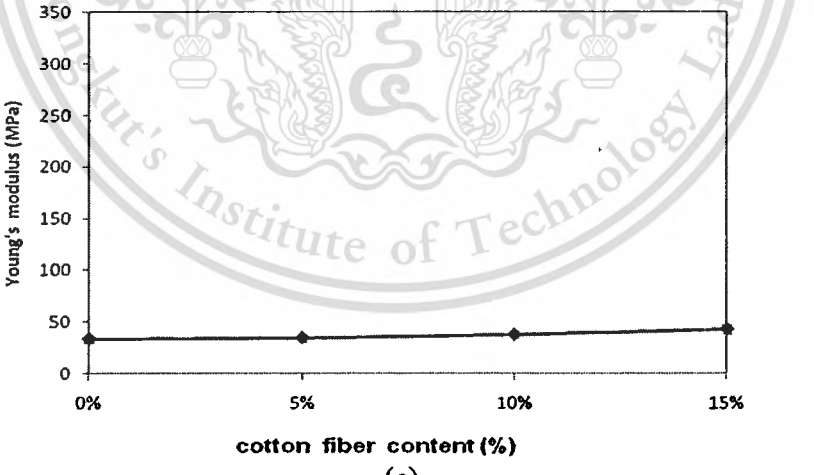
Figure 4.15 Effect of cotton fiber content on mechanical properties of the TPS at the ratio 100:0 (rice : glutinous rice) using 5 mm length of cotton fiber (a) maximum load and stress at maximum load (b) extension and strain at maximum load and (c) Young's modulus



(a)



(b)



(c)

Figure 4.16 Effect of cotton fiber content on mechanical properties of the TPS at the ratio 50:50 (rice : glutinous rice) using 5 mm length of cotton fiber (a) maximum load and stress at maximum load (b) extension and strain at maximum load and (c) Young's modulus

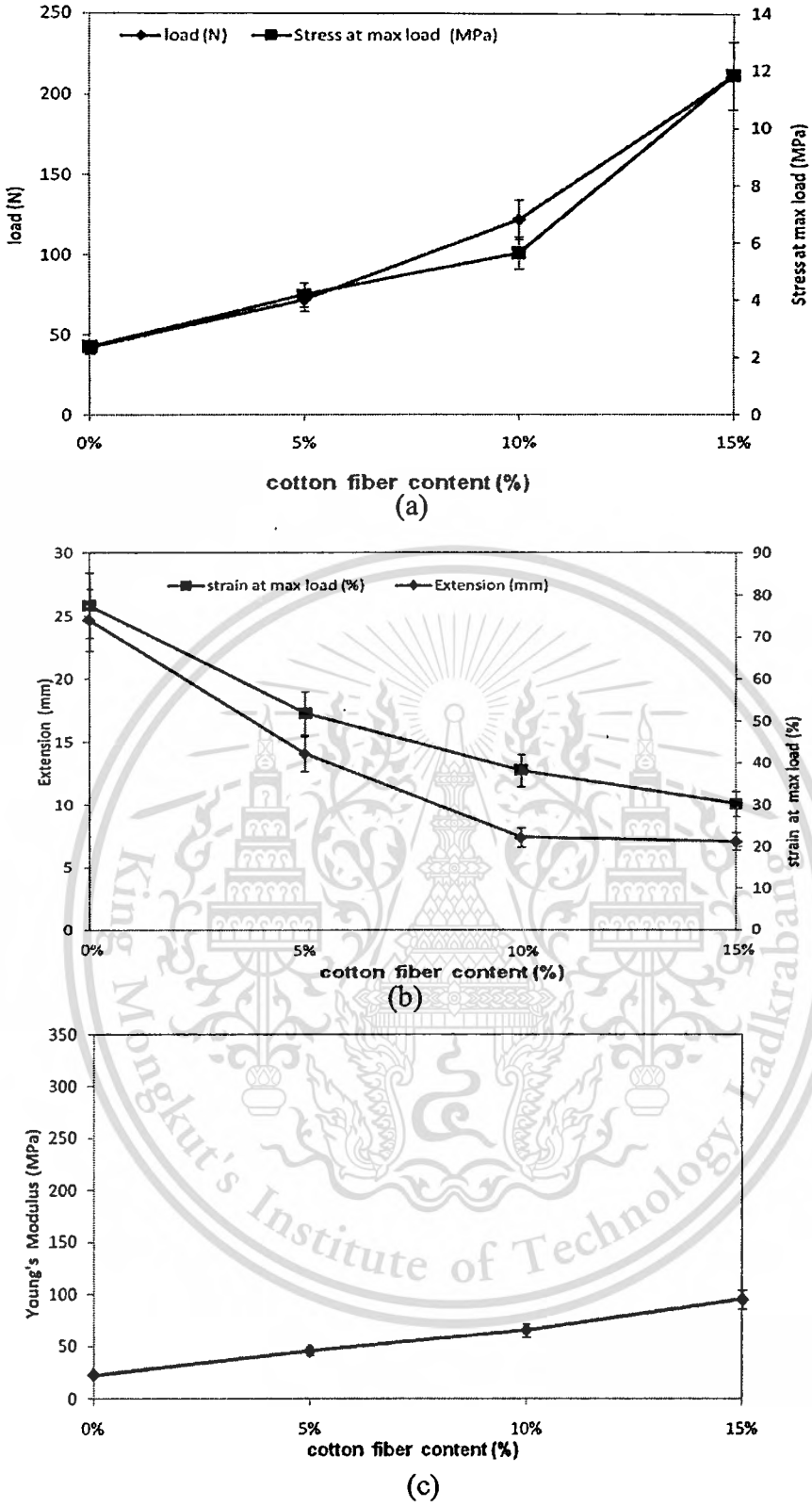
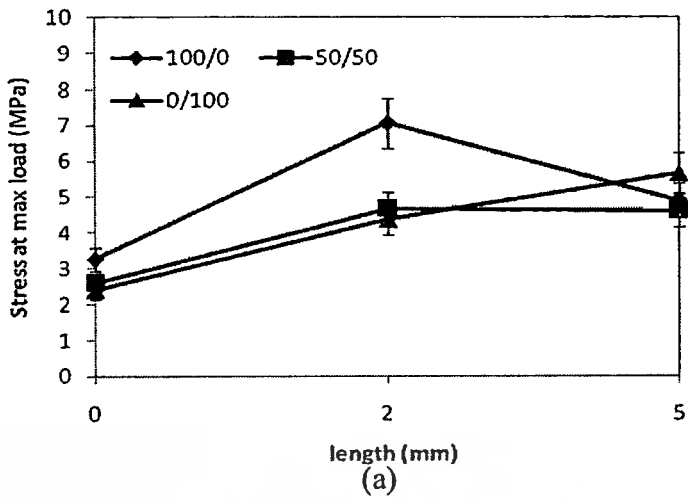


Figure 4.17 Effect of cotton fiber content on mechanical properties of the TPS at the ratio 0:100 (rice : glutinous rice) using 5 mm length of cotton fiber (a) maximum load and stress at maximum load (b) extension and strain at maximum load and (c) Young's modulus

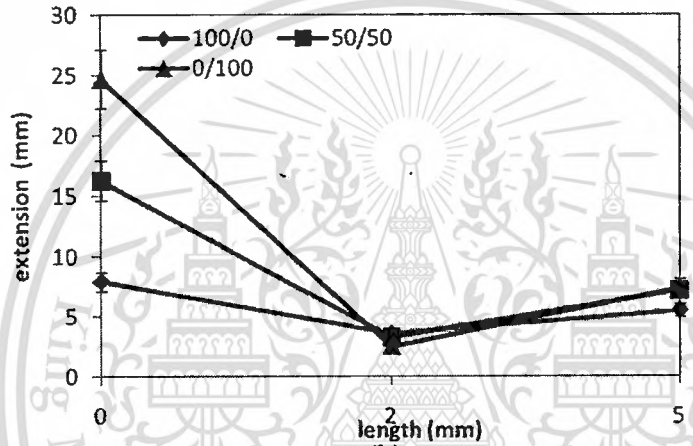
4.2.3 Effect of cotton fiber lengths on mechanical properties of TPS

The effect of fiber lengths i.e. 2 mm and 5 mm on mechanical properties is shown in Figure 4.18 It was found that the TPS with 2 mm cotton fiber gave higher maximum load, stress at maximum load and Young's modulus than those of 5 mm (Figure 4.18 (a) and 4.18 (c)). On the other hand, the extension and %strain at maximum load of TPS with 2 mm cotton fiber were lower than those 5 mm as shown in Figure 4.18 (b). This could be explained by the fiber dispersion in the TPS matrix. The use of 2 mm fiber could be well dispersed into the TPS matrix due to the higher surface area of cotton fibers as observed from SEM micrographs (Figures 4.21-4.23). Therefore, the mechanical overall properties of TPS with 2 mm length cotton fiber were higher than those of 5 mm.

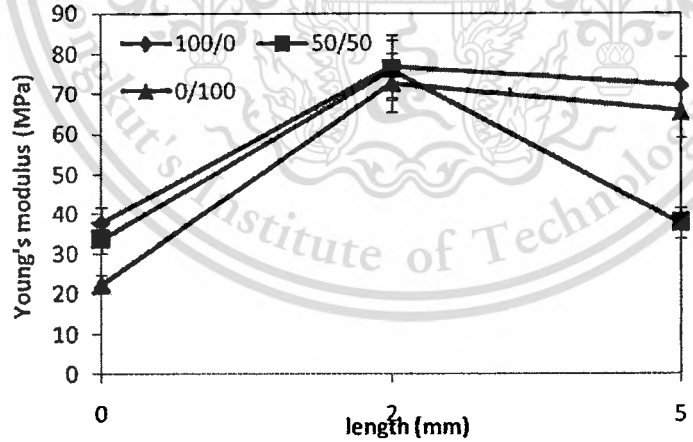
The effect of rice ratios on mechanical properties of TPS reinforced by using cotton fiber 2 mm and 5 mm length at 10 %wt cotton fiber is also shown in Figure 4.19 From this study the TPS from rice starch (100:0) showed the maximum overall mechanical properties.



(a)



(b)

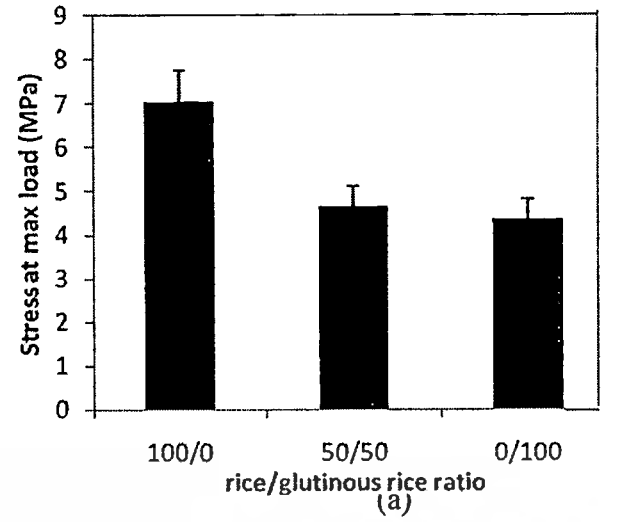


(c)

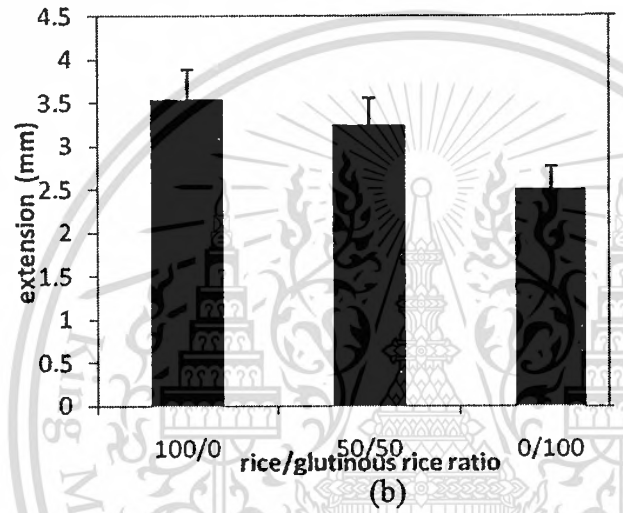
Figure 4.18 Effect of cotton fiber length on mechanical properties of TPS at different ratios of 100:0, 50:50 and 0:100 (rice : glutinous rice) (a) maximum load and stress at maximum load (b) extension and strain at maximum load and (c) Young's modulus

4.2.4 Comparison between different rice ratios on mechanical properties of TPS

From sections 4.1.2 - 4.1.4, it was found that the best mechanical properties of TPS were obtained by using 10 %wt and 2 mm cotton fiber. By comparison between different ratio of rice and glutinous rice i.e. 100:0, 50:50 and 0:100 (Figure 4.19) the result shows that the maximum stress at maximum load and Young's modulus was observed in 100:0 rice : glutinous rice ratio. From this study, the best mechanical properties were obtained in 100:0 reinforced by 2mm length and 10%wt cotton fibers as shown in Figure 4.19.



(a)



(b)

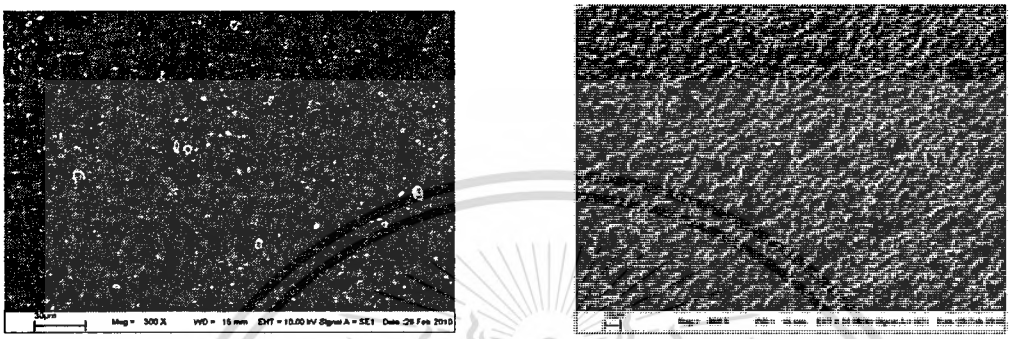
(c)

Figure 4.19 Effect of rice ratio (rice : glutinous rice) on mechanical properties of TPS reinforced by 2 mm length and 10%wt cotton fiber. (a) stress at maximum load (b) strain at maximum load and (c) Young's modulus

4.3 Morphological properties

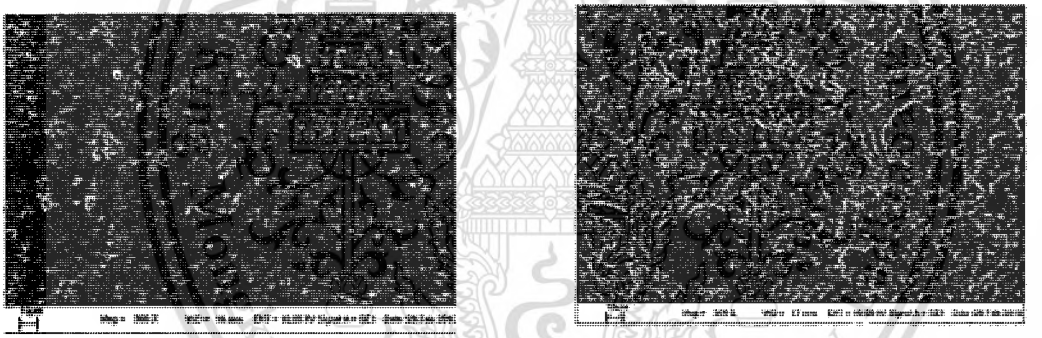
4.3.1 Effect of rice ratio (rice : glutinous rice ratio) on morphological property of TPS

- Rice starch (100:0)



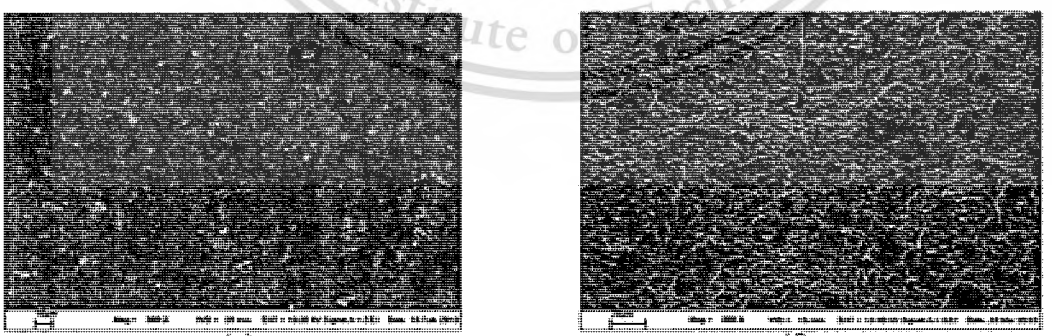
(a) (b)

- Blended rice starch (50:50)



(c) (d)

- Glutinous rice starch (0:100)



(e) (f)

Figure 4.20 SEM micrographs at 300X magnification of (a),(b) rice starch (100:0) (c), (d) blended rice starch (50:50) (e), (f) glutinous rice starch (0:100) ((a), (c), (e) – surface view and (b), (d), (f) – fractured view)

Morphological structure of polymer is a very important characteristic because it determines property of polymer. SEM micrographs of the surface view and fractured view of fragile test specimens of TPS are shown in Figures 4.21 - 4.22. Rough surface of rice starch could be observed as presented in Figures 4.21 (a) - 4.21 (b). For the surface of the TPS from the blended rice starch (50:50) was observed as shown in Figures 4.21 (c) - 4.21 (d). It was found that, the surface of blended rice starch contained smooth and rough surfaces. This is due to the part of glutinous rice starch. Figures 4.21 (e) and 4.23 (f) were showed both smooth and rough surfaces of the TPS from glutinous rice starch.

