

อิทธิพลของระดับชั้นการแทนที่ต่อสมบัติทางกายภาพและความสามารถในการย่อยสลายทาง  
ชีวภาพของฟิล์มเซลลูโลสดัดแปรจากไบโสับปะรดเปลือกข้าวโพดและเศษผ้าฝ้าย  
ภายใต้พลังงานไมโครเวฟ

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต  
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INFLUENCE OF DEGREE OF SUBSTITUTION ON PHYSICAL PROPERTIES AND  
BIODEGRADABILITY OF MODIFIED CELLULOSE FILMS FROM PINEAPPLE LEAF,  
CORN HUSK, AND WASTE COTTON FABRICS UNDER MICROWAVE ENERGY

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A Thesis Submitted in Partial Fulfillment of the Requirements  
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Department of Materials Science

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 ความสามารถในการย่อยสลายทางชีวภาพของฟิล์มเซลลูโลสดัดแปรจากใบสับปะรด  
 เปลือกข้าวโพดและเศษผ้าฝ้ายภายใต้พลังงานไมโครเวฟ. (INFLUENCE OF DEGREE  
 OF SUBSTITUTION ON PHYSICAL PROPERTIES AND BIODEGRADABILITY OF  
 MODIFIED CELLULOSE FILMS FROM PINEAPPLE LEAF, CORN HUSK, AND  
 WASTE COTTON FABRICS UNDER MICROWAVE ENERGY) อ.ที่ปรึกษา  
 วิทยานิพนธ์หลัก : รศ.ดร. ดวงดาว อัจจงค์, 146 หน้า.

งานวิจัยนี้ได้ศึกษาอิทธิพลของระดับชั้นการแทนที่ต่อสมบัติทางกายภาพและความสามารถในการย่อย  
 สลายทางชีวภาพ ด้วยภาวะการย่อยสลายแบบการใช้ปุ๋ยหมักชีวภาพ การใช้เอนไซม์ และการแช่ในบ่อน้ำบาดน้ำ  
 เสียของฟิล์มเซลลูโลสดัดแปรจากใบสับปะรดเปลือกข้าวโพดและเศษผ้าฝ้าย โดยได้เตรียมเซลลูโลสดัดแปรด้วย  
 ปฏิกิริยาเอสเทอร์ฟิเคชัน ในตัวทำละลายของลิเทียมคลอไรด์กับไดเมทิลอะซิทาไมด์ ซึ่งใช้ลอโรอิลคลอไรด์เป็น  
 สารดัดแปร ภายใต้การให้ความร้อนด้วยพลังงานไมโครเวฟในรูปของกำลัง (วัตต์) และเวลา จากนั้นวิเคราะห์  
 โครงสร้างทางเคมีของเซลลูโลสดัดแปรได้ด้วยเทคนิคฟูริเออร์ทรานฟอร์มอินฟราเรดสเปกโทรสโกปีและเทคนิค  
 นิวเคลียร์แมกเนติกเรโซแนนซ์ ผลการทดลองพบว่า โครงสร้างทางเคมีของเซลลูโลสดัดแปรที่มีหมู่คาร์บอนิลของ  
 สารดัดแปรเกิดขึ้นที่เลขคลื่นตำแหน่ง  $1740\text{ cm}^{-1}$  และมีการลดลงของหมู่ไฮดรอกซิลในโครงสร้างของเซลลูโลสที่  
 เลขคลื่นตำแหน่ง  $3340\text{ cm}^{-1}$  รวมถึงลักษณะสัณฐานวิทยาของเซลลูโลสดัดแปรมีขนาดใหญ่อขึ้นตามปริมาณการ  
 เข้าแทนที่ของสารดัดแปรในโครงสร้างของเซลลูโลส และเซลลูโลสดัดแปรที่ได้มีสมบัติในการทนต่อความร้อน  
 ลดลง ซึ่งเป็นการยืนยันถึงความสำเร็จในการดัดแปรเซลลูโลส โดยภาวะเหมาะสมที่ให้ค่าน้ำหนักเพิ่มขึ้นสูงสุด  
 และให้ค่าระดับชั้นการแทนที่สูง กลาง และต่ำ สำหรับใบสับปะรดอยู่ที่ 160 วัตต์ 90 วินาที 240 วัตต์ 60 วินาที  
 และ 240 วัตต์ 30 วินาที สำหรับเปลือกข้าวโพดอยู่ที่ 240 วัตต์ 60 วินาที 160 วัตต์ 150 วินาที และ 320 วัตต์ 90  
 วินาที และสำหรับเศษผ้าฝ้ายอยู่ที่ 240 วัตต์ 90 วินาที 160 วัตต์ 90 วินาที และ 240 วัตต์ 30 วินาที ตามลำดับ

จากนั้นทำการขึ้นรูปเป็นฟิล์มเซลลูโลสดัดแปรที่มีระดับชั้นการแทนที่สูง กลาง และต่ำ โดยกระบวนการ  
 หล่อแบบด้วยสารละลายคลอโรฟอร์ม ผลการศึกษาพบว่า เมื่อฟิล์มเซลลูโลสดัดแปรมีระดับชั้นการแทนที่เพิ่ม  
 สูงขึ้น สมบัติด้านความมันเงาและสมบัติความทนแรงดึงมีค่าเพิ่มขึ้น ขณะที่สมบัติการเปียกที่พื้นผิวและการดูด  
 ชีมน้ำมีค่าลดลง ส่วนความสามารถในการย่อยสลายทางชีวภาพของฟิล์มเซลลูโลสดัดแปรพบว่า ฟิล์มเซลลูโลส  
 ดัดแปรที่มีความสามารถในการย่อยสลายทางชีวภาพได้มากขึ้นเมื่อระดับชั้นการแทนที่น้อยลง ซึ่งฟิล์ม  
 เซลลูโลสดัดแปรจากใบสับปะรดและเปลือกข้าวโพดสามารถเกิดการย่อยสลายทางชีวภาพได้ดีที่สุดในภาวะการ  
 ใช้ปุ๋ยหมักชีวภาพ ในขณะที่ฟิล์มเซลลูโลสดัดแปรจากเศษผ้าฝ้ายสามารถเกิดการย่อยสลายทางชีวภาพได้ดีที่สุดใน  
 ภาวะการแช่ในบ่อน้ำบาดน้ำเสีย

ภาควิชาวัสดุศาสตร์..... ลายมือชื่ออนิสิต.....  
 สาขาวิชาวิทยาศาสตร์พอลิเมอร์ประยุกต์และเทคโนโลยีสิ่งทอ..... ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์หลัก.....  
 ปีการศึกษา...2552.....