4.3.2 Effect of cotton fiber on morphology of rice starch (100:0)

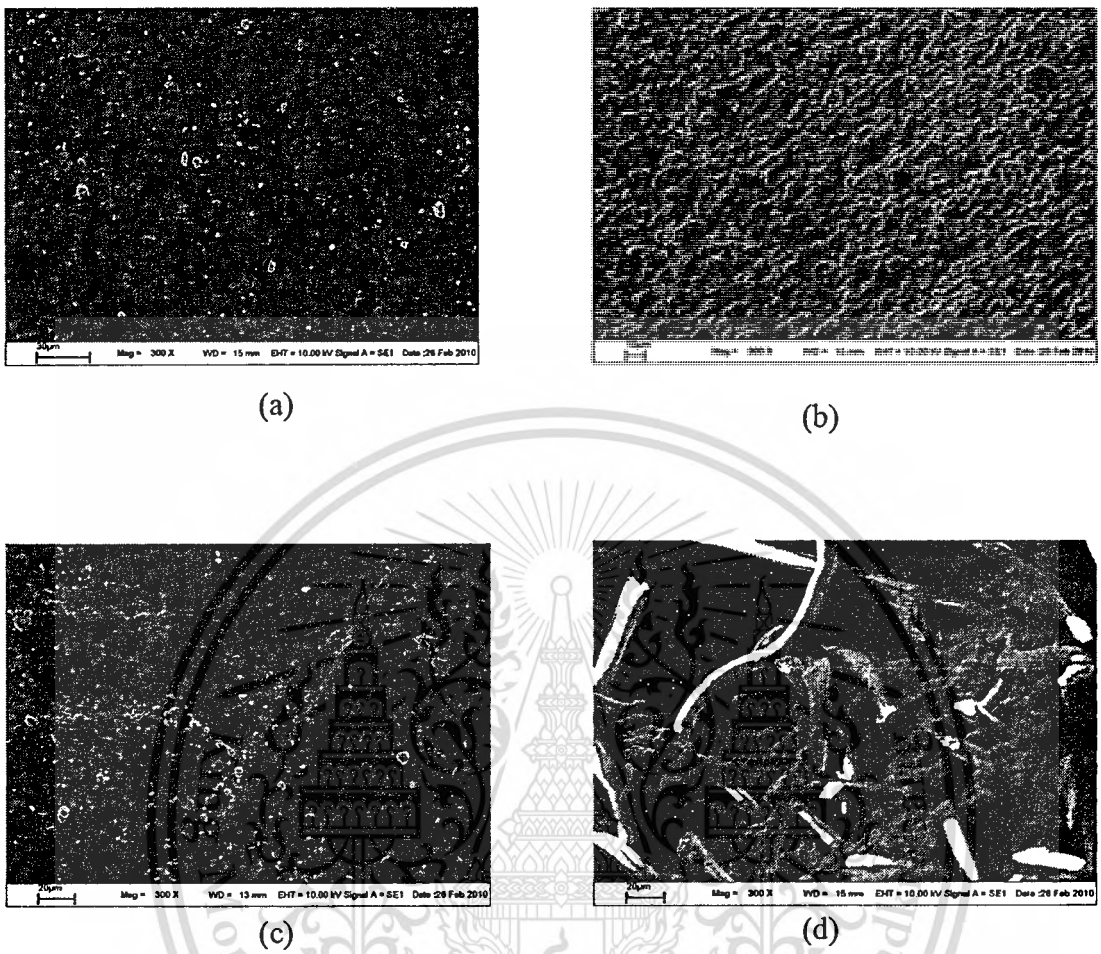
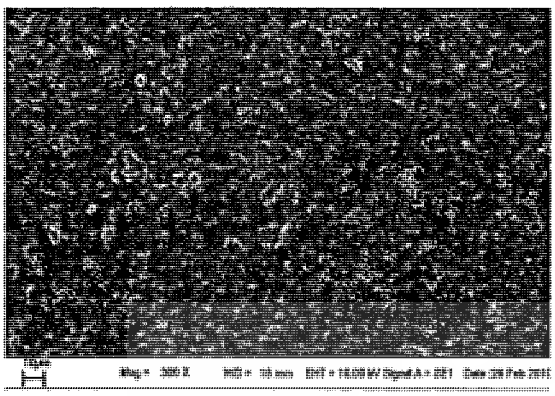
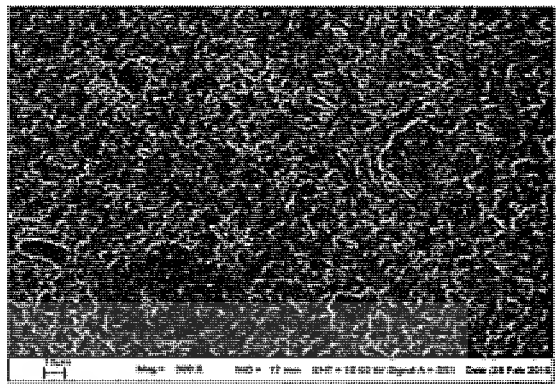


Figure 4.21 SEM micrographs at 300X magnification of (a) rice starch (100:0) at surface (b) rice starch (100:0) at fractured surface (c) rice starch (100:0) reinforced by using cotton fiber 10%wt, 2 mm at surface and (d) rice starch (100:0) reinforced by using cotton fiber 10%wt, 2 mm at fractured surface

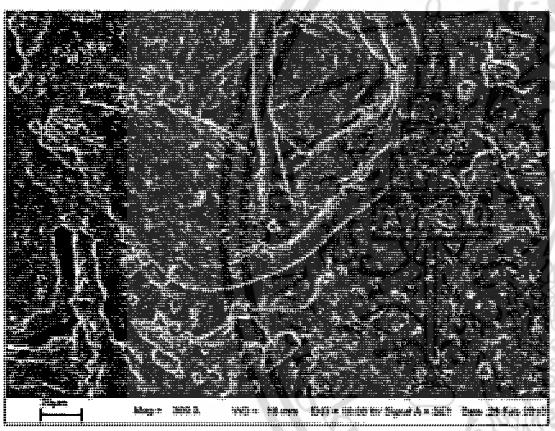
4.3.3 Effect of cotton fiber on morphology of blended rice starch (50:50)



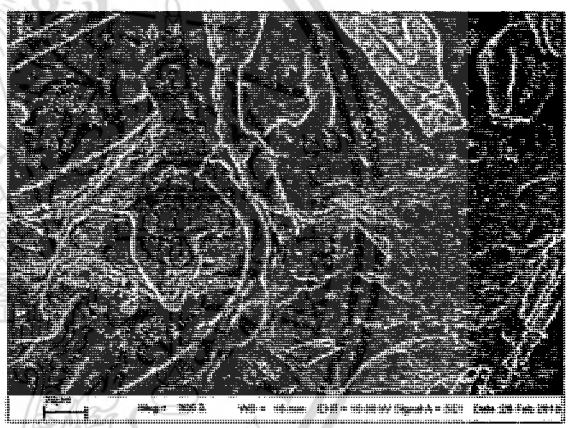
(a)



(b)



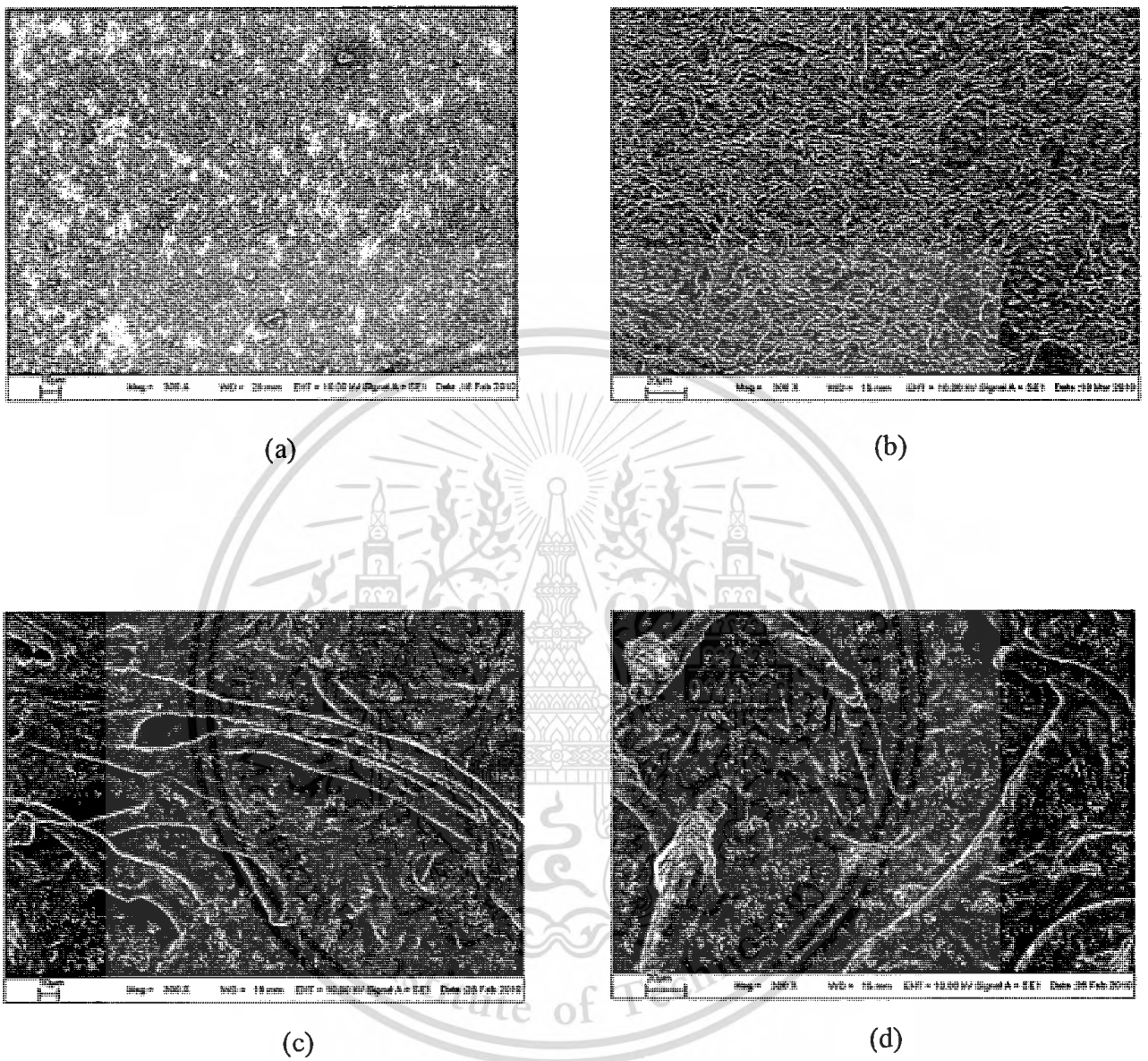
(c)



(d)

Figure 4.22 SEM micrographs at 300X magnification of (a) blended rice starch (50:50) at surface (b) blended rice starch (50:50) at fractured surface (c) blended rice starch (50:50) reinforced by using cotton fiber 10%wt, 2 mm at surface and (d) blended rice starch (50:50) reinforced by using cotton fiber 10%wt, 2 mm at fractured surface

4.3.4 Effect of cotton fiber on morphology of glutinous rice starch (0:100)



(a) (b)

(c) (d)

Figure 4.23 SEM micrographs at 300X magnification of (a) glutinous rice starch (0:100) at surface (b) glutinous rice starch (0:100) at fractured surface (c) glutinous rice starch (0:100) reinforced by using cotton fiber 10%wt, 2 mm at surfaces and (d) glutinous rice starch (0:100) reinforced by using cotton fiber 10%wt, 2 mm at fractured surface

SEM micrographs of surface and fractured views of the TPS from rice starch and TPS reinforced by using cotton fiber (10%wt, 2 mm) are shown in Figures 4.21-4.23. The SEM micrographs showed the long cotton fiber embedded into the rice starch matrix and the fiber surface was wetted by rice starch matrix (Figures 4.21(c) – (d)), indicating of the phase compatibility ,which could be observed on the increasing of mechanical properties of TPS reinforced by using cotton fiber (Figures 4.12-4.17). Similar result was found in the TPS from blended rice starch (50:50) and glutinous rice starch (Figures 4.22 and 4.23, respectively). It should be noted that more voids could be observed in the TPS from the blended and glutinous rice starches.

4.3.5 Effect of fiber content on morphology of rice starch (100:0)

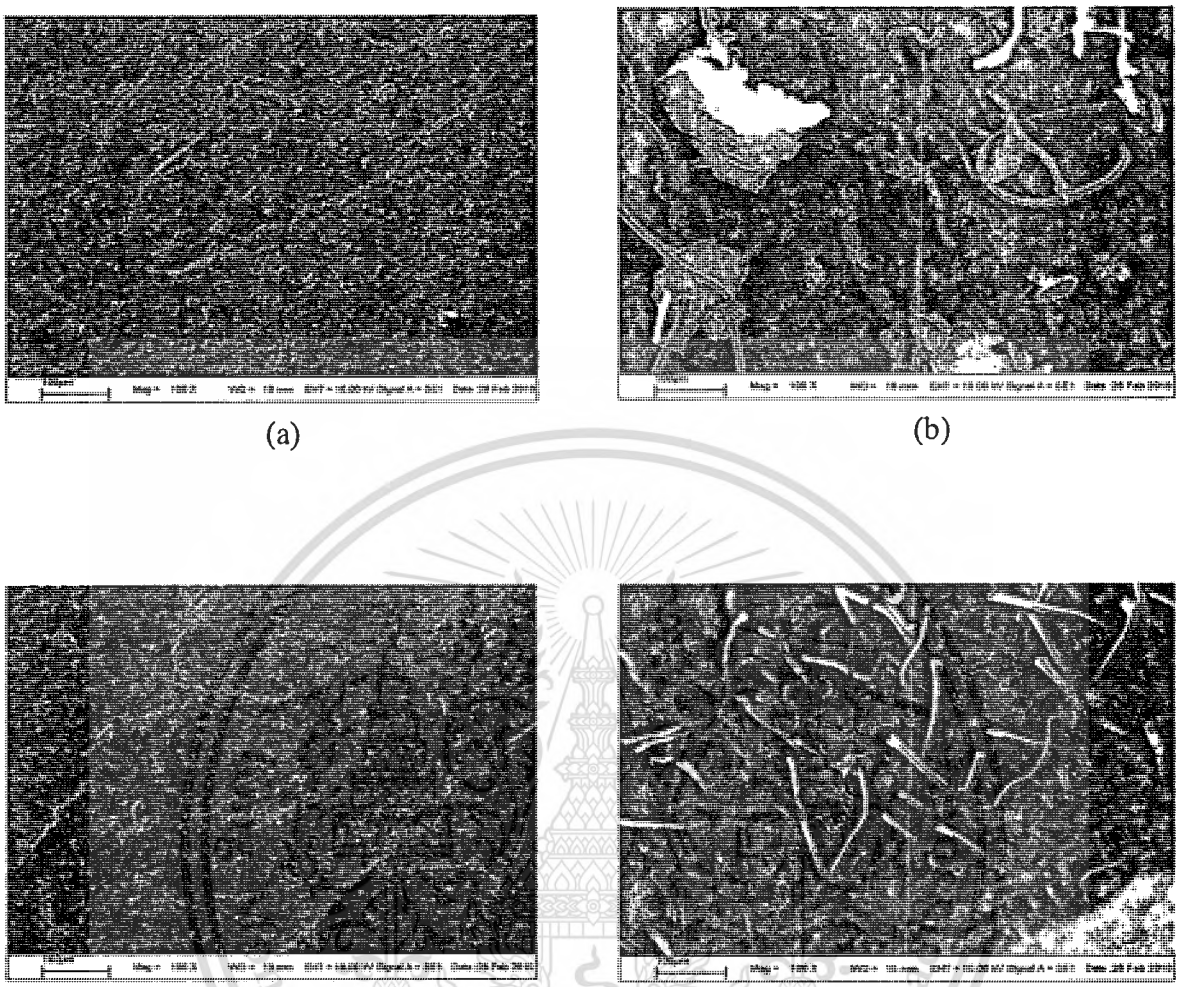
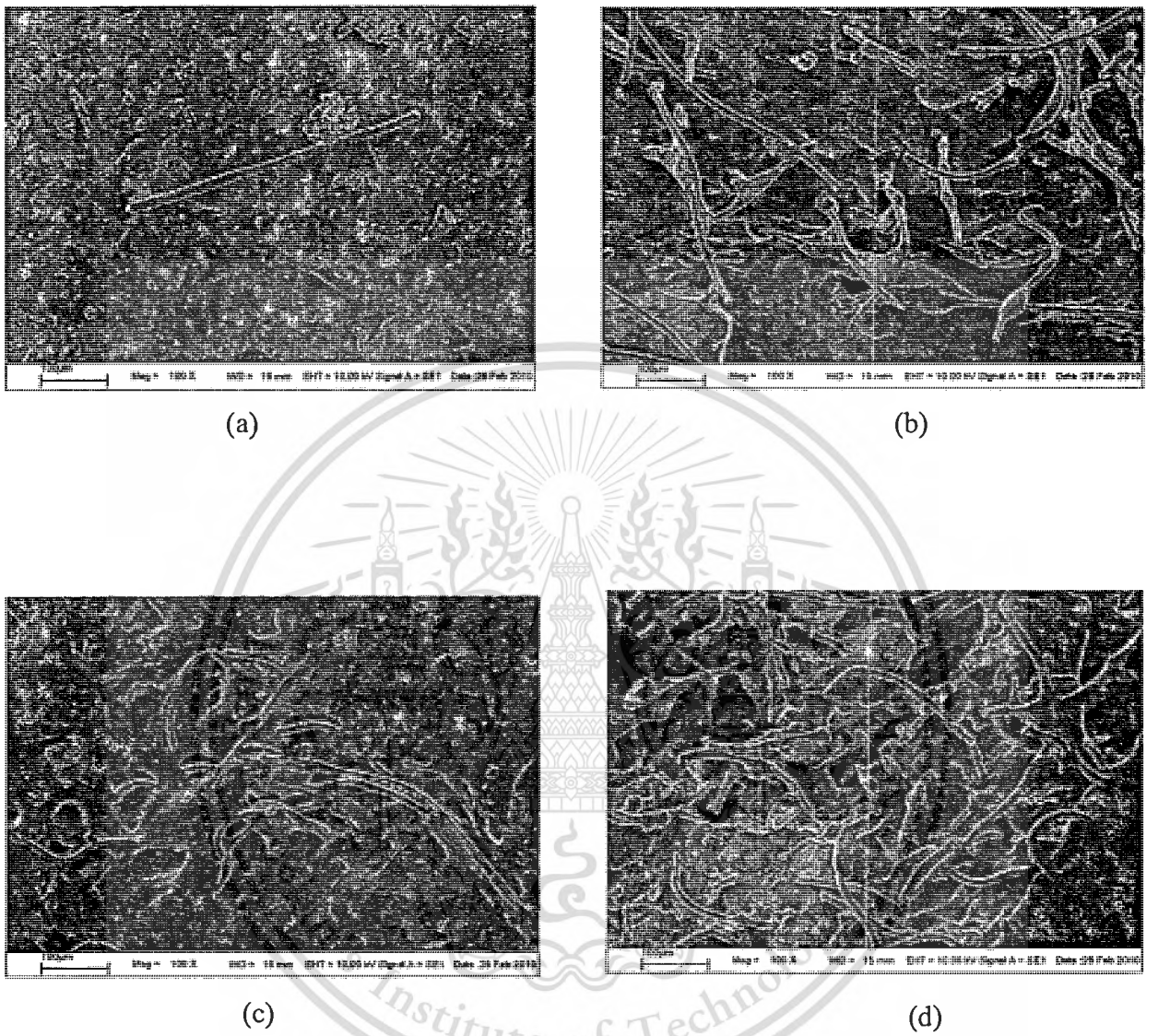


Figure 4.24 SEM micrographs at 100X magnification of (a) rice starch (100:0) reinforced by using cotton fiber 5%wt, 2 mm at surface (b) rice starch (100:0) reinforced by using cotton fiber 5%wt, 2 mm at fractured surface (c) rice starch (100:0) reinforced by using cotton fiber 10%wt, 2 mm at surface and (d) rice starch (100:0) reinforced by using cotton fiber 10%wt, 2 mm at fractured surface

4.3.6 Effect of fiber content on morphology of glutinous rice starch (0:100)

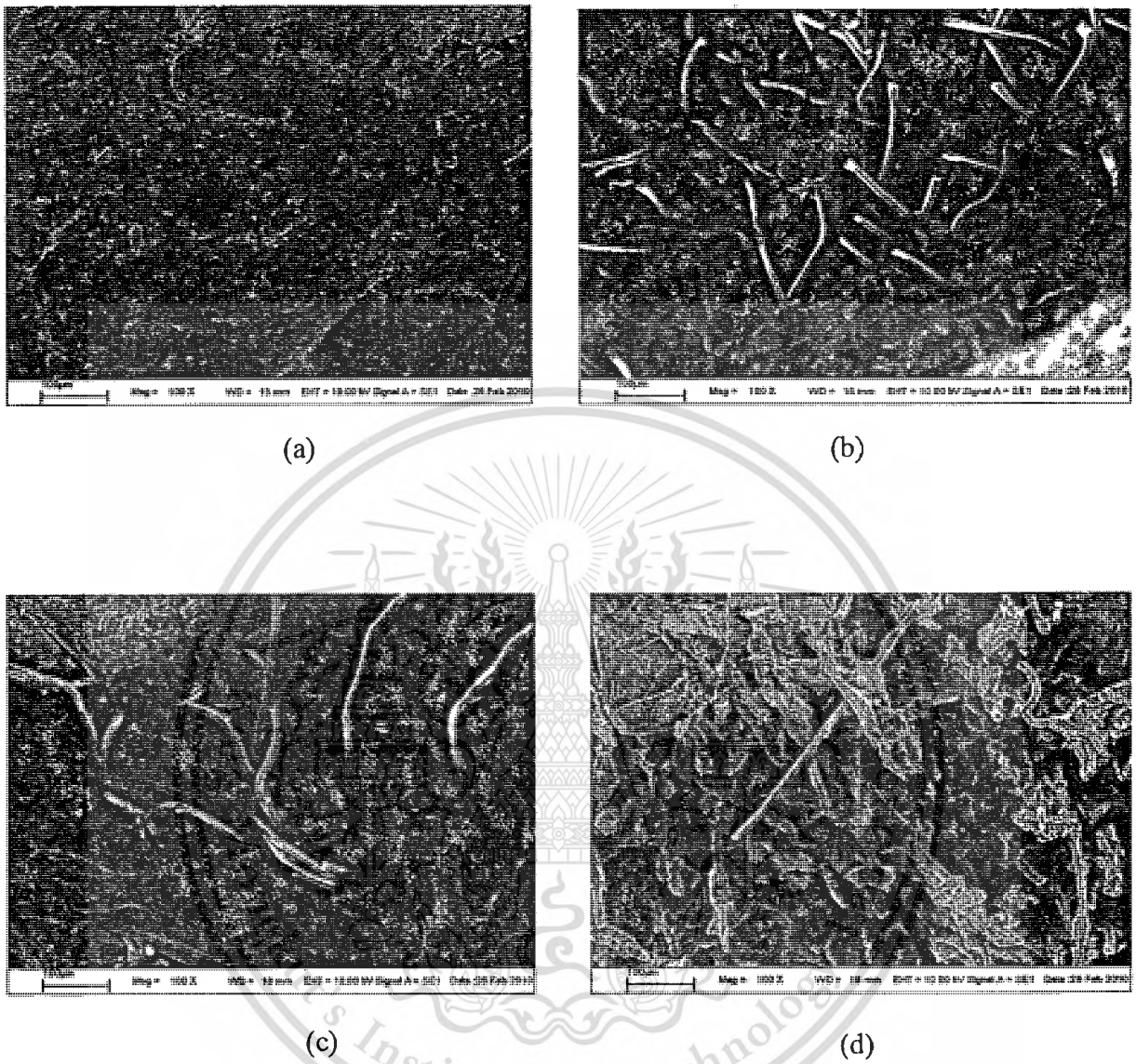


(a) (b)

(c) (d)

Figure 4.25 SEM micrographs at 100X magnification of (a) glutinous rice starch (0:100) reinforced by using cotton fiber 5%wt, 2 mm at surface (b) glutinous rice starch (0:100) reinforced by using cotton fiber 5%wt, 2 mm at fractured surface (c) glutinous rice starch (0:100) reinforced by using cotton fiber 10%wt, 2 mm at surface and (d) glutinous rice starch (0:100) reinforced by using cotton fiber 10%wt, 2 mm at fractured surface

4.3.7 Effect of fiber length on morphology of rice starch (100:0)

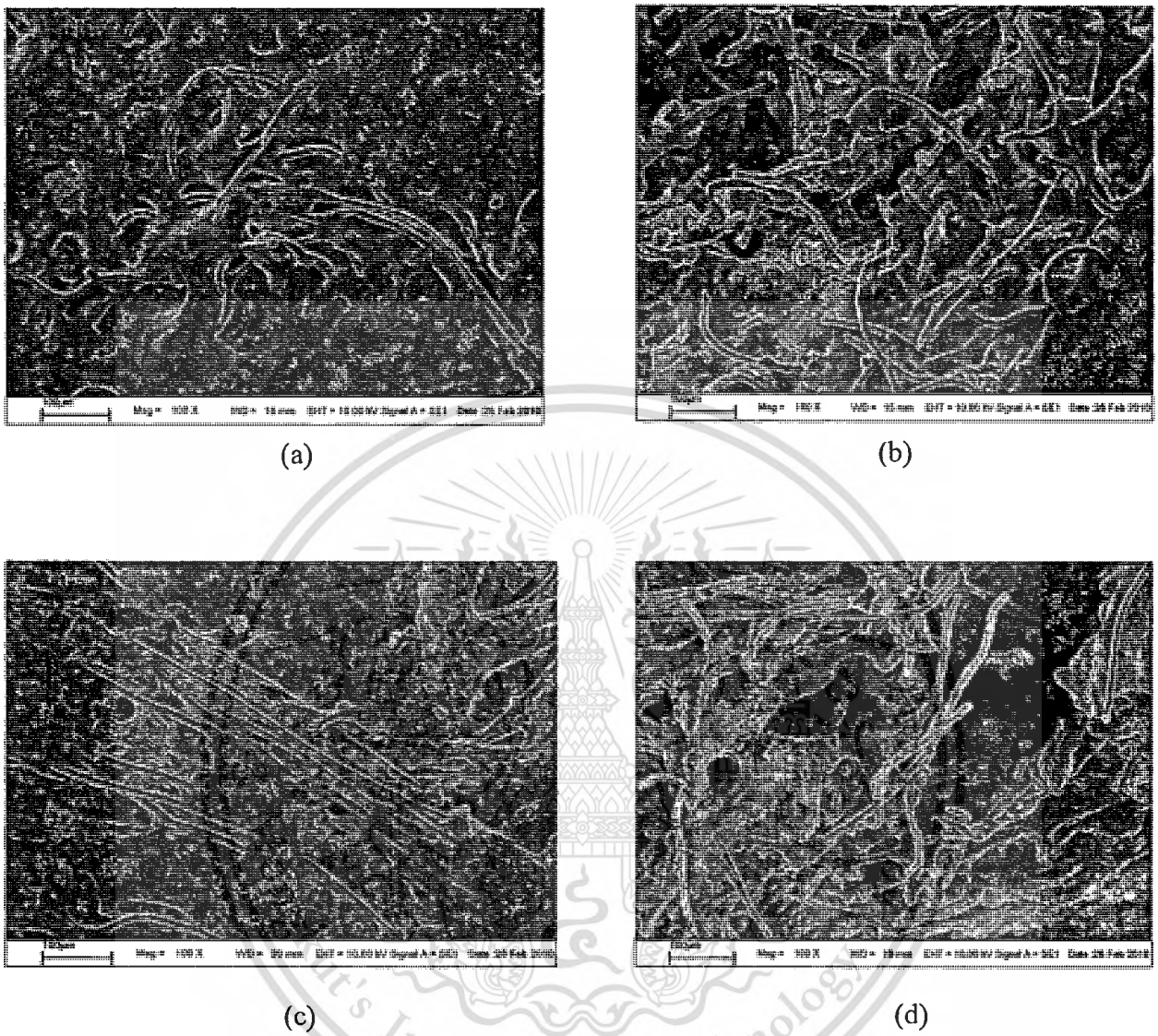


(a) (b)

(c) (d)

Figure 4.26 SEM micrograph at 100X magnification of (a) rice starch (100:0) reinforced by using cotton fiber 10%wt, 2 mm at surface (b) rice starch (100:0) reinforced by using cotton fiber 10%wt, 2 mm at fractured surface (c) rice starch (100:0) reinforced by using cotton fiber 10%wt, 5 mm at surface and (d) rice starch (100:0) reinforced by using cotton fiber 10%wt, 5 mm at fractured surface

4.3.8 Effect of fiber length on morphology of glutinous rice starch (0:100)



(a) (b)

(c) (d)

Figure 4.27 SEM micrographs at 100X magnification of (a) glutinous rice starch (0:100) reinforced by using cotton fiber 10%wt, 2 mm at surface (b) glutinous rice starch (0:100) reinforced by using cotton fiber 10%wt, 2 mm at fractured surface (c) glutinous rice starch (0:100) reinforced by using cotton fiber 10%wt, 5 mm at surface and (d) glutinous rice starch (0:100) reinforced by using cotton fiber 10%wt, 5 mm at fractured surface

SEM micrographs of surface and fractured surfaces of the TPS from rice starch and TPS reinforced by using different cotton fiber content (5%wt 2 mm and 10%wt 2mm) are shown in Figures 4.24 – 4.25. It can be seen that the cotton fibers were embedded and wetted by the TPS matrix from both rice starch and glutinous rice starch. More void can be observed in the TPS/cotton fiber from glutinous rice starch.

The effect of fiber lengths on morphology of TPS was presented in Figures 4.26 - 4.27. It was found that the TPS from rice starch showed long fibers embedded into and floated on the TPS matrix; but, the TPS from glutinous rice starch showed long fibers embedded in to the TPS matrix. The use of 2 mm length leaded to better fiber distribution in the TPS from both rice and glutinous rice starches. Therefore, the mechanical overall properties of the TPS with 2 mm length cotton fiber were higher than those of 5 mm (Figure 4.18).

4.4 Water absorption

Water absorption of different TPS samples with unreinforced and reinforced cotton fibers were carried out at 30±2 °C and 50% RH in a close container. Weight increase expressed as the percentage of water absorption is shown in Figure 4.27.

Water absorption of different TPS was examined and shown in Figure 4.27. It can be seen that the TPS samples from rice starch, blended rice starch and glutinous rice showed the increase of water absorption at the first stage, but the quickest water absorption was found in the TPS from glutinous rice starch. After that, the percentage water absorption tend to increase slowly and reached its maximum within 7 days, for the TPS from rice starch, 5 days for the TPS from blended starch and 4 days for the TPS from glutinous rice starch.

The addition of cotton fiber into the TPS matrix caused the decrease of water absorption for all of the TPS samples, as shown in Figures 4.27 (b)-(c). This result can be attributed to the establishment of hydrogen bonding between the fibers and the hydroxyl function of TPS. Thus, the interaction at the interface level avoided the presence of void between both components which decreasing the capacity of the entrance of water inside the material. The higher content of cotton fibers also leaded to lower water absorption of TPS. The lowest water absorption was obtained from the TPS from rice starch with addition of 10%wt. In addition, the TPS-reinforced from rice starch samples have better phase compatibility than that of the TPS-reinforced from blend starch and glutinous rice starch (Figures 4.21-4.23), leading to lower an entrance of water into the materials at void regions. Beside, length of cotton fiber did not show the significant effect on the water absorption of the TPS samples.

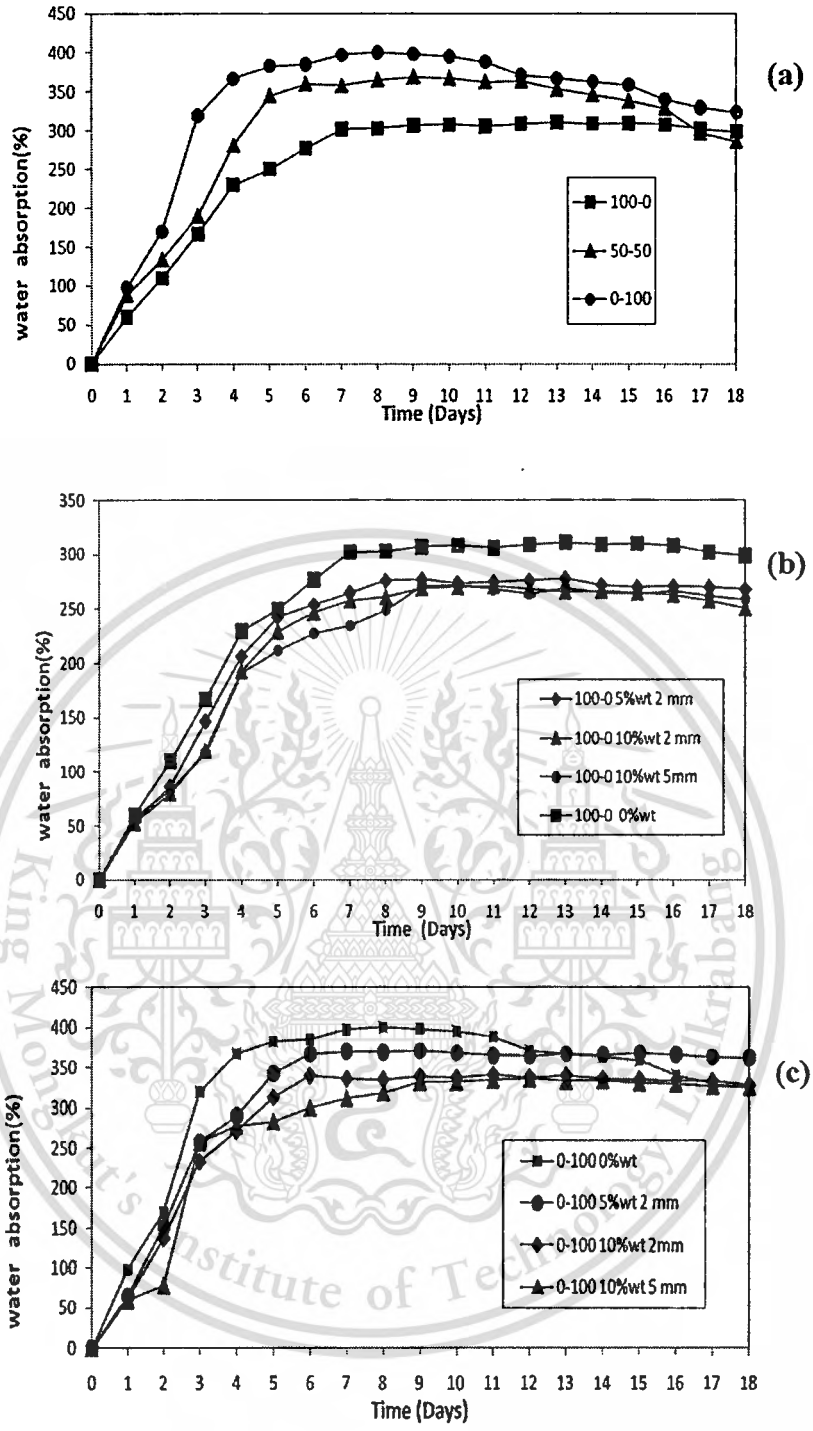


Figure 4.28 Water absorption behavior of (a) TPS unreinforced, (b) TPS reinforced cotton fiber from rice starch (100:0) and (c) TPS reinforced cotton fiber from glutinous rice starch.

4.5 Thermal property

Thermogravimetric analysis was used to study thermal properties of TPS with and without cotton fibers (Figure 4.29 and Table 4.1). The decomposition temperatures of the TPS-unreinforced i.e. 100:0, 50:50 and 0:100 were characterized by two steps. The first step was attributed to the evaporation of glycerol occurs at the ranged of 146-169 °C. The second step, corresponded to starch degradation, started at about 293-296 °C. The TPS-reinforced samples showed the additional decomposition peak of cotton fiber in the range of 397-407 °C as the third step.