# # 5072235423 : MAJOR APPLIED POLYMER SCIENCE AND TEXTILE TECHNOLOGY

KEYWORDS : CELLULOSE / ESTERIFICATION / MICROWAVE / DEGREE OF SUBSTITUTION / BIODEGRADABILITY

JITTIPORN SAENG-ON : INFLUENCE OF DEGREE OF SUBSTITUTION ON PHYSICAL PROPERTIES AND BIODEGRADABILITY OF MODIFIED CELLULOSE FILMS FROM PINEAPPLE LEAF, CORN HUSK, AND WASTE COTTON FABRICS UNDER MICROWAVE ENERGY. THESIS ADVISOR : ASSOC. PROF. DUANGDAO AHT-ONG, Ph.D., 146 pp.

This research investigated the effects of degree of substitution (DS) on physical properties and biodegradability (i.e., real composting condition, waste water treatment system condition and enzymatic degradation) of modified cellulose films from pineapple leaf, corn husk, and waste cotton fabric. The modified cellulose were prepared in homogeneous LiCl/DMAc solvent system by esterification reaction under microwave energy in terms of microwave power and time and using lauroyl chloride as an esterifying agent. Additionally, the chemical structure of the obtained product was characterized by FTIR and  $^1\text{H-NMR}$ . The results showed that modified cellulose from all cellulose sources exhibited evidence of esterification by showing the increasing in the ester bands at  $1750\text{ cm}^{-1}$  (carbonyl C=O stretching of ester), and the decreasing in the intensity of O-H band at  $3300\text{ cm}^{-1}$ . In addition, all celluloses revealed aggregation of fatty acid side chain groups on the surface thus resulted in rough surface and larger dimension. The optimum conditions for modification of pineapple leaf, corn husk, and waste cotton fabric that yield low, medium, and high degree of substitution (DS) values with reasonable %weight increase under microwave heating were 30 second 240 watt (DS 1.93), 60 second 240 watt (DS 2.23), and 90 second 160 watt (DS 2.46) for pineapple leaf, 90 second 320 watt (DS 1.99), 150 second 160 watt (DS 2.44), and 60 second 240 watt (DS 2.73) for corn husk, and 30 second 240 watt (DS 1.95), 90 second 160 watt (DS 2.27), and 90 second 240 watt (DS 2.48) for waste cotton fabrics, respectively.

Then, modified cellulose powder with DS value was formed the film by casting method with chloroform. It was found that the degree of substitution (DS) affected the physical and mechanical properties of esterified cellulose films that the gloss value and tensile properties increased with increasing of DS value while the wettability and water absorption decreased with increasing of DS value. In addition, biodegradability of esterified cellulose films was also dependent upon DS value where biodegradation rate increased with decreasing of DS value. Considering biodegradation condition, it was found that pineapple leaf and corn husk films had the highest biodegradability in real composting condition; while cotton films had the highest biodegradation rate in waste water treatment system condition.

Department : Materials Science ..... Student's Signature .....

Field of Study : Applied Polymer Science and Textile Technology ..... Advisor's Signature .....

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# CHAPTER I

## INTRODUCTION

Nowadays, we are confronting with a number of environmental problems such as pollutions (e.g., air, water and soil) and a decrease in natural resources. Especially, petroleum resources which have been used every day for producing plastics so they are being exhausted in less than one century because they are not renewable resources. Moreover, synthetic plastic waste is becoming an importantly environmental problem since has been dumped and accumulated in nature due to its biodegradable resistance. The development and utilization of biodegradable cellulose-based plastic film may be a good candidate or solution to both problems.

Cellulose is the most abundant renewable raw material, and biodegradable polymer. It is estimated that about  $5 \times 10^{10}$  tons of cellulose are generated each year throughout the world [1]. It is a glucose polymer photosynthesized by solar energy and is the main component of plant cell wall [2]. Cellulose structure is a linear homopolymer composed of macromolecule of D-glucose units (so called anhydroglucose units) which link continuously through the  $\beta$ -1,4-glycosidic linkage. The interaction between oxygen and hydrogen atoms in the cellulose molecule forms the intra- and intermolecular hydrogen bonds. The cellulose polymer contains three reactive hydroxyl groups at C-2, C-3, and C-6 atoms, which are accessible to the typical conversions of primary and secondary alcoholic OH groups. In general, cellulose exhibits a highly ordered microcrystalline structure alternating with regions of distinctly lower order (amorphous regions). The crystalline nature of cellulose creates from intermolecular force between neighboring cellulose chain over long lengths. For this reason, cellulose is insoluble in common organic solvents and it is not melt-processible due to the large amount of intra- and intermolecular hydrogen bondings and its high crystallinity in structure. As a result,

it cannot be converted into the thermoplastic. However, after chemical modification, cellulose can be soluble in common organic solvents and is easy to process; hence, it can have a wide range of applications such as coatings, laminates, composites, and plastics [3]. The most widely used reactions for chemical modification of cellulose are esterification, etherification, and crosslinking. Among them, the esterification of cellulose with fatty acid has been very interested. The reaction of cellulose modification is occurred by fatty acids substitution on hydroxyls groups available on each anhydroglucose ring. The success of modification reaction of cellulose can be evaluated from the degree of substitution or DS value which is the parameter determining substituted value of hydroxyls groups in cellulose structure. It is indicated as the average number of hydroxyl groups substituted by modifying agent in a glucose unit. Theoretically, the maximum degree of substitution value is 3. Nevertheless, in general, the degree of substitution values were found to be in the range of 0.5-2.92, depending on reaction system, catalyst, modifying agent, heating method, and reaction time. The degree of substitution value of modified cellulose can define the properties of modified cellulose such as solubility, swelling, and biodegradability which are strongly affected by changing the degree of substitution value [4].