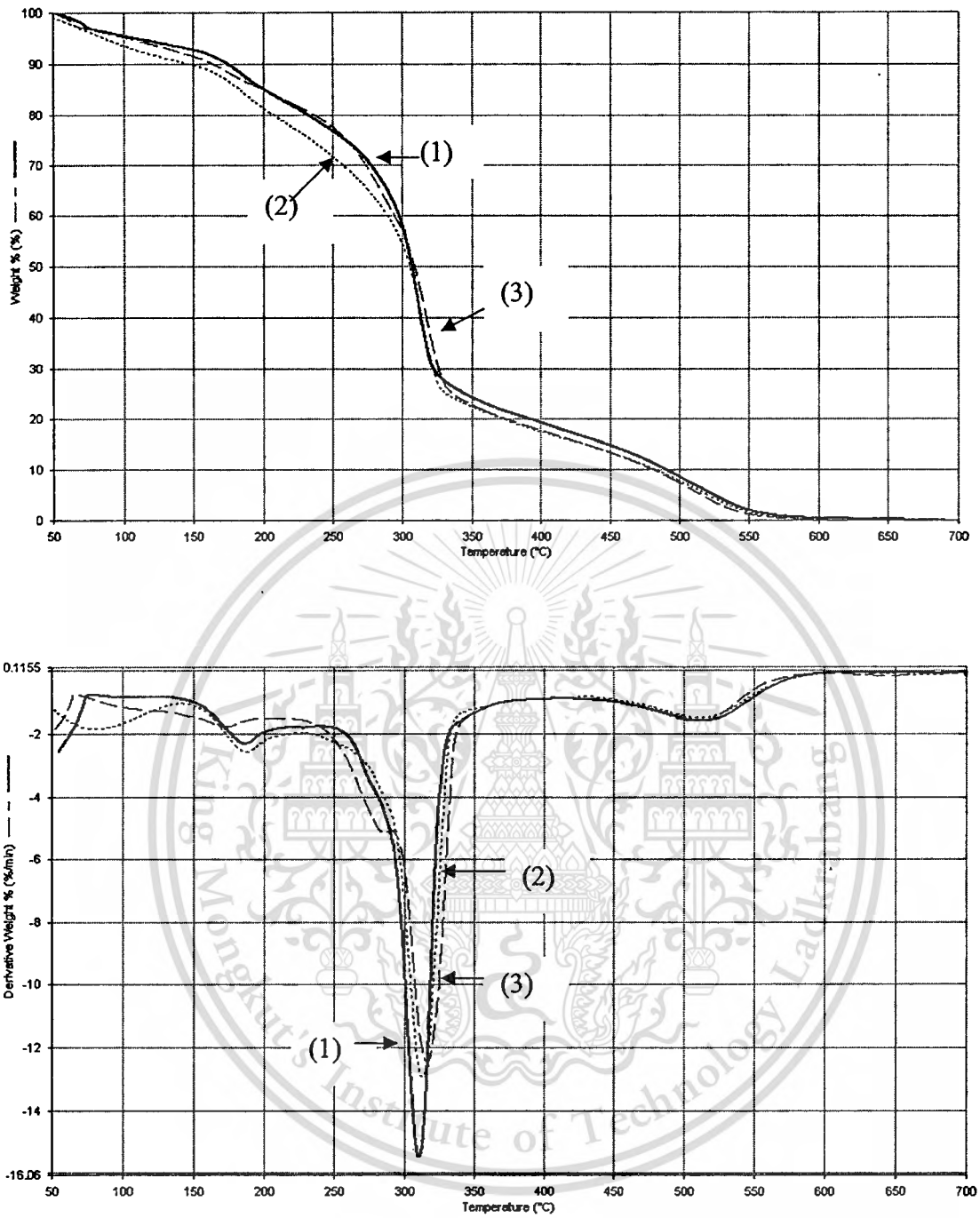


Figure 4.29 (a) TGA and (b) DTG thermograms of TPS-unreinforced (1) 100:0 (2) 50:50 and (3) 0:100

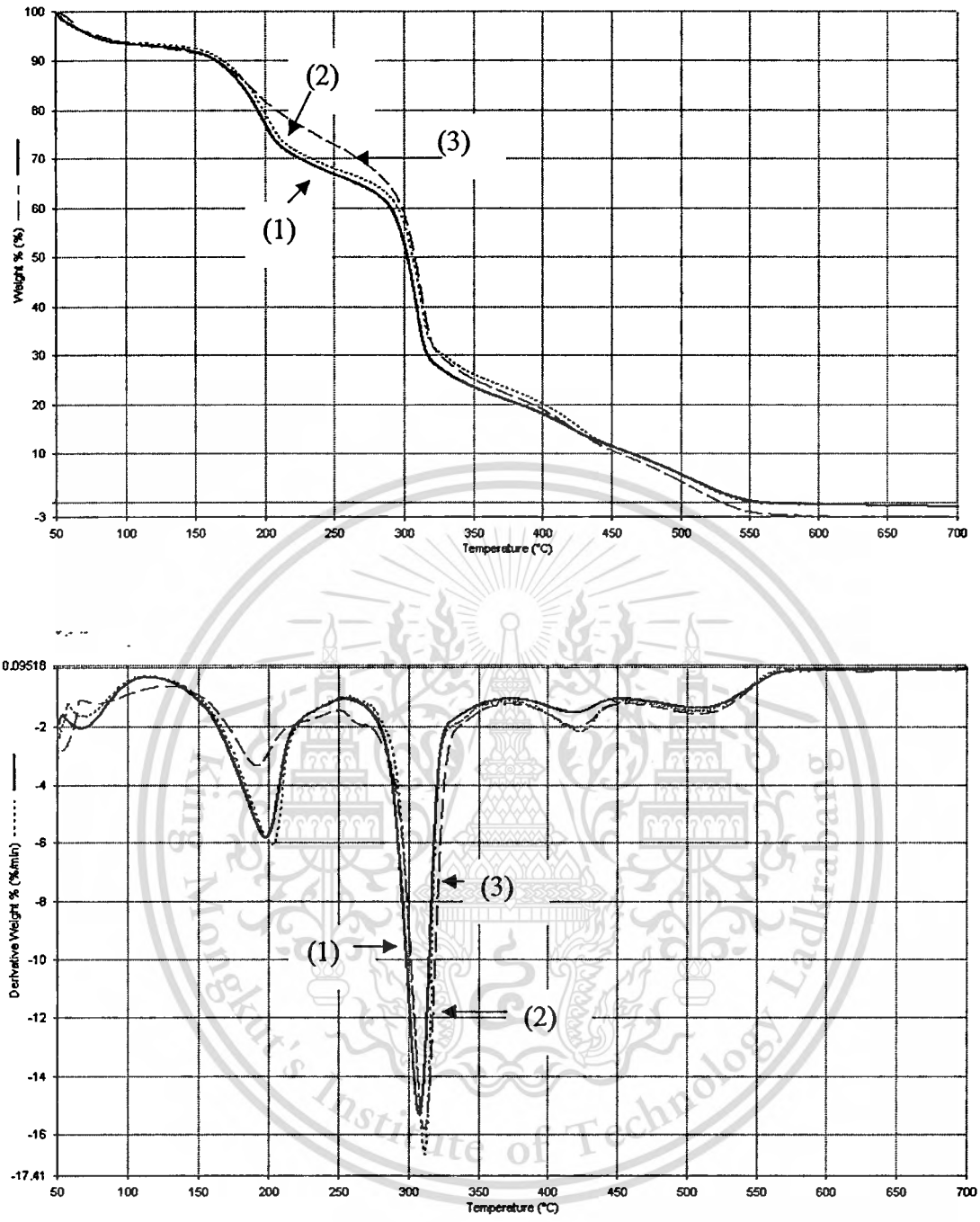


Figure 4.30 (a) TGA and (b) DTG thermograms of TPS-reinforced cotton fiber from rice starch (100:0) (1) 5% 2mm cotton (2) 10% 2mm cotton and (3) 10% 5mm cotton

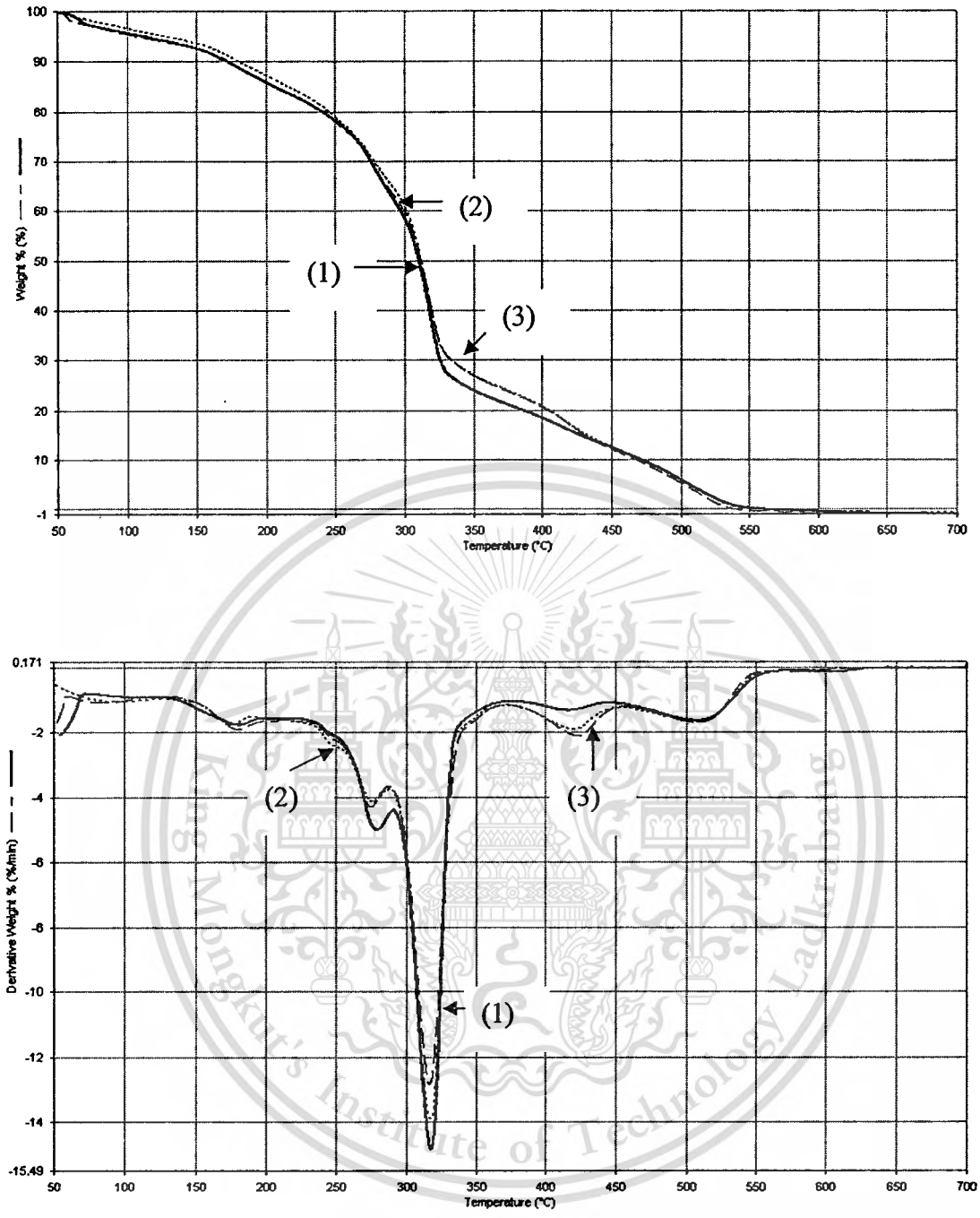


Figure 4.31 (a) TGA and (b) DTG thermograms of TPS-reinforced cotton fiber from glutinous rice starch (0:100) (1) 5% 2mm cotton (2) 10% 2mm cotton and (3) 10% 5mm cotton

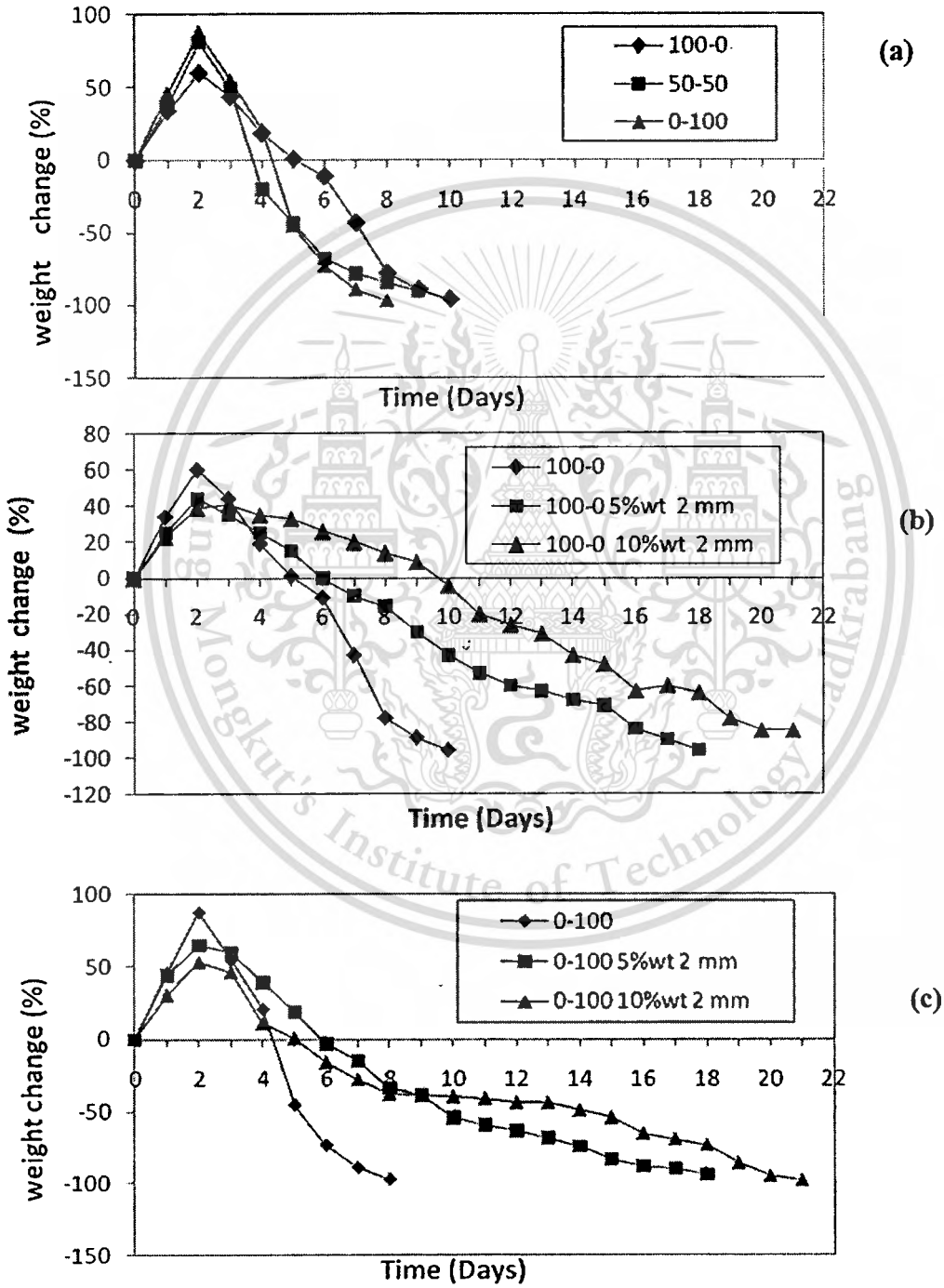
Table 4.1 Thermogravimetric results for TPS subjected to different reinforcement

Samples	Onset degradation temperature (°C)			Weight loss(%)
	Step 1 (glycerol)	Step 2 (starch)	Step 3 (fiber)	
Unreinforced				
100:0	165.2	294.3	-	59.8
50:50	168.6	296.3	-	58.7
0:100	145.5	292.5	-	65.8
Reinforced				
5% 2mm cotton				
100:0	173.5	296.3	400.5	44.9
0:100	150.4	294.9	398.0	63.0
10% 2mm cotton				
100:0	174.9	297.8	400.7	43.3
50:50	166.0	304.6	403.4	41.3
0:100	158.7	295.0	407.3	61.7
10% 5mm cotton				
100:0	169.6	299.1	405.0	50.3
0:100	161.8	307.5	399.2	41.1

From Figure 4.29 and Table 4.1, the TPS prepared from rice starch (100:0) showed higher onset degradation temperature and lower weight loss than the TPS prepared from glutinous rice starch (0:100). However, the TPS prepared from rice and glutinous rice starch blended (50:50) showed similar degradation temperature and %wt loss to the TPS from rice starch (100:0). The TPS-reinforced cotton fiber (Figures 4.30 - 4.31 and Table 4.1) promoted an increase in the onset decomposition temperature. This could be described as the TPS is phase compatible with cotton fiber by hydrogen bond linkages. In addition, the weight loss decreased by the addition of the cotton fiber showing higher thermal stability of the TPS/cotton fiber composites, regardless of the cotton fiber contents and lengths.

4.6 Soil burial test

TPS samples with the dimension of 20x50 mm were burial under soil surface of approximately 10 cm. The pH and temperature of soil were maintained at 7 and 32±2°C, respectively.



Figures 4.32 Percentage weight loss of different TPS and TPS reinforced by using cotton fiber under soil burial test

Biodegradable properties of different TPS samples can be determined by soil burial test. Figure 4.32 showed the percent weight change of different TPS. All of the TPS samples, showed the increment in weight after few days of soil immersion due to water uptake from the soil; after that, the TPS samples weight tended to decrease and then the sample started to degrade by microorganisms in soil. Especially, the TPS from glutinous rice starch (0:100) and blended rice starch (50:50) degraded within 8 days, but the TPS from rice starch (100:0) degraded within 10 days. Regardless of starch type, the percentage weight change in TPS reinforced by using cotton fiber was lower than that of the pure TPS and the TPS/cotton fiber-composite degraded within approximately 20 days. Moreover, the compatibility of rice starch and cotton fibers (Figure 4.26), leading to improve enzyme prevention by avoiding attack of the enzymes at voids.

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

5.1.1 The addition of cotton fiber in TPS caused the change of X-ray diffraction pattern, showing more main peaks than TPS, due to cotton fiber reinforcement.

5.1.2 The poor mechanical properties of TPS was improved by the modification of the TPS using cotton fiber as reinforcement. The TPS from rice starch showed higher stress and modulus than those from glutinous rice starch. It was found that the best overall mechanical properties was obtained rice starch (100:0) reinforced by cotton fiber 10%wt, 2 mm .

5.1.3 From SEM micrographs, cotton fiber were embedded and wetted by the TPS matrix, and the use of 2 mm length of cotton fiber caused good dispersion into the starch matrix.

5.1.4 The cotton fiber could effectively restrain the water absorption and reduced the water sensitivity of TPS. Thus, the increase of cotton fiber involved a decrease in the water absorption. The best performance of water resistance showed in the TPS from rice starch with 10% 2 mm and 10% 5 mm cotton fiber.

5.1.5 The enhancement in thermal stability in TPS was obtained by the addition of cotton fiber.

5.1.6 Under soil burial test, the TPS degraded quicker than the TPS/cotton fiber composites. The results showed that the quickest degradation was glutinous rice starch (0:100) in 8 days. Whereas, the TPS from rice starch with 10% 2 mm and 10% 5 mm cotton fiber showed the slowest within 20 days.

5.1.7 The best performance in this study was found in the TPS from rice starch with 10% 2 mm cotton fiber by the maximum mechanical properties and the lowest water absorption.

5.2 Recommendations

5.2.1 Study on the other types of natural fibers such as flax stand, bamboo, kenaf, hemp, banana.

5.2.2 Study on the other plasticizers such as 1,4-butanediol (BUT), ethylene glycol (EG), propylene glycol(PG), D-sorbitol (SOR) and diethyleneoxide glycol (DEG).

5.2.3 Study on additives which can increase the durability properties of TPS reinforced by using cotton fiber such as preservatives.

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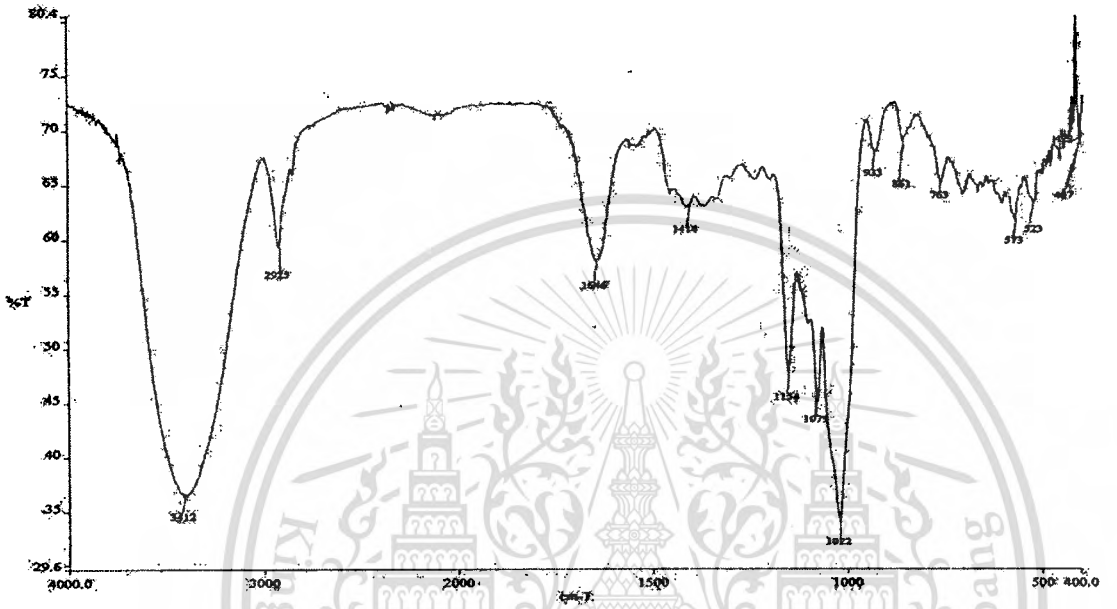
Appendices