Biodegradation is a biochemical transformation of compounds into mineralization by microorganisms. Commonly, microorganisms (e.g., bacteria and fungi) behave differently and are also quite specific with respect to the degradation of polymer. Parameters such as humidity, temperature, pH, salinity, the presence or absence of oxygen, and the supply of different nutrients have important effects on the microbial degradation of polymer, and so these conditions must be considered when the biodegradability of polymer is investigated [5]. The most important factor in determination of biodegradation is the proper selection of test procedure based on the nature of plastic and the climatic conditions of the study environment. There are wide varieties of methods currently available for measuring the biodegradability of polymeric materials such as soil burial method, pure culture method, compost method, enzymatic

degradation, and an aerobic degradation in the presence of sewage sludge. Biodegradation can be characterized with loss of weight, change in tensile strength, change in dimensions, change in chemical and physical properties, carbon dioxide production, bacterial activity in soil and change in molecular weight distribution.

From our previous work [6], we have found that the modified cellulose films from pineapple leaf, corn husk, and cotton fabric had a very good potential to be degraded under soil burial test. Pineapple leaf, corn husk, and cotton fabric were used as cellulose resources because they are agricultural and industrial wastes generated in large amount every year. All of them are annually renewable, low cost, and copious source for cellulose. Furthermore, the cotton fabric has the highest cellulose content (95%); whereas, pineapple leaf and corn husk have relatively low lignin content and are easy to be delignified. The compositions of pineapple leaf are cellulose (70-80%), hemicellulose (18-19%), lignin (5-12%), and ash (0.7-0.9%); whereas those of corn husk are cellulose (38-40%), hemicellulose (28%), lignin (7-21%), and ash (3.6-7.0%) [7]. The obtained modified cellulose films were tested in the terms of mechanical properties and biodegradability and the results showed that the tensile properties of modified cellulose films increased with increasing DS value. The biodegradability of modified cellulose films presented an increasing of %weight loss and appearance of numerous small holes caused by microorganisms consumption on the film surface after 30 days of soil burial test. However, in reality, after the useful life-time plastics will be both intentionally and unintentionally discarded or exposed to different disposal environments besides landfill or soil burial test where the biodegradation rate of biodegradable plastics is strongly dependent upon the disposal environment (soil, landfill, composting environment, fresh water or sea water, etc.) and its conditions (temperature, moisture level, oxygen, pH value, microorganisms, etc.). Accordingly, in some environments a very efficient degradation mechanism may be occurred; while in other environments the same mechanism might not be worked due to lack of suitable conditions in particular microorganisms (their concentration, the concentration of enzymes, the nutrients for

microorganisms, etc). Hence, the biodegradability of esterified-cellulose films in other disposal environments such as under composting condition and waste water treatment system should be determined to find the appropriate disposal environments and condition for these biodegradable films.

Therefore, the objective of this work was to study the biodegradability of esterified-cellulose films from pineapple leaf, corn husk, and waste cotton fabric as a function of DS values under different biodegradation methods. The microwave energy was selected as a heating source for the esterification reaction to reduce time and energy used. By varying the microwave power and reaction time, modified cellulose with different degree of substitution values was achieved. The influences of DS values on physical, mechanical, and biodegradability of esterified-cellulose film were investigated. In particular, the effects of DS values and cellulose source on the biodegradability of modified cellulose film under different conditions, i.e., real composting condition, waste water treatment system, and enzymatic degradation were compared and evaluated.

## CHAPTER II

### LITERATURE REVIEWS

#### 2.1 Cellulose

##### 2.1.1 Cellulose Source

Cellulose is the most abundant renewable polymer in nature. It has been estimated that, by photosynthesis,  $10^{11}$ - $10^{12}$  tons are synthesized annually in a rather pure form, e.g., in the seed hairs of the cotton plant, but mostly are combined with lignin and other polysaccharides (so-called hemicelluloses) in the cell wall of woody plants [8].

Cellulose is found in plants as microfibrils (2-20 nm in diameter and 100-40,000 nm in length). These form the structurally strong framework in the cell walls. The structure strength of plant cell walls is due to the ease with which cellulose molecules form stabilizing networks of intra- and interchain secondary forces, resulting in straight, stable supramolecular fiber of great tensile strength.

Wood pulp is the most important raw material source for the processing of cellulose. Although generally considered a plant material, cellulose is also produced by some bacteria, algae, and fungi. Commercial cellulose supplies an annual world consumption of about 150 million tons of fibrous raw materials. The greatest portion of this amount, derived mostly from pulped wood, is used for the production of paper. Another significant amount, mostly from cotton, goes into the manufacturing of textiles.

Table 2.1 presents chemical composition of some cellulose sources [7]. As a naturally occurring material, cellulose may contain by-products, in which application problems and difficulties in chemical modifications are possible.