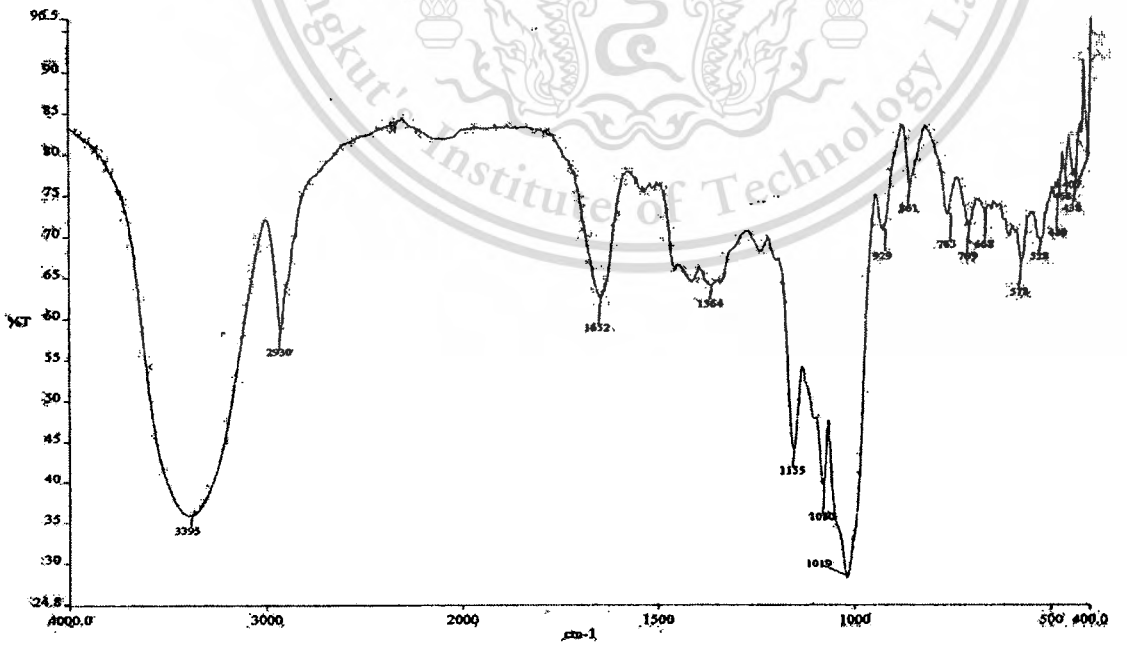
Appendix A

Native starch

- Rice starch

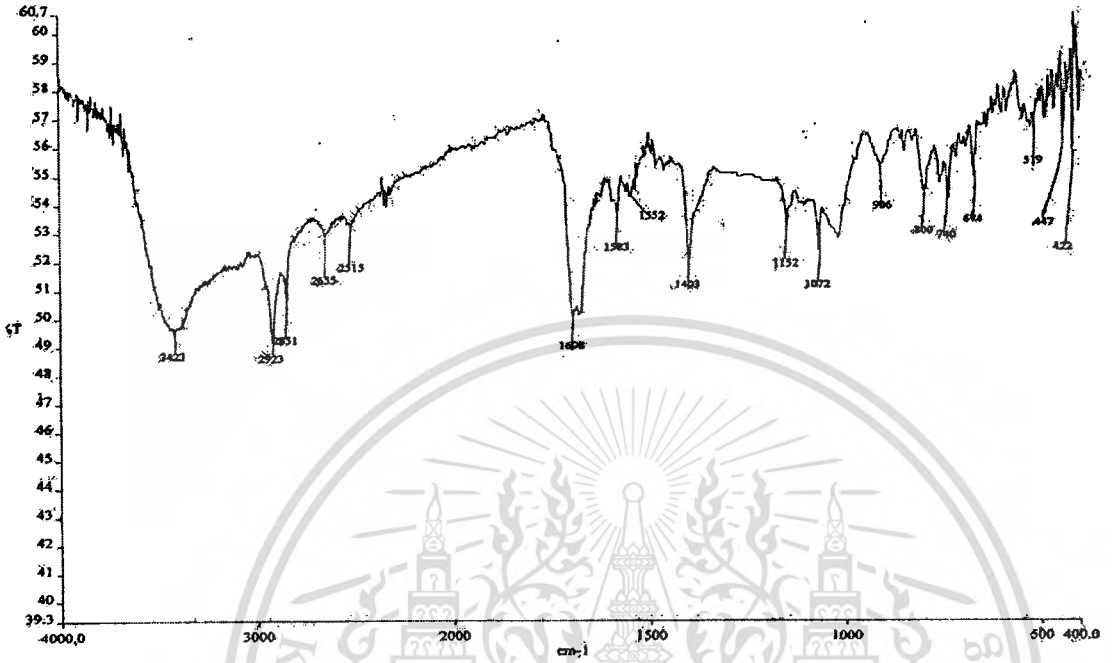


- Glutinous rice starch

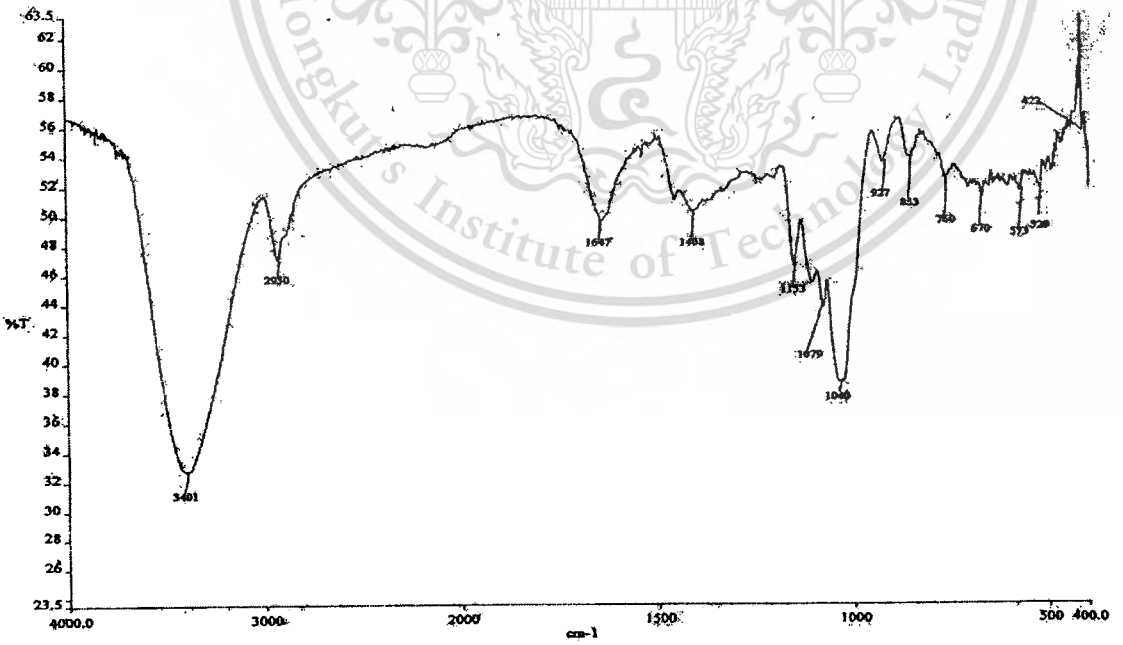


TPS-unreinforced

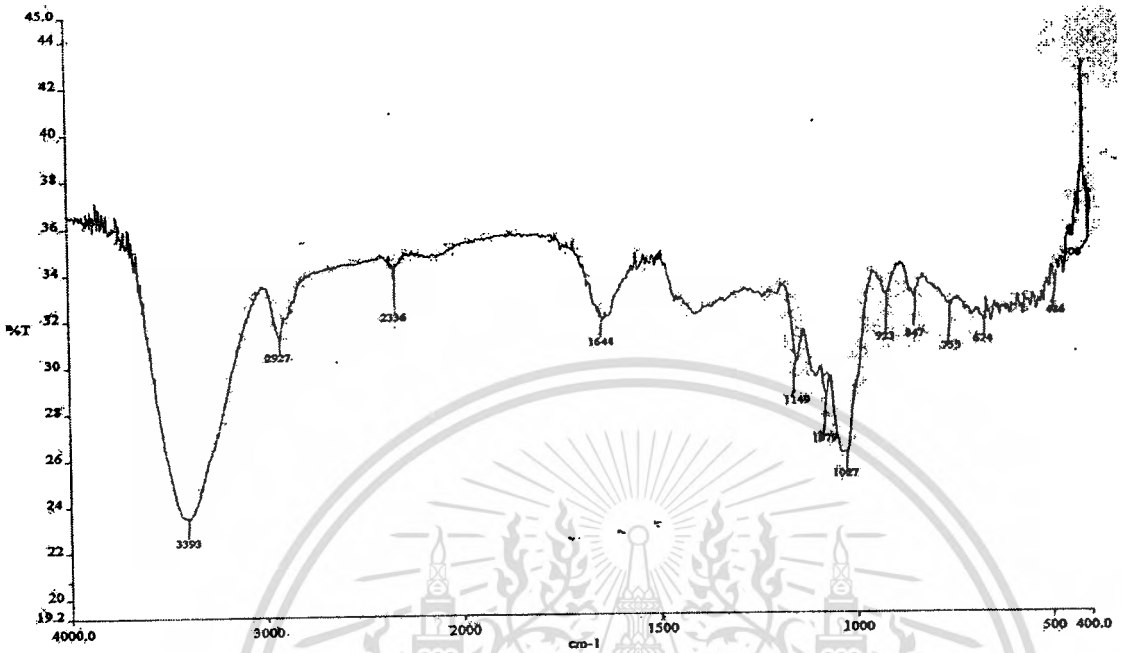
- 100:0



- 50:50



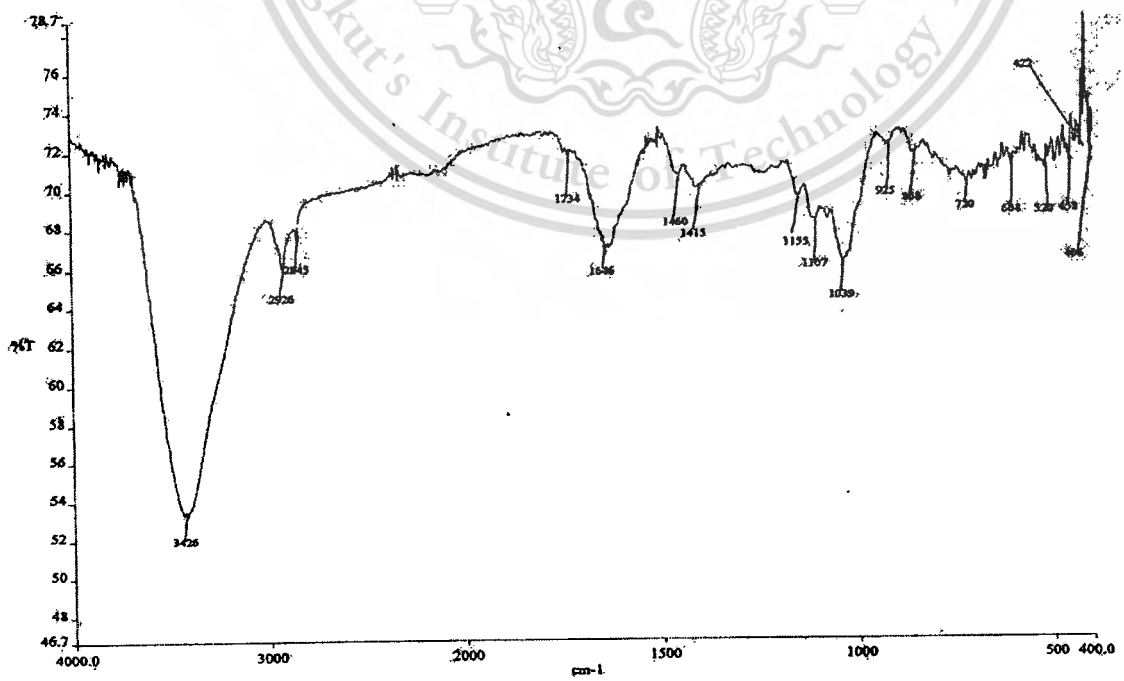
- 0:100



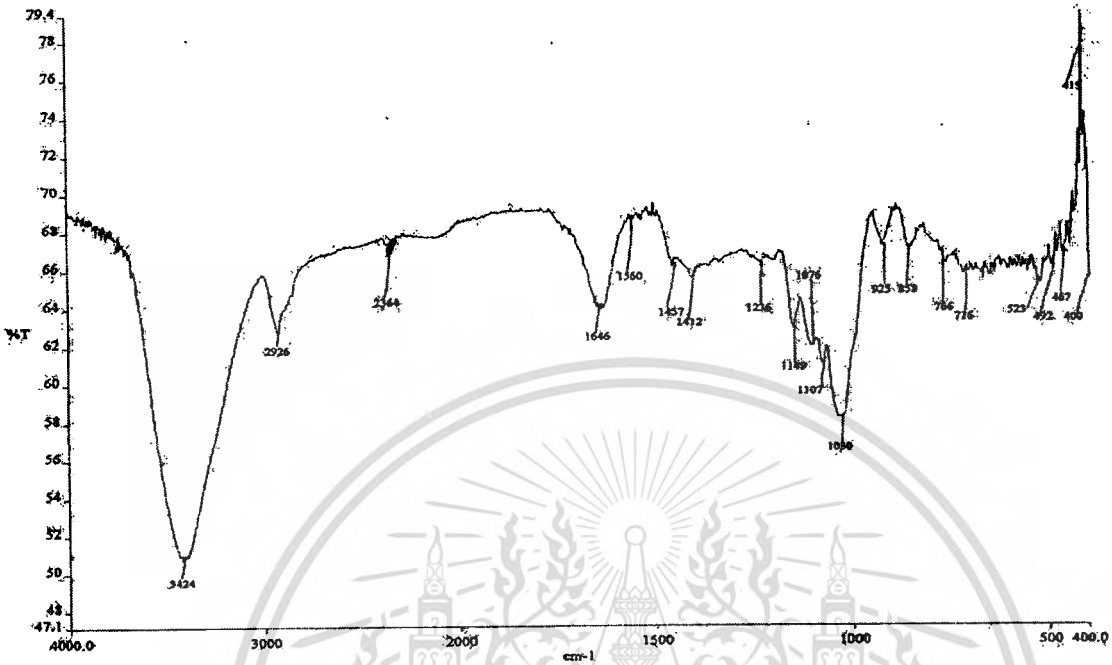
TPS-reinforced cotton fiber

5% 2mm cotton

- 100:0

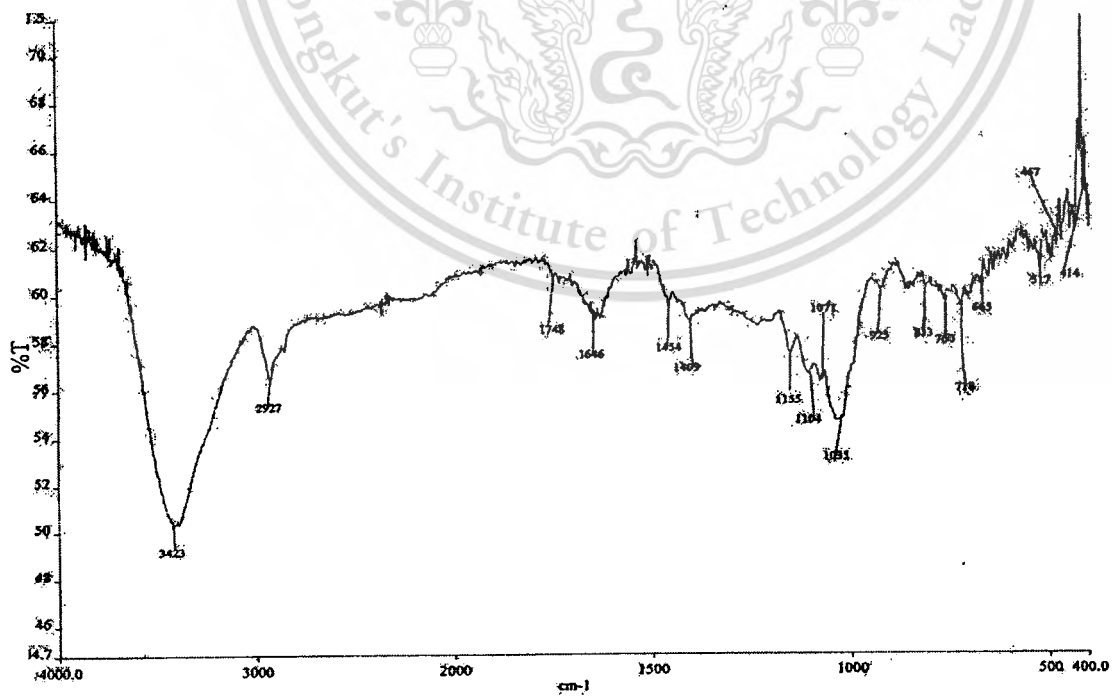


- 0:100

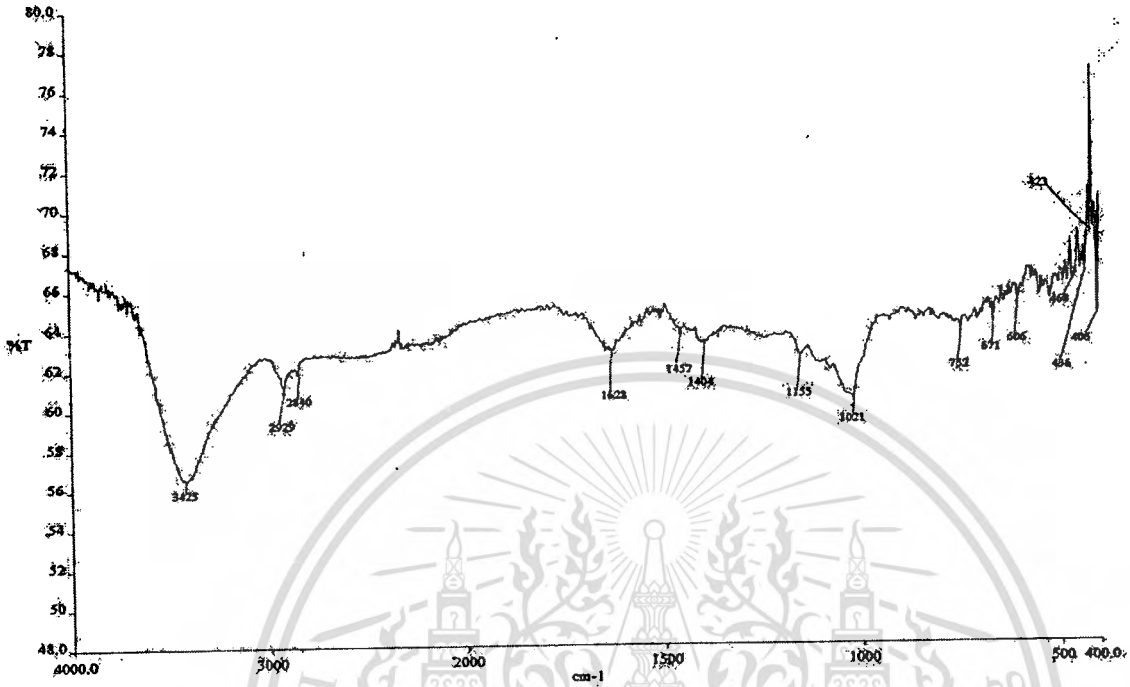


10% 2mm cotton

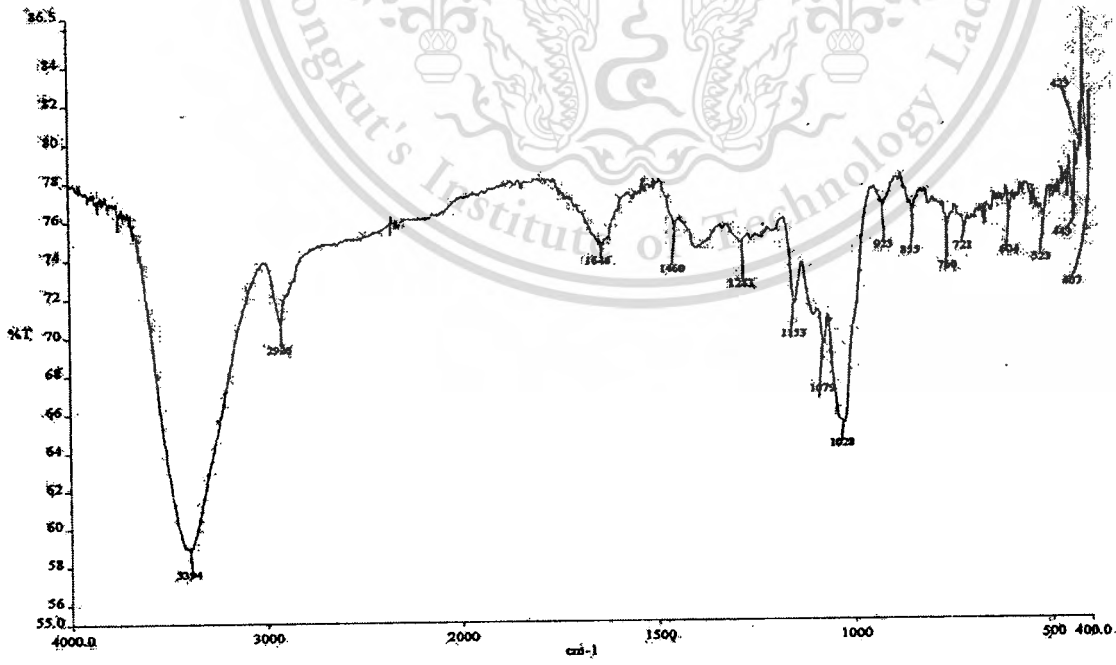
- 100:0



- 50:50

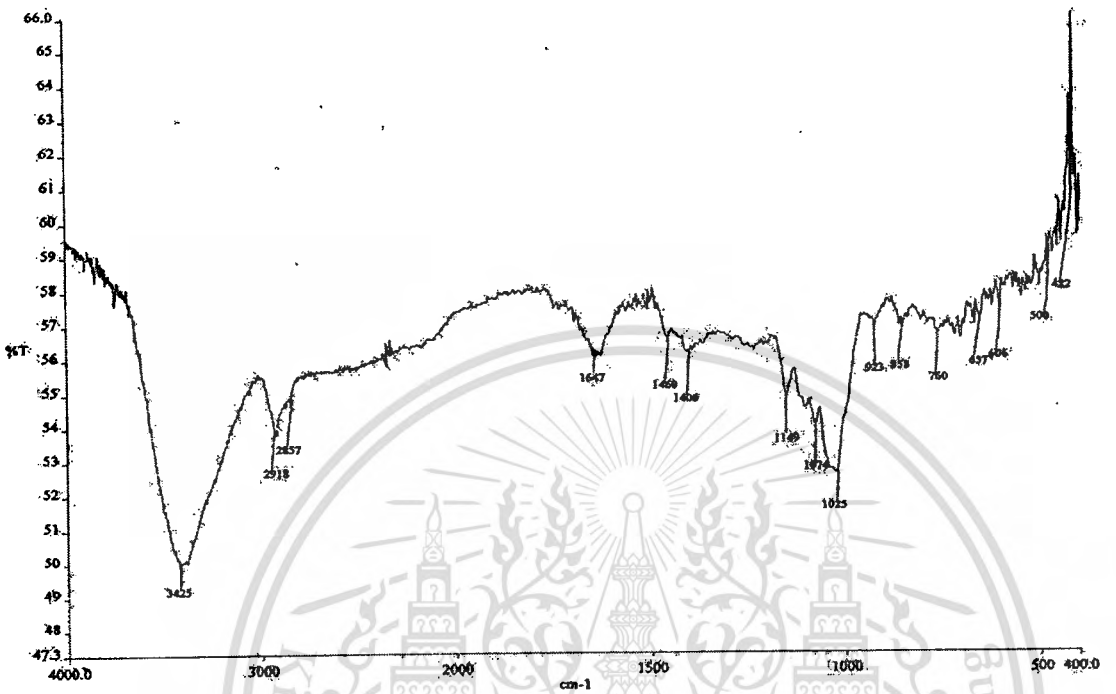


- 0:100

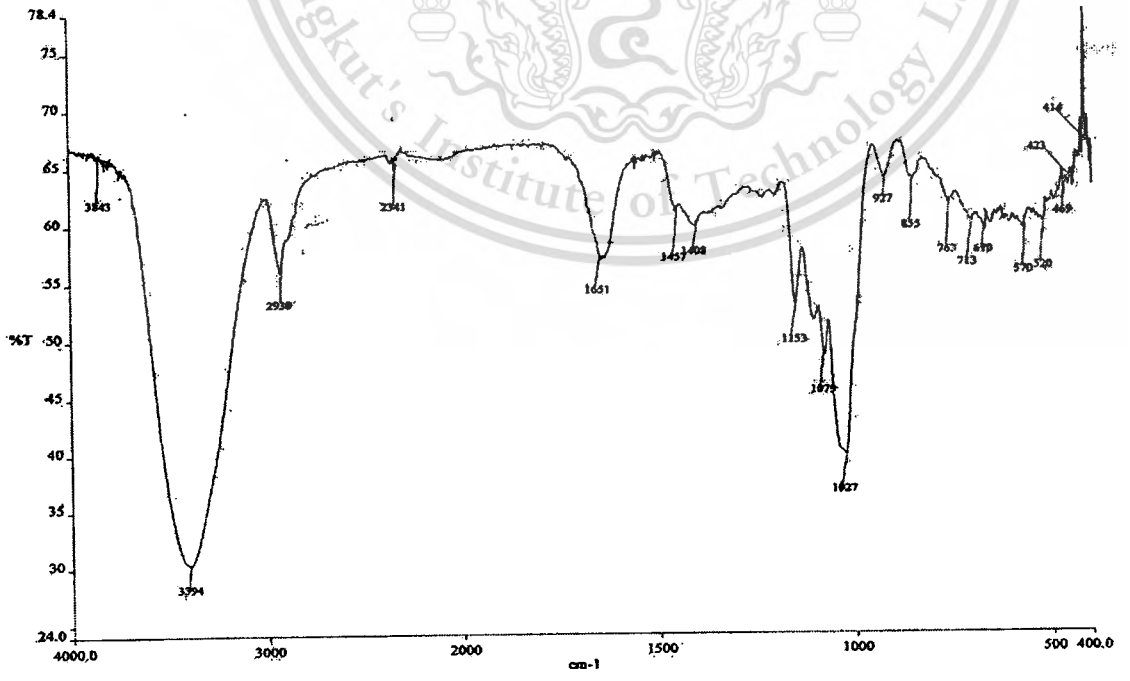


10% 5mm cotton

- 100:0



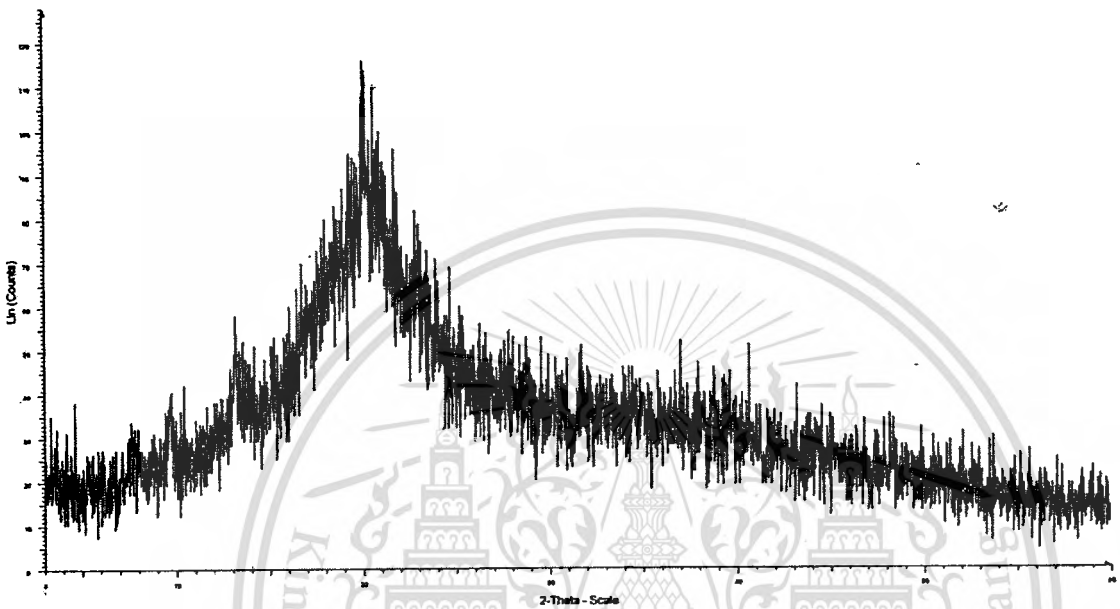
- 0:100



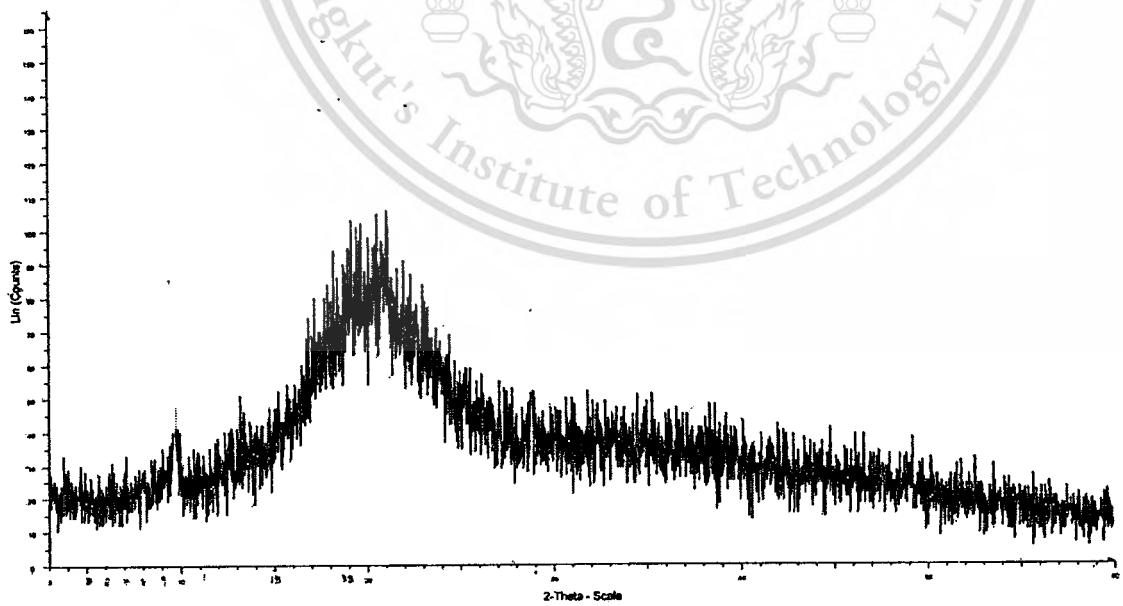
Appendix B

TPS-unreinforced

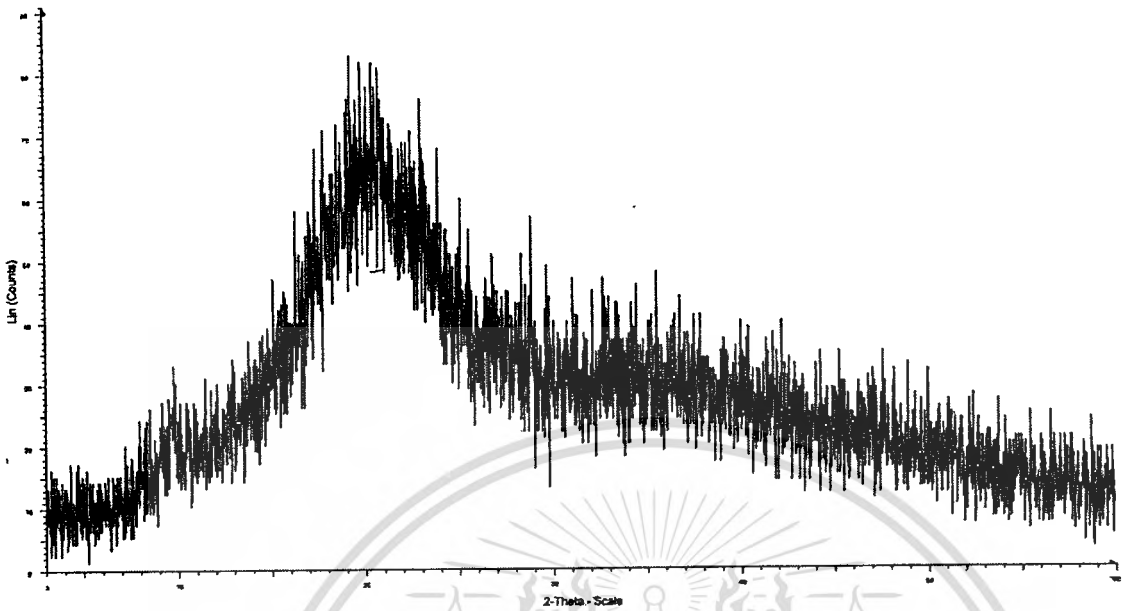
- 100:0



- 50:50

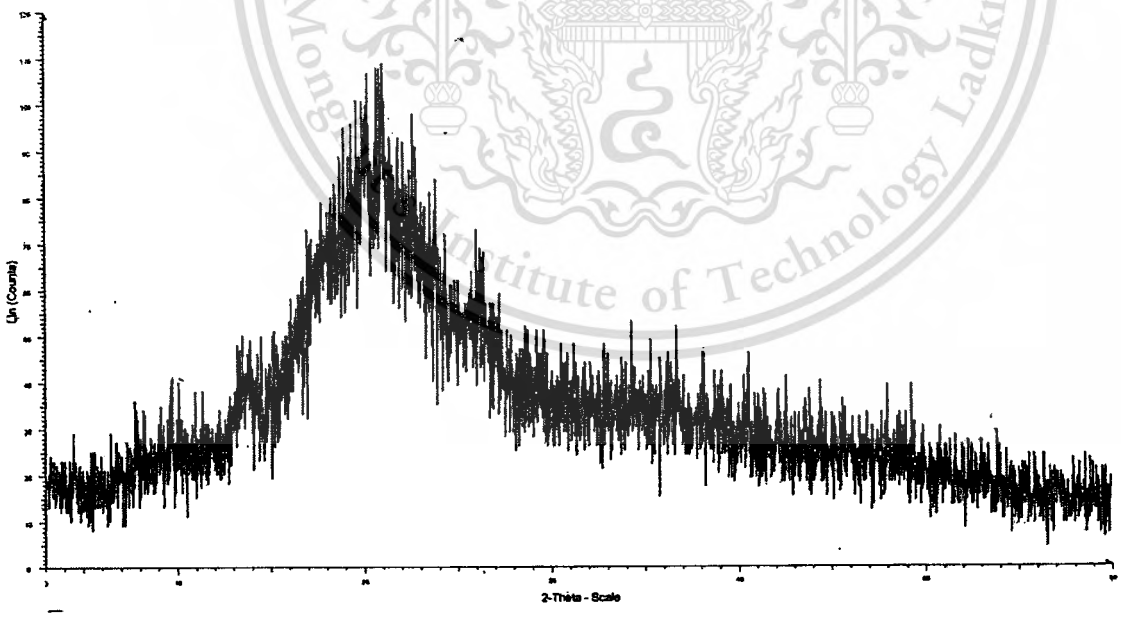


- 0:100



TPS-reinforced cotton fiber
5% 2mm cotton

- 100:0



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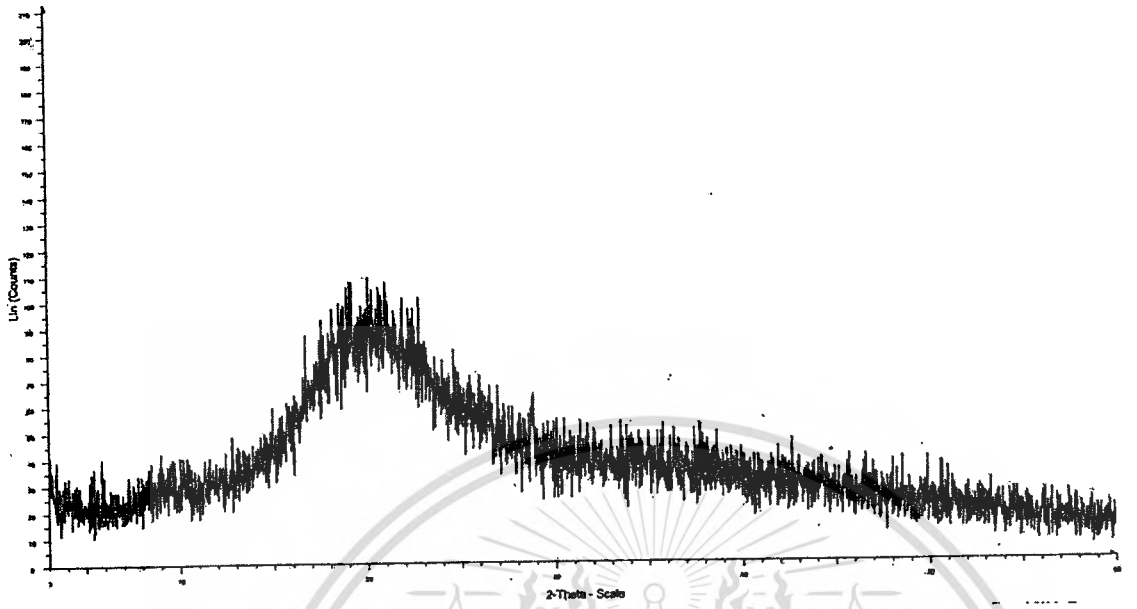
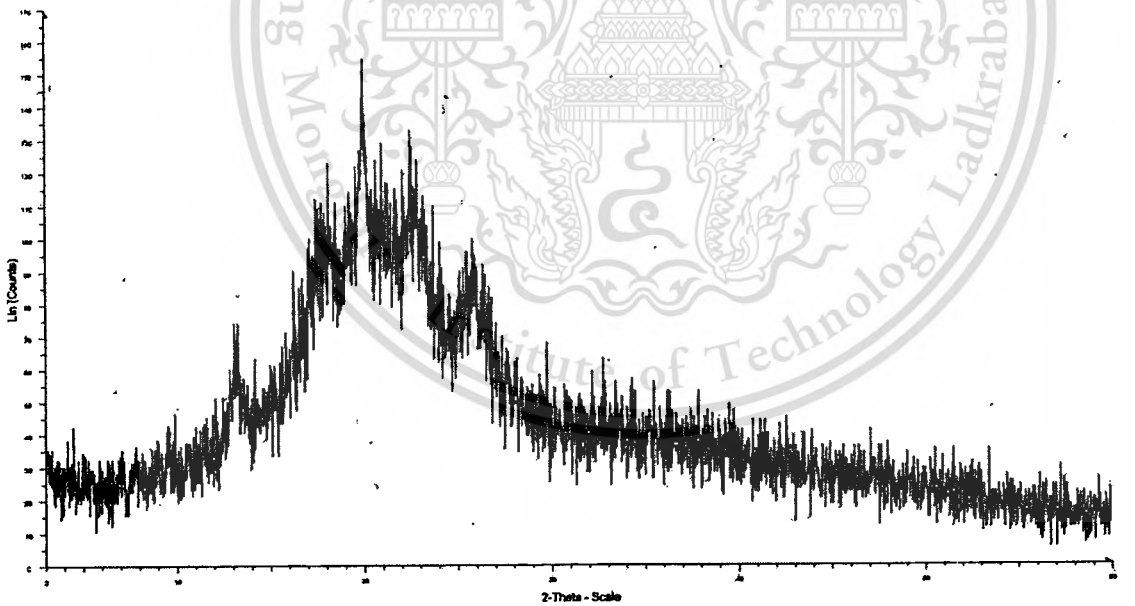


10% 2mm cotton

- 100:0



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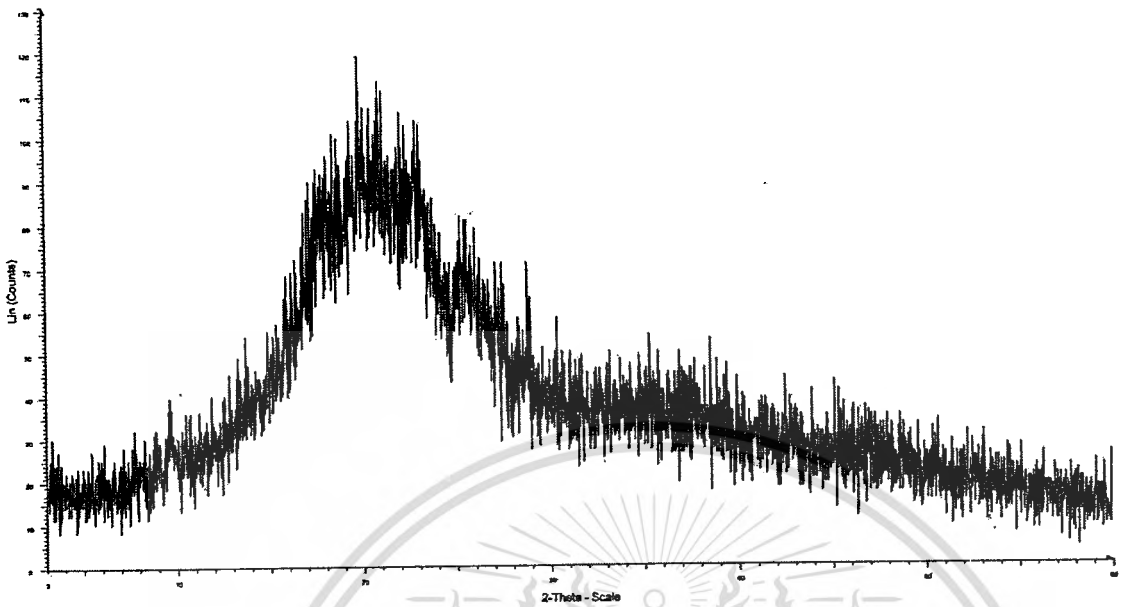

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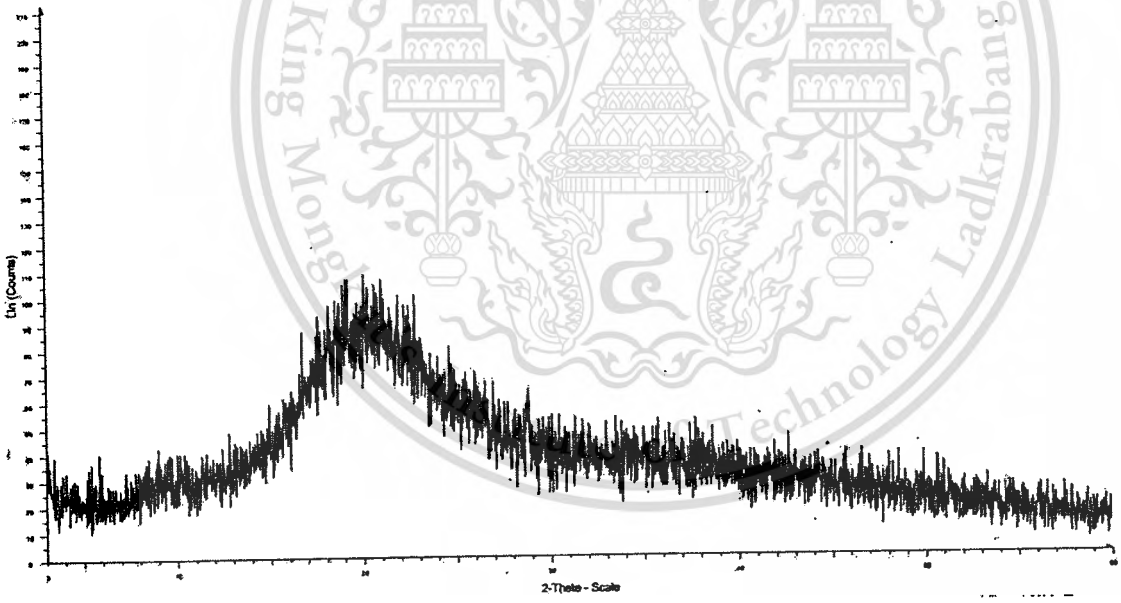
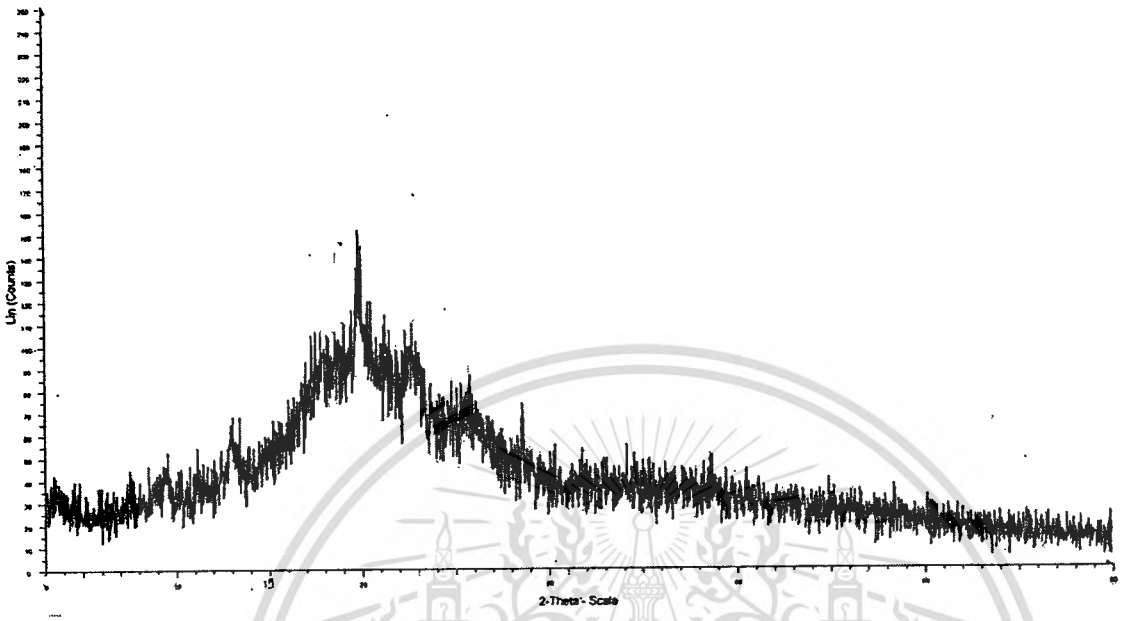


10% 5mm cotton

- 100:0



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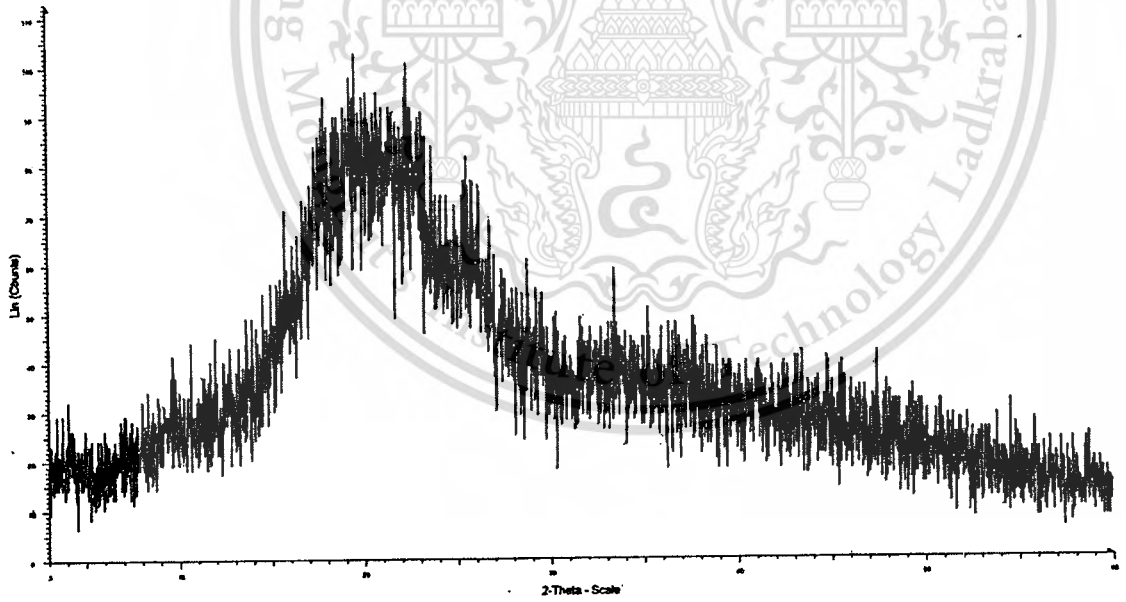


Appendix C

The results of Mechanical properties

100/0 (2mm)

Cotton content	Ftm	Rm	Extremax_load	%Ag	E(R0)
0%	75.21±15.51	3.26±0.48	7.98±2.83	36.61±5.63	37.79±8.66
5%	104.18±20.51	5.25±0.87	7.63±1.94	34.28±7.63	50.05±9.69
10%	151.23±25.21	7.06±1.18	3.53±0.46	10.67±5.54	76.82±11.23
15%	191.66±14.37	7.71±0.66	2.34±0.47	10.33±2.25	80.24±6.16

50/50 (2mm)

Cotton content	Ftm	Rm	Extremax_load	%Ag	E(R0)
0%	48.1±8.7	2.6±0.81	16.3±5.301	58.6±0.56	33.65±2.03
5%	54.05±6.11	3.2±0.39	11.44±4.031	45.15±0.47	35.79±1.08
10%	149.1±14.37	5.16±0.66	3.23±2.25	13.032±0.49	75.93±6.16
15%	174.6±12.3	8.45±0.53	1.367±3.31	5.47±0.67	76.67±5.43

0/100 (2mm)

Cotton content	Ftm	Rm	Extremax_load	%Ag	E(R0)
0%	42.3±7.3	2.4±0.69	24.7±6.08	77.6±1.24	22.6±1.43
5%	77.54±12.3	3.5±0.43	8.23±4.07	36.77±0.55	48.39±2.59
10%	94.1±13.2	4.37±0.57	2.598±5.3	17.17±0.69	72.76±4.57
15%	128.8±14.2	7.07±0.41	2.58±3.34	8.34±0.81	73.15±3.46

100/0 (5mm)

Cotton content	Fm	Rm	Ext@max load	%Agt	E(Rt)
0%	75.2±6.5	3.26±.0.75	7.98±5.2	36.61±0.65	37.79±3.02
5%	96.47±10.23	4.67±0.65	7.08±4.03	30.81±0.87	56.29±5.46
10%	132.125±8.9	4.89±0.75	5.5±3.04	23.25±0.45	71.95±6.7
15%	137.62±12.1	5.47±0.31	3.69±2.4	13.46±0.56	74.79±7.1

50/50 (5mm)

Cotton content	Fm	Rm	Ext@max load	%Agt	E(Rt)
0%	48.1±5.5	2.6±0.87	16.3±6.5	58.6±0.95	33.65±3.5
5%	75.19±9.8	4.38±0.96	8.49±5.8	35.69±0.84	34.35±3.8
10%	85.83±8.4	4.6±0.74	7.16±5.9	27.94±0.77	37.64±4.1
15%	95.41±10.2	4.79±0.56	4.76±3.2	19.69±0.59	42.82±4.6

0/100 (5mm)

Cotton content	Fm	Rm	Ext@max load	%Agt	E(Rt)
0%	42.3±6.4	2.4±0.45	24.7±6.9	77.6±0.48	22.6±2.1
5%	71.67±8.2	4.18±0.59	14.1±4.5	51.95±0.51	45.67±3.5
10%	121.7±11.3	5.66±0.61	7.41±4.8	38.305±0.55	65.59±4.2
15%	211.4±12.1	11.85±0.66	7.09±3.2	30.28±0.63	95.02±6.7

Appendix D

The results of water absorption

Time (Days)	weight (g)									
	TPS-unreinforced			100 5%wt 2mm		10%wt 2mm			10%wt 5mm	
	100-0	50-50	0-100	100-0	0-100	100-0	50-50	0-100	100-0	0-100
0	0	0	0	0	0	0	0	0	0	0
1	60	88	98	55	65	53	88	61	58	59
2	110	134	170	87	152	80	114	137	83	78
3	167	189	320	147	257	120	179	233	118	257
4	230	281	367	207	290	193	261	271	191	277
5	250	345	383	243	343	230	311	313	212	283
6	277	360	385	254	367	247	320	340	228	300
7	302	358	397	265	370	258	346	336	235	312
8	303	365	400	276	369	261	355	335	249	319
9	307	369	398	277	371	269	358	339	271	332
10	308	367	395	274	368	270	359	337	272	332
11	306	363	388	275	365	271	359	341	268	335
12	309	364	371	276	364	268	360	338	264	336
13	311	353	367	278	367	266	361	340	269	333
14	309	346	363	272	366	267	358	336	265	334
15	310	338	359	270	368	265	357	335	264	331
16	308	329	340	271	366	263	357	334	267	330
17	302	297	330	270	363	258	356	333	262	327
18	299	286	324	268	362	251	356	328	259	326

Appendix E

The results of soil burial test

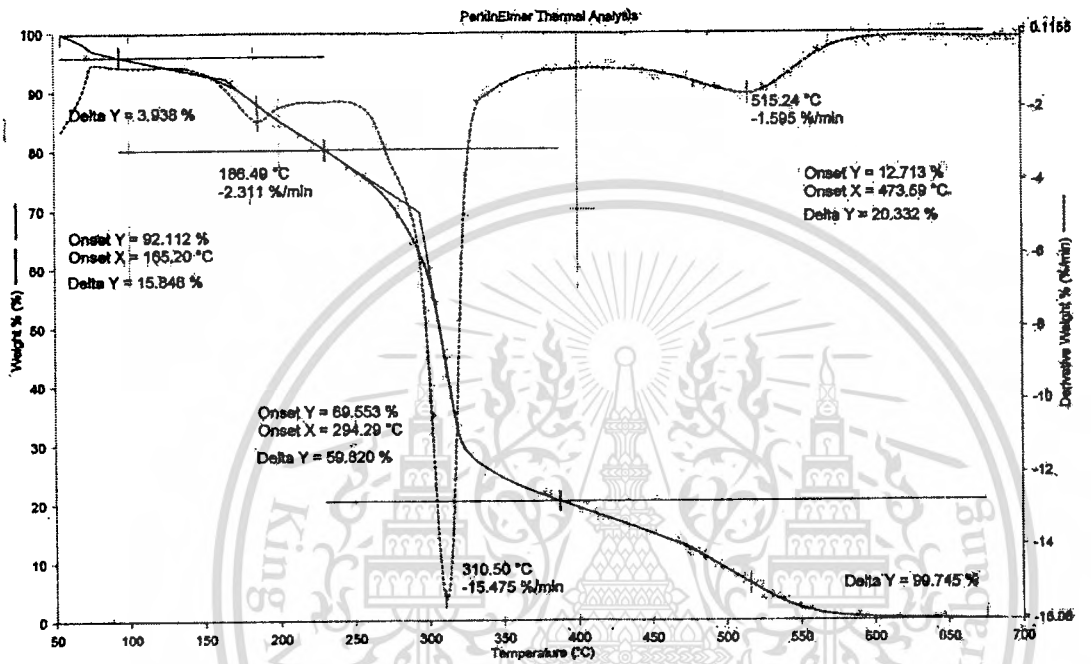
days	weight change (%)							
	pure TPS			5% 2mm cotton		10% 2mm cotton		
	100-0	50-50	0-100	100-0	0-100	100-0	50-50	0-100
1	0	0	0	0	0	0	0	0
2	34	38	46	25	44	23	36	30
3	60	81	65	44	81	39	74	53
4	61	49	79	35	84	41	78	46
5	44	6	21	25	39	35	33	11
6	19	-30	-33	15	19	33	18	1
7	1	-43	-65	0	-3	26	-1	-16
8	-11	-68	-80	-10	-15	20	-14	-28
9	-43	-74	-89	-16	-34	14	-29	-38
10	-48	-78	-93	-30	-39	9	-31	-39
11	-55	-84	-98	-43	-54	-4	-31	-40
12	-73	-80		-53	-59	-20	-33	-41
13	-78	-93		-60	-63	-26	-39	-44
14	-89	-95		-63	-68	-31	-41	-44
15	-96			-66	-74	-43	-46	-49
16				-68	-83	-48	-49	-54
17				-70	-88	-63	-63	-65
18				-71	-90	-60	-65	-69
19				-75	-94	-64	-69	-73
20				-84		-78	-80	-86
21				-90		-78	-80	-86
22				-96		-85	-90	-98
23						-85	-90	-98