Table 2.1 Chemical composition of some cellulose sources [7]

| Source      | Composition (%) |               |        |         |
|-------------|-----------------|---------------|--------|---------|
|             | Cellulose       | Hemicellulose | Lignin | Extract |
| Wheat Straw | 30              | 50            | 15     | 5       |
| Bagasse     | 40              | 30            | 20     | 10      |
| Soft wood   | 40-44           | 25-29         | 25-31  | 1-5     |
| Hard wood   | 43-47           | 25-35         | 16-24  | 2-8     |
| Flax        | 71.5            | 20.6          | 2.2    | 6       |
| Jute        | 71.2            | 13.6          | 13.1   | 1.8     |
| Henequen    | 77.6            | 4.8           | 13.1   | 3.6     |
| Ramie       | 76.2            | 16.7          | 0.7    | 6.4     |
| Cotton      | 95              | 2             | 0.9    | 0.4     |

### 2.1.2 Pineapple Leaf and Corn Husk Cellulose

In Thailand, pineapple is one of the popular tropical fruits. It is available in a large quantity every year. Thailand is now one of the major producers and exporters of pineapple in the world. During the past five years, the average annual production amounted to two million tons. While the total production area of approximately 100,000 ha [9] is spread over thirteen provinces, most of the pineapple farms are located along the East and the West Coasts of the Gulf of Thailand. After harvesting pineapple for domestic fresh consumption and food industry, there are many leaves of pineapple turned to be waste.

Pineapple Leaf is waxy, strap-shaped leaves having 2 to 6 feet in length. It usually has a sharp point on the tip of the leaf and spines along the margins of the leaves. The leaf may be green or variegated in color. Pineapple leaf is multi-cellular and lignocelluloses materials extracted from the leaf of plant *Ananas cosomus* belonging to the Bromeliacea family by retting (separation of fabric bundles from the cortex). Pineapple leaf has a ribbon-like structure and is cemented together by lignin, pentosan-link materials, which contribute to the strength of the fiber. Approximately 70-82% of pineapple leaf is cellulose, another 18% is hemicellulose, 5-12% is a lignin, and 0.7-0.9% is ash [10]. It is rich in cellulose content; therefore, pineapple leaf residues are suitable for using as a source of cellulose production.

Corn husk is another interesting source for cellulose production. Corn husk is an agricultural residue with a Thailand annual yield of ~3.60 million tons [11]. Corn husk offers annually renewable, low cost, and copious source for cellulose production. In addition, the process of cellulose extraction from corn husk requires relatively lesser energy and is also environmentally friendly. Corn husk has the following compositions: 38-40% cellulose, 44% hemicellulose, 7-21% lignin, and 2.8-7% ash [10, 12].

### 2.1.3 Cellulose Structure

Cellulose is a polydisperse linear homopolymer consisting of macromolecule of D-glucose units (so-called anhydroglucose units [AGU]), as shown in Figure 2.1, which link successively through a glycosidic linkage in the  $\alpha$ -configuration between C-1 and C-4 of adjacent units to form long chain 1,4-glucans.

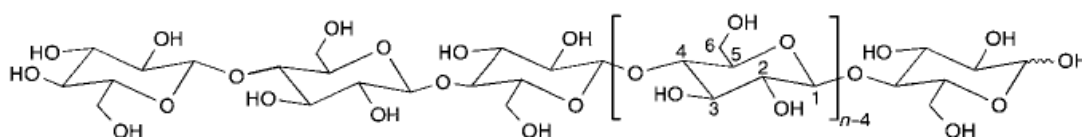


Figure 2.1 Molecular structure of cellulose

The interaction between oxygen and hydrogen atom in the cellulose molecule form the intra- and intermolecular hydrogen bonds. Figure 2.2 displays the intra- and intermolecular hydrogen bond in the cellulose structure.

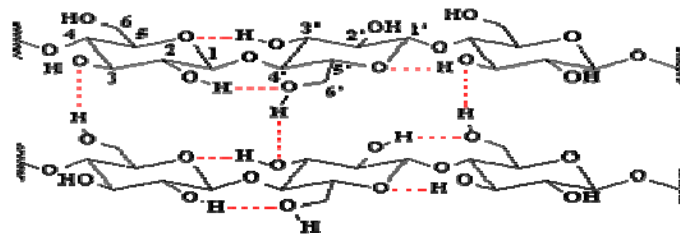


Figure 2.2 Intra- and intermolecular hydrogen bond in cellulose structure [13]

The  $\beta$ -glucosidic linkage in cellulose and the resulting intramolecular hydrogen bonds render the cellulose molecule straight and stiff. The cellulose polymer comprises three reactive hydroxyl groups at C-2, C-3, and C-6 atom, which are accessible to the typical conversion of primary and secondary alcoholic OH groups.

### 2.1.3.1 Crystalline Structure [8]

Solid cellulose presents a highly ordered microcrystalline structure alternating with regions of distinctly lower order (amorphous regions). The crystalline nature of cellulose originates from intermolecular forces between neighboring cellulose chains over long lengths. All native cellulose shows the same crystal lattice structure, called cellulose I. However, various modification of native cellulose can alter the lattice structure to yield other types of crystals (cellulose II, III, and IV). The intermolecular forces in the crystalline domains are mainly hydrogen bonds between adjacent cellulose chains in the same lattice plane, which results in a sheet-like structure of packed cellulose chains. In addition, the sheets are probably connected to one another by hydrogen bonds and/or Van der Waal's forces. The organization of cellulose molecules into parallel arrangements is responsible for the formation of crystallites. The length of



an elementary crystallite ranges from 12 to 20 nm (~24-40 glucose units) and width from 2.5 to 4 nm.

### 2.1.3.2 Supramolecular Structure

The tendency of hydroxyl groups to form intermolecular hydrogen bonds between neighboring cellulose chains, in combination with the stiff, strength nature of the cellulose molecules, results in the formation of crystallite strands. Such a strand of several crystals linked together by segments of long cellulose molecules constitutes the so-called elementary fibril, which is the basic structure component of the cellulose fiber. The interlinking regions between the crystalline areas in the strands have a distinctly less pronounced organization and thus constitute the amorphous cellulose. The elementary fibrils are packed together to form larger aggregates called micro- and microfibrils, these aggregations are then further organized in a typical manner (depending on source) in the cell wall. The lateral dimensions of these structural units are between 1.5 and 3.5 nm (elementary fibrils), between 10 and 30 nm (microfibrils), and on the order of 100 nm (microfibrillar bands). The length of the microfibrils is on the order of several hundred nm. Figure 2.2 shows electron micrographs of the fibrillar structure of samples of varying origins.

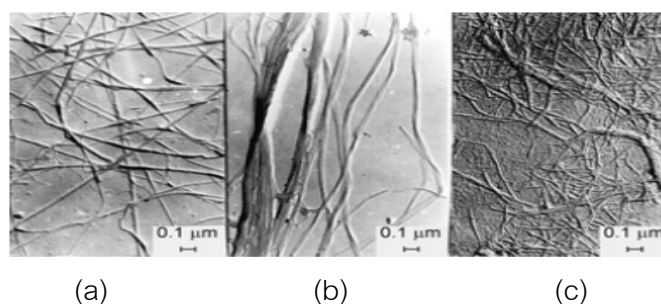


Figure 2.3 Electron micrographs of cellulosic microfibrils of varying origins (a) *Valonia* spp. (algae) cellulose, (b) cotton linters, (c) spruce sulfite pulps [8].

The fringed fibrillar model with crystalline regions of varying dimensions (crystallites) and noncrystalline regions has proven successful for the description of the structure of microfibrils and the partial crystalline structure of cellulose (Figure 2.4).

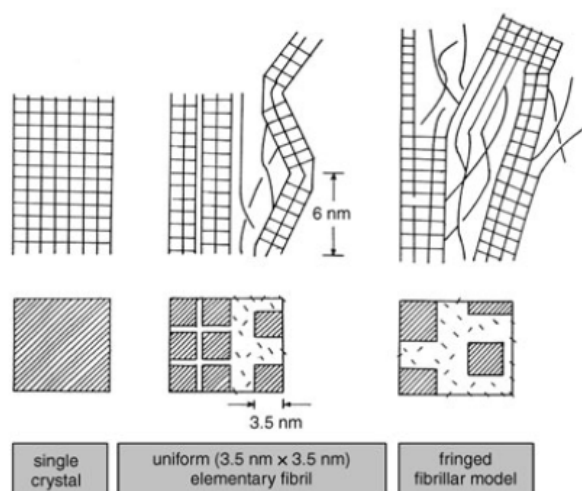


Figure 2.4 Various models of the supramolecular structure of cellulose microfibrils [8]

The degree of crystallinity of cellulose and the dimensions of the crystallites have been the subject of extensive investigations, some results of X-ray diffraction measurements of native celluloses have been compiled in Table 2.2.

Table 2.2 Degree of crystallinity ( $\chi_c$ ), crystallite sizes ( $D_{(hkl)}$ ), and lateral dimensions ( $d$ ) of microfibrils of native celluloses [8]

| Cellulose Source    | $\chi_c$ (%) | Crystallite sizes (nm) |             |             | $d$ (nm) |
|---------------------|--------------|------------------------|-------------|-------------|----------|
|                     |              | $D_{(1\bar{1}0)}$      | $D_{(110)}$ | $D_{(020)}$ |          |
| Algal cellulose     | >80%         | 10.1                   | 9.7         | 8.9         | 10-35    |
| Bacterial cellulose | 65-79        | 5.3                    | 6.5         | 5.7         | 4-7      |
| Cotton linters      | 56-65        | 4.7                    | 5.4         | 6.0         | 7-9      |
| Ramie               | 44-47        | 4.6                    | -           | 5.0         | 3-12     |
| Flax                | 44(56)*      | 4-5                    | 4-5         | 4-5         | 3-18     |
| Hemp                | 44(59)*      | 3-5                    | 3-5         | 3-5         | 3-18     |
| Dissolving pulp     | 43-56        | -                      | -           | 4.1-4.7     | 10-30    |

\*Degree of crystallinity relative to cellulose.

#### 2.1.4 Cellulose Modification

Cellulose is the most abundant and renewable biopolymer with outstanding properties and a variety of useful applications. However, some of the inherent properties of cellulose limit its utility in certain applications. The interactions between oxygen and hydrogen atoms in the cellulose molecule form the intra- and intermolecular hydrogen bonds. The  $\beta$ -glucosidic linkage in cellulose and the resulting intramolecular hydrogen bonds render the cellulose molecule straight and stiff.

From both a physical and chemical basis cellulose is a rather intractable material. It cannot be converted into different shapes by injection molding, or melt extrusion as due to its high melting point it thermally degrades prior to obtaining the ability to flow. Similarly, it is not soluble in common organic solvents, as a result, a major obstacle for utilizing cellulose in many industrial applications. Therefore, native cellulose is commonly modified by physical, chemical, enzymatic or genetic means in order to obtain specific functional properties.

Chemical modification is based on reactions of the free hydroxyl groups in the anhydroglucose monomers, resulting in changes in the chemical structure of the glucose units and ultimately, the production of cellulose derivatives. Chemically modified cellulose was developed primarily in order to overcome this insoluble nature of cellulose, thus extending the range of applications of polymer. Usually, these modifications involve esterification or etherification reactions of the hydroxyl groups. The cellulose molecule contains three different kinds of anhydroglucose units, as shown in Figure 2.5, with the reducing end with a free hemi-acetal (or aldehyde) group at C-1, the non-reducing end with a free hydroxyl at C-4, and the internal ring joined at C-1 and C-4.