Appendix F

Thermal property

TPS-unreinforced

- 100:0



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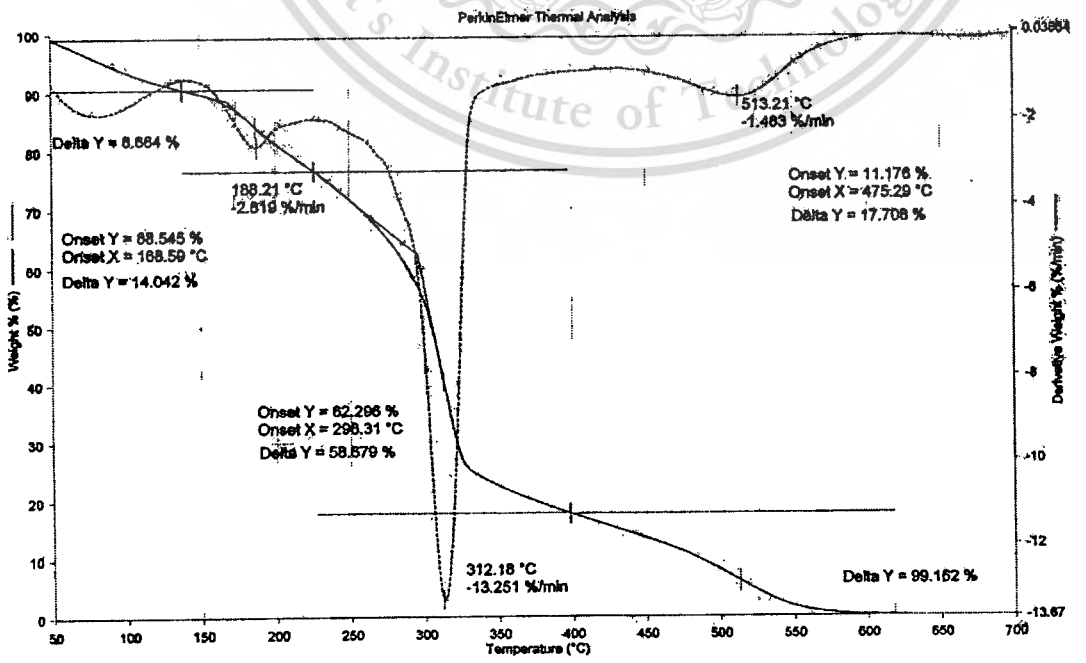

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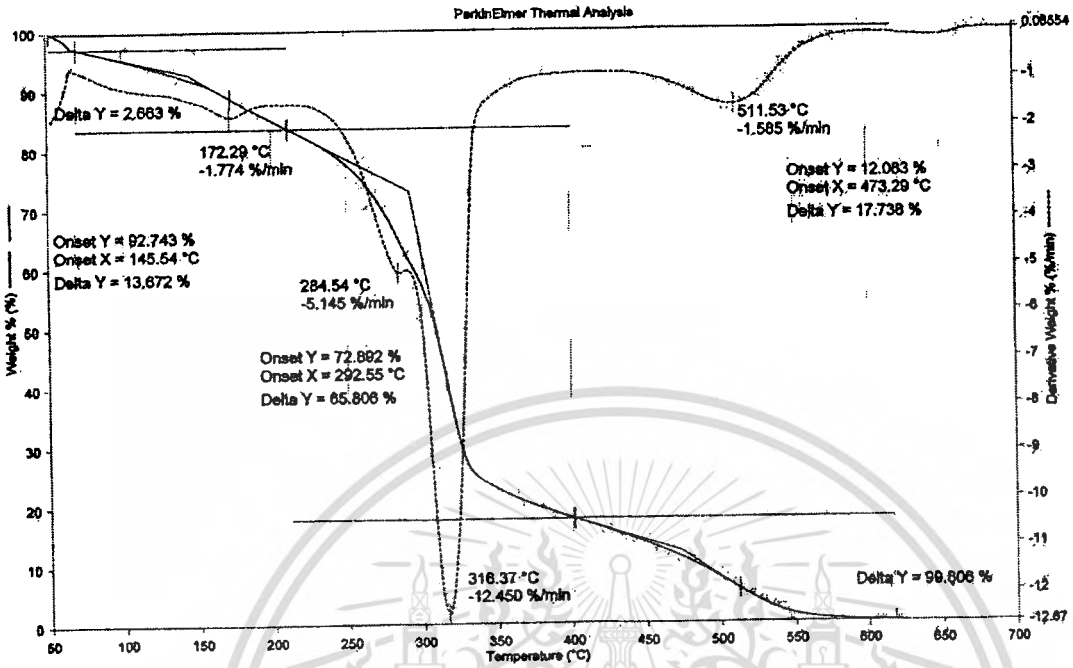
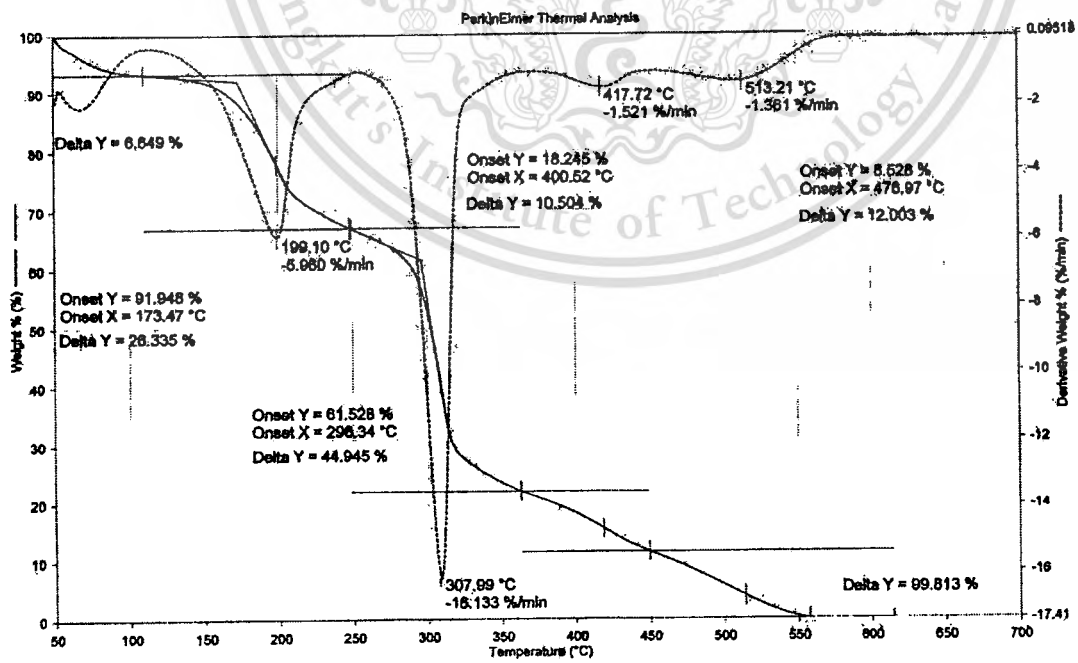


TPS-reinforced cotton fiber

5% 2mm cotton

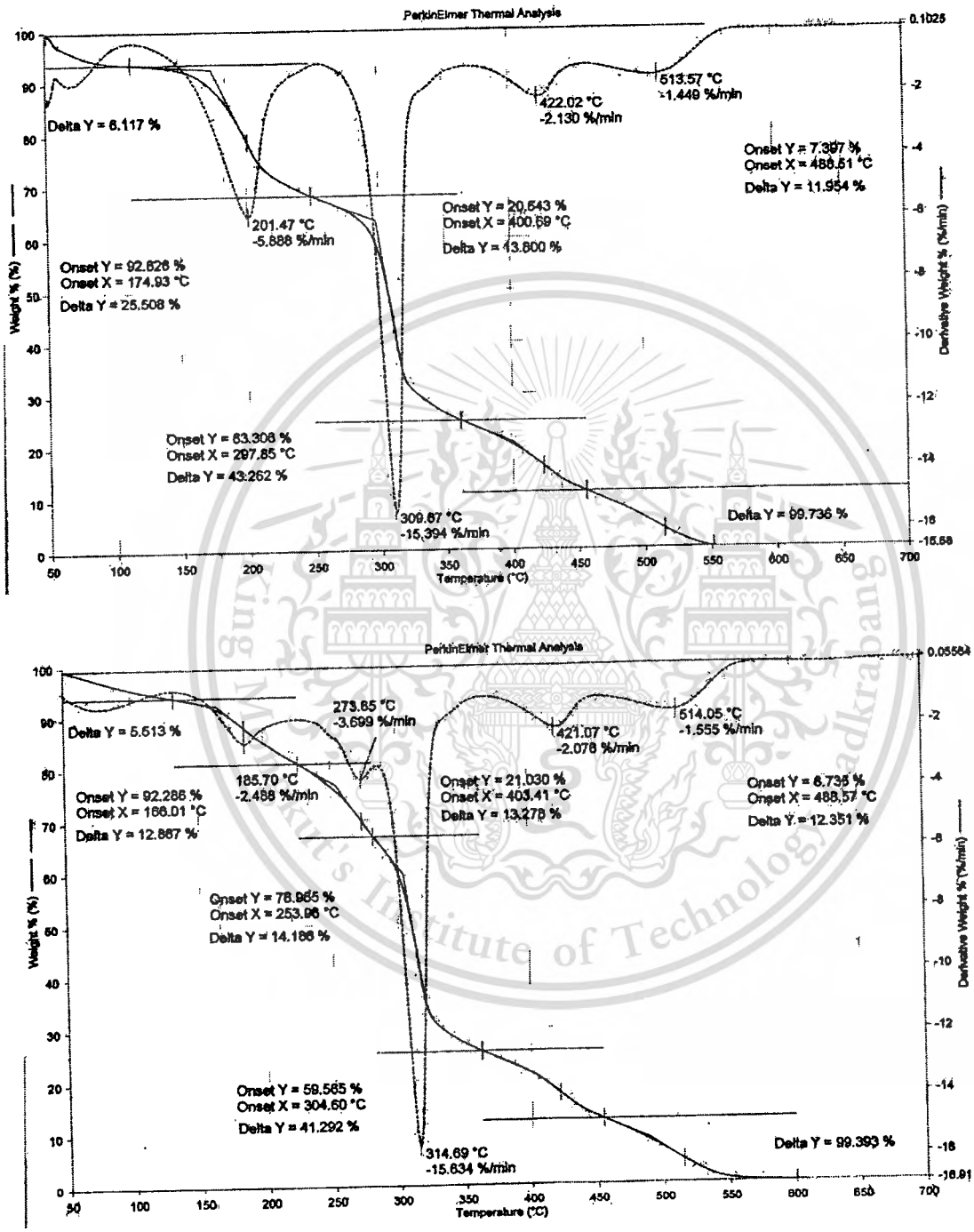
- 100:0



- 0:100

10% 2mm cotton

- 100:0



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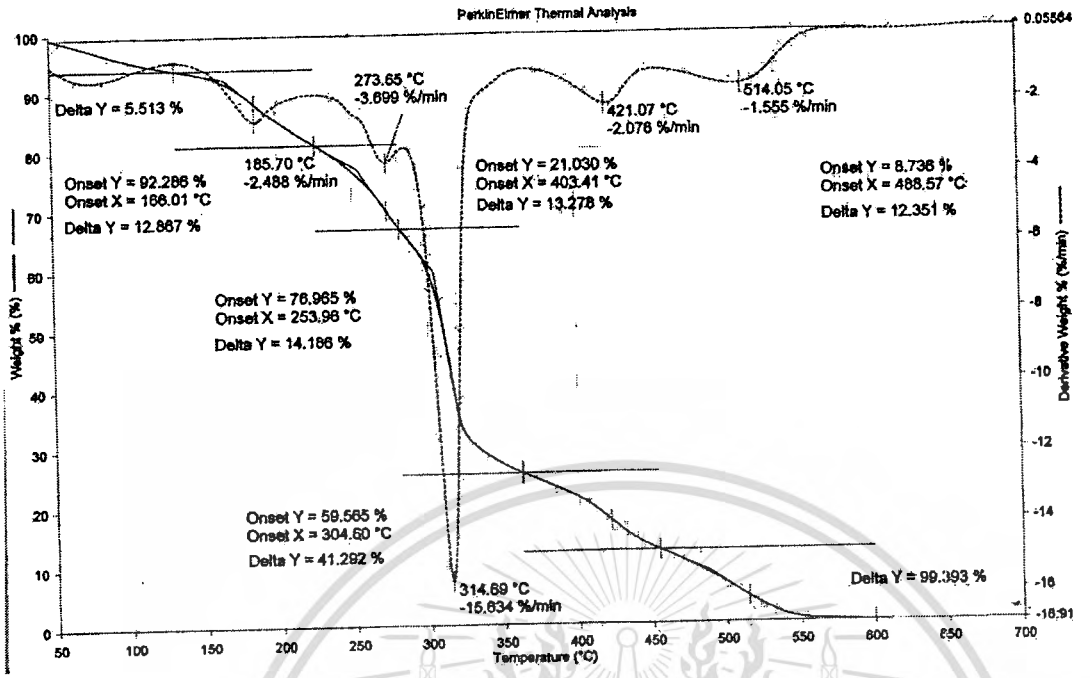

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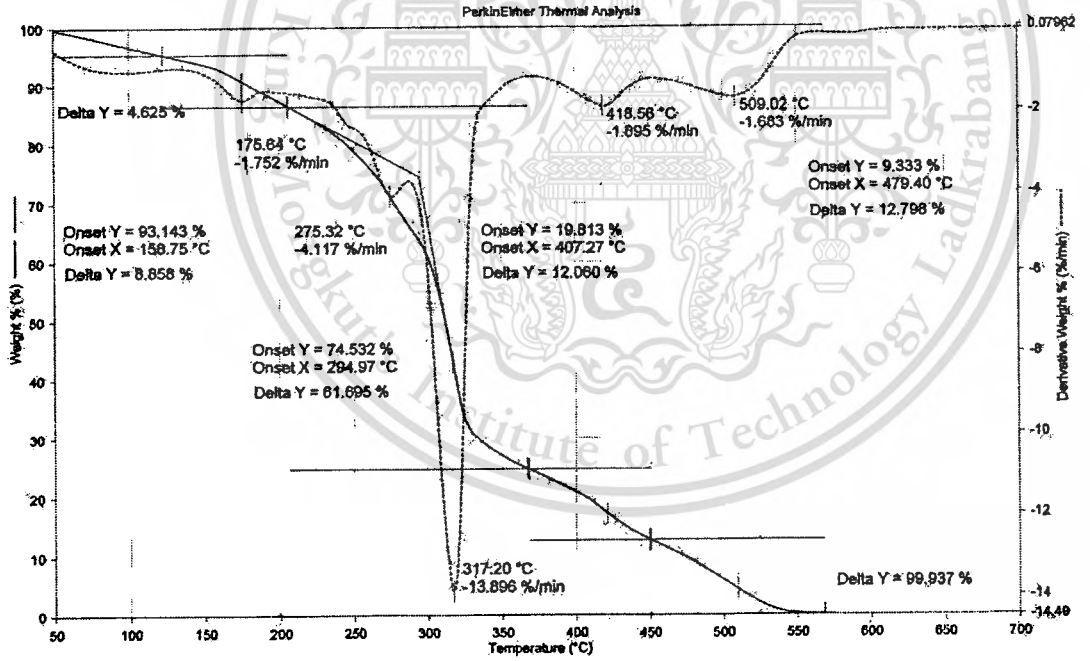
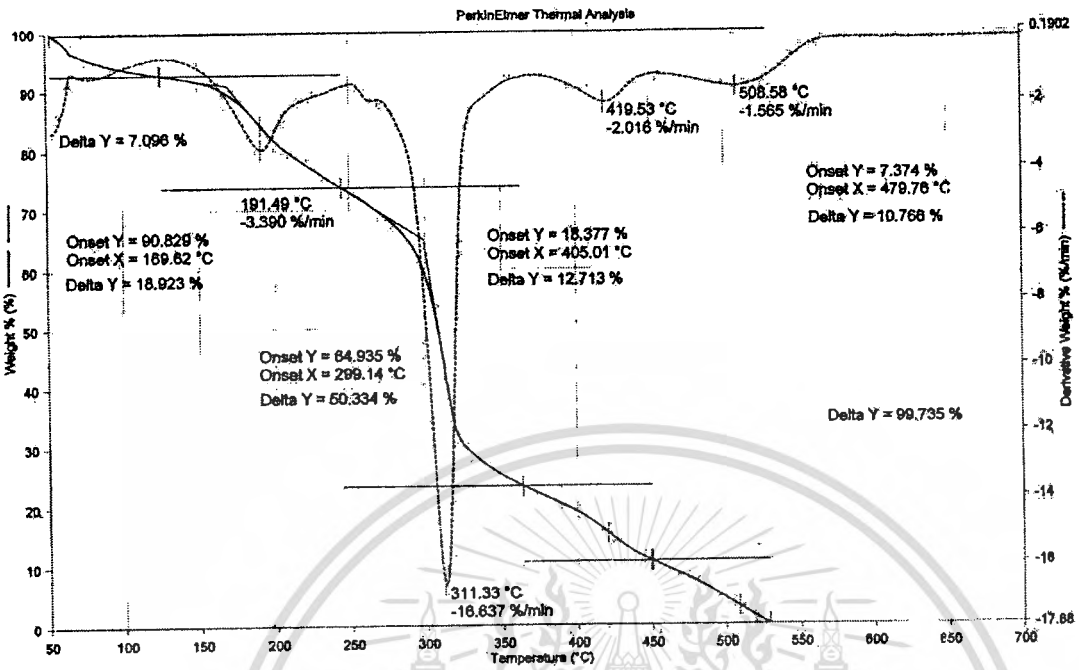


10% 5mm cotton

- 100:0



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