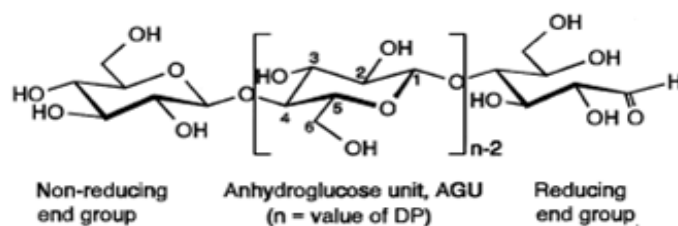


Figure 2.5 Molecular structure of cellulose [14]

But because of the long chain length, the chemistry of alcohol groups of the internal units predominates, so long as the chains are not cleaved by the reaction conditions. Cellulose reacts as trihydric alcohol with one primary and two secondary hydroxyl groups per glucose units. Thus, it can undergo esterification, etherification, oxidation, and other reactions such as halogenation. A great number of cellulose derivatives have been prepared by using these reactions and various reagents. However, unlike simple alcohols, cellulose reactions are usually controlled more by steric factor than would be expected on the basis of the inherent reactivity of the different hydroxyl groups. Each AGU is available for up to three sites of substitution; the hydroxyl group on C-2, C-3, and C-6. Therefore, derivatives are usually characterized in terms of a “degree of substitution (DS)”. The degree of substitution is defined as the average number of substituted hydroxyl groups per AGU and ranges from 0 to 3. Higher degree of substitution, or reaction conditions which disrupt the crystalline regions, can be used to reduce inter-chain hydrogen bonding and force the chain apart. This can result in a cellulose derivative that is soluble in common organic solvents, and thus capable of extrusion to form filaments, or other structure.

The manifold reactions of cellulose may be conveniently divided into two main kinds: those involving the hydroxyl groups and those comprising a degradation of the chain molecules. The former includes the following reactions [15]:

- (1) Esterification: nitration, acetylation, and xanthation
- (2) Etherification: alkylation and benzylation
- (3) Replacement of  $-OH$  by  $-NH_2$  and halogen

- (4) Replacement of -H in -OH by Na
- (5) Oxidation of -CH<sub>2</sub>OH to -COOH
- (6) Oxidation of secondary -OH groups to aldehyde and carboxyl
- (7) Formation of addition compounds with acids, bases, and salts

### 2.1.5 Esterification of Cellulose

Figure 2.6 shows the esterification process for making esters, which are the compound of chemical structure RCOOR', where R and R' are either alkyl or aryl groups. The most common method for preparing esters is to heat a carboxylic acid, R-CO-OH, with an alcohol R'-OH, while removing the water that is formed. In the reaction, the hydroxyl group (OH) of carboxylic acid is replaced by the alkoxy group (R'O) of alcohol. The reverse of reaction is an example of hydrolysis. A mineral acid catalyst is usually needed to make the reaction occur at a useful rate.

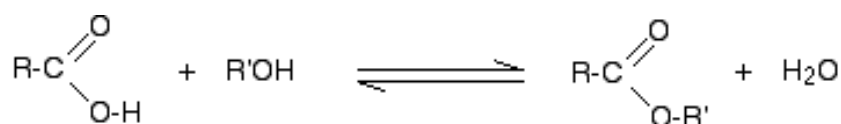


Figure 2.6 Esterification reaction

For example, esterification reaction of acetic acid in excess ethanol (possibly as the solvent) in the presence of concentrated sulfuric acid as a catalyst results in an ester (ethyl acetate) is shown in Figure 2.7.

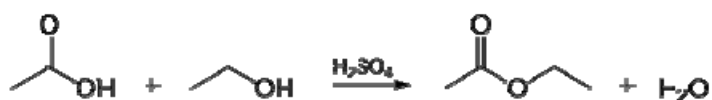


Figure 2.7 Esterification reaction of acetic acid and ethanol

Ester can also be formed by various other reactions. These include the reaction of an alcohol with an acid chloride ( $R-CO-Cl$ ) or an anhydride ( $R-CO-O-COR'$ ). Early studies into the chemical mechanism of esterification concluded that the ester product ( $R-CO-OR'$ ) is the union of the acyl group ( $R-C=O-$ ) from the acid,  $RCO-OH$ , with the alkoxide group ( $R'O-$ ) from the alcohol,  $R'-OH$ , rather than other possible combinations.

Similar to simple alcohols, the hydroxyl groups of cellulose can be esterified by reaction with acids or other acylating agents. In general, esters of organic acids are prepared by the reaction of cellulose with an acid anhydride or its mixture with acid in the presence of an acid catalyst (sulfuric acid, perchloric acid, etc.). They also may be prepared with an acyl halide or an acid anhydride in the presence of base (pyridine, sodium acetate, etc). Nitration with a mixture of nitric and sulfuric acids was used to produce the first man-made fibers. Acetylation with acetic acid or acetic anhydride produces a variety of different products with properties that depend on the DS.

Esterification of cellulose with carboxylic acids and carboxylic acid derivatives is among the most versatile transformations of this biopolymer. It gives ready synthetic access to a wide range of valuable products. Commercial processes are carried out exclusively under heterogeneous condition, due to the high viscosity of cellulose solutions, the high costs of solvents, and the ease of workup procedure in the case of multiphase conversions. One aims for completely functionalized derivatives because partial conversion leads mainly to insoluble polymer, specifically in the case of cellulose.

### 2.1.6 Applications of Cellulose

Cellulose has many uses as an anti-oxidant agent, emulsifier, stabilizer, dispersing agent, thickener, and gelling agent. Novel cellulose derivatives are beginning to play an important role in the "design for the environment" concept being adopted for materials in general and packaging materials in specific. Derivative of cellulose affords materials

that are possible into various useful forms, such as three dimensional objects fibers, and solutions to be used for coating or casting (of films or membranes). Additionally, the physical properties of cellulose can be greatly modified by derivatization. Cellulose derivatives were used into wide ranges of application such as coating, control release, plastics, biodegradable, optical films, membrane structure, composites and laminates [10]. Examples of some type of cellulose and applications are given in Table 2.2. The modified properties of these cellulose derivatives give entry into a range of applications greatly expanded from those available to the parent polysaccharide. It is important to gain a fundamental understanding of how structural changes are effected by cellulose esterification, the ability to predict how those changes will impact properties and an understanding of how those property changes translate into performance between application requirements, in some cases in cooperation with other materials or ingredients.

Table 2.3 Some types of cellulose and their applications [10]

| Type of Cellulose   | Applications  |
|---|---|
| Cellulose acetate   | Extruded tape, packaging film, blister packs, skins, containers, premium toys, electrical appliances housings and electrical insulation |
| Cellulose acetate butyrate (CAB) and cellulose propionate | Tooth brush handles, safety goggles, blister packs  |
| Ethyl cellulose   | Flashlight cases, fire extinguisher components and electrical appliance parts   |
| Cellulose triacetate                                      | Photographic albums, electrical insulation applications and photographic films base   |
| Cellulose nitrate   | Toilet articles and industrial items fabricated from sheet, rod and tube  |

## 2.2 Microwave Chemistry

### 2.2.1 Introduction

In the past 20 years, the microwave oven has become an essential appliance in most kitchens. Faster cooking times and energy saving over conventional cooking methods are the primary benefits. Although the use of microwave for cooking food is widespread, the application of this technology to the chemical reaction is a relatively new development. The use of microwave energy for synthesis reaction has potential to offer similar advantages in reduced synthesis times and energy savings.

While fire is now rarely used in synthetic chemistry, it was not until Robert Bunson invented the burner in 1855 that the energy from this heat source could be applied to a reaction vessel in a focused manner. The Bunson burner was later superseded by the heating mantle, oil bath, or hot plate as a source of applying heat to a chemical reaction. In the past few years, heating and driving chemical reaction by microwave energy has been an increasingly popular theme in the scientific community. This non-classical heating technique is slowly moving from a laboratory curiosity to an established technique having been used in both academic and industry. Microwave chemistry involves the use of microwave radiation to conduct chemical reaction, and essentially pertains to chemical analysis and chemical synthesis. Microwave radiation has been successfully applied to numerous industrial applications (drying, heating, sintering, etc).

Generally, most organic reactions have been heated using traditional heat transfer equipment such as oil baths, sand baths, and heating jackets. These heating techniques are, however, rather slow and a temperature gradient can develop within the sample. In addition, local overheating can lead to product, substrate, and reagent decomposition.



In microwave dielectric heating, the microwave energy is introduced into the chemical reactor remotely and direct access by the energy source to the reaction vessel is obtained. The microwave radiation passes through the walls of the vessel and heats only the reactants and solvent, not the reactor vessel itself. If the apparatus is properly designed, the temperature increase will be uniform throughout the sample, which can lead to less by-products and/or decomposition products. In pressurized systems, it is possible to rapidly increase the temperature far above the conventional boiling point of the solvent used.

### 2.2.2 Microwave Radiation

Microwaves are electromagnetic radiation which is discharged from mobile, electric charges and spreads out as a wave. The wavelength of this radiation decreases with increasing energy. If the wavelength of microwave is in the range 1 mm to 1 m which correspond to frequency of 300 MHz to 300 GHz. Household microwave ovens produce radiation with a fixed frequency of 2.45 GHz. In the electromagnetic spectrum microwaves lie between radio waves (1 m to 104 m) and infrared waves (760 nm to 0.5 mm) (Figure 2.8).

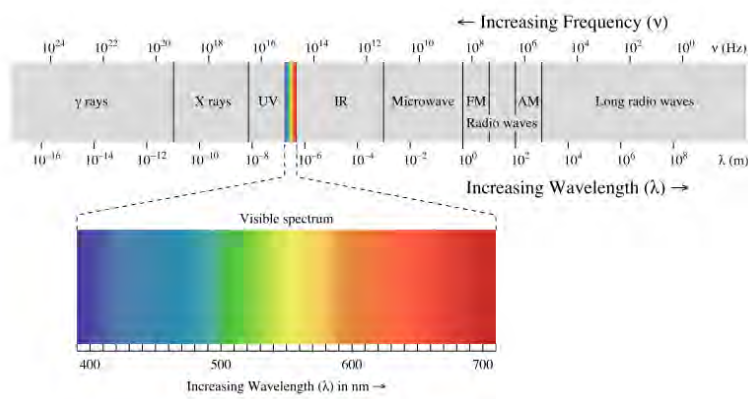


Figure 2.8 Electromagnetic spectrum [16]

Microwaves represent a non-ionizing radiation that influences molecular motions such as ion migration or dipole rotation, but not altering the molecular structure. In 2.45 GHz microwaves the oscillation of the electric field of the radiation occurs  $4.9 \times 10^9$  times per second; the timescales in which the field changes is about the same as the response time (relaxation time) of permanent dipoles present in most organic and inorganic molecules. This fact represents a fundamental characteristic for an efficient interaction between the electromagnetic field of microwave and a chemical system. The absorption of microwaves causes a very rapid increase of the temperature of reagents, solvents, and products. Moreover, in the case of solutions containing salts or strong acids and bases the energy can also be dissipated through ionic conduction, causing heating or overheating of the solvent (together with a possible increase of the pressure when the reaction is carried out in closed vessels)

### 2.2.3 Interaction of Microwave with Materials

One can broadly characterize how bulk materials behave in a microwave field. Materials can absorb the energy, they can reflect the energy, or they can simply pass the energy. It should be noted that few materials are either pure absorbers, pure reflectors, or completely transparent to microwaves. The chemical composition of the material, as well as the physical size and shape, will affect how it behaves in a microwave field. Since the response of various materials to microwave radiation is diverse, not all materials are amenable to microwave heating. Based on their response to microwaves, materials can be broadly classified as follows:

- Materials that are transparent to microwaves, e.g., sulphur
- Materials that reflect microwaves, e.g., copper
- Materials that absorb microwaves, e.g., water

Their interaction with matter is characterized by a penetration depth. That is, microwave can penetrate only a certain distance into a bulk material. If the penetration

depth of material is less than sample size, it is considered as a “surface heating”. On the contrary, a “volumetric heating” will occur in a bulk material when the penetration depth is larger than a sample size.

Materials which absorb the radiation are able to start the heating or to activate a chemical reaction. Many materials are practically transparent (quartz) and can be penetrated by the radiation; some other materials, such as metals, reflect the radiation; other materials, such as dielectrics, interact with microwaves to different extents. Chemical reactors must be transparent to microwave and are made of Teflon or polyethylene; glass is also a suitable material, especially for high temperature reactions, but it is not completely transparent to microwaves.

Material that absorbs microwaves can display different rates of heating, according to their composition and the dimension of their particles, when solids. The inclusion of such materials in the form of powder or fibers within the mass of polymer can improve microwave absorption and locally raise the temperature, thus increasing the hardening or improving the compaction of polymeric materials, indirectly acting as an adhesive.

#### **2.2.4 Microwave Heating Mechanism**

There are two specific mechanisms of interaction between materials and microwaves: (1) Dipole interactions and (2) ionic conduction. Both mechanisms require effective coupling between components of the target material and the rapidly oscillating electrical field of the microwaves.

Dipole interactions occur with polar molecules. The polar ends of a molecule tend to align themselves and oscillate in step with the oscillating electrical field of the microwaves. Collisions and friction between the moving molecules result in heating.

Broadly, the more polar a molecule, the more effectively it will couple with (and be influenced by) the microwave field.

Ionic conduction is only minimally different from dipole interactions. Obviously, ions in solution do not have a dipole moment. They are charged species that are distributed and can couple with the oscillating electrical field of the microwaves. The effectiveness or rate of microwave heating of an ionic solution is a function of the concentration of ions in solution.

Materials have physical properties that can be measured and used to predict their behavior in a microwave field. One calculated parameter is the dissipation factor, often called the loss tangent. The dissipation factor is a ratio of the dielectric loss (loss factor) to the dielectric constant. Taken one more step, the dielectric loss is a measure of how well a material absorbs the electromagnetic energy to which it is exposed, while the dielectric constant is a measure of the polarizability of a material, essentially how strongly it resists the movement of either polar molecules or ionic species in the material. Both the dielectric loss and the dielectric constant are measurable properties.

Microwave heating can have effects that are different from conventional heating technique, one must focus on what in the reaction mixture is actually absorbing the microwave energy. One must recognize the simple fact that materials or components of a reaction mixture can differ in their ability to absorb microwaves. Differential absorption of microwaves will lead to differential heating and localized thermal inhomogeneities that cannot be duplicated by conventional heating techniques. The several examples are presented with considering of microwave absorption by a bulk solvent and/or by the minor concentration of reactants in the solvent [17]:

#### Example 1: Solvent and reactants absorb microwaves equally

If the bulk solvent and reactants absorb microwaves equally, then energy transfer and heating will occur to the allowed depth of penetration into the bulk mixture. Homogeneous reaction conditions can be established with thorough mixing, and at equilibrium (chemical and thermal), the temperature of the reactants will be the same as that of the bulk solvent.

In this case, reaction rates can be increased by increasing the temperature of the reaction mixture. This can easily be achieved using closed-vessel microwave techniques, using the same reaction chemistry and solvent. Alternatively, using conventional heating techniques, higher reaction temperatures can be achieved in a closed reactor system, or by using a higher-boiling solvent in an open vessel.

#### Example 2: Solvent absorbs microwaves, reactants much less so

If the bulk solvent absorbs microwaves, but the reactants do not absorb (or absorb to a lesser extent than the solvent), then energy transfer and heating of the solvent will occur to the allowed depth of penetration. The bulk solvent will, in turn, heat the reactants by conduction. Homogeneous reaction conditions can be established with thorough mixing, and at equilibrium the temperature of the reactants will be the same as that of the bulk solvent.

This case is little different from conventional heating techniques. Reaction rates can be increased by increasing the temperature of the reaction mixture. Using closed-vessel microwave techniques previously mentioned. In conventional heating techniques, higher reaction temperatures can be achieved in a closed-vessel reactor system, or by using a higher-boiling solvent in an open vessel.

#### Example 3: Reactants absorb microwaves, solvent much less so

If the bulk solvent does not absorb microwaves, but the reactants do, then direct energy transfer and heating of the reactant molecules will occur to the allowed depth of penetration. The bulk solvent will, in turn, be heated by conduction

from the reactants. Although homogeneous reaction conditions can be established with thorough mixing, the temperature of the reactants will always be higher than that of the solvent, as long as the solvent continues to lose heat to the environment through the vessel wall.

This case is significantly different from conventional heating techniques. Reaction rates can be increased by increasing the temperature of the reactants, heat transfer from reactant to bulk solvent must be fast enough to overcome the heat loss from the reaction mixture to the environment. For this effect to be sustainable, careful attention must be paid to vessel design and vessel cooling. This effect can be achieved using microwave reflux techniques. It must be recognized that only the bulk temperature can be measured by direct insertion of a monitoring probe, so there really isn't any practical way of measuring a temperature differential between the reactants and the solvent. Multimode cavities, with their higher output power (1,000 watts or more), are best suited to creating the necessary conditions for obtaining this unique microwave effect.

#### Example 4: Catalysts on microwave absorbing supports

Some unusual reaction conditions can be created in a microwave field when catalysts are present in the mixture, particularly when the catalyst is deposited on a microwave-absorbing material. Palladium on carbon is a common catalyst in some reaction mechanisms. Carbon or graphite is an excellent absorber of microwave energy, with a dissipation factor significantly higher than most solvents.

An unexpected effect of the microwave field is that it can directly heat some catalyst supports, and create a condition where the catalyst is at a substantially higher temperature than the rest of the bulk mixture. The catalyst support will transfer heat to the bulk mixture by conduction. There really is not any practical way to measure the temperature at the surface of the catalyst support. The enhanced reactivity, however, can be quite dramatic, as evidenced by the reaction products. This superheating of the catalyst cannot be duplicated by conventional means. Multimode

cavities, with their higher output power (1,000 watts or more), are better suited to creating the necessary conditions for obtaining this unique microwave effect.

### 2.2.5 Application of Microwave Chemistry

Due to the successful development of commercial instrumentation, microwave dielectric heating is now being increasingly applied in chemical reactions. It has been successfully applied in varied industries such as the biotechnology, pharmaceuticals, petroleum, plastics, chemicals, etc. However, most of these applications have been limited to small-scale use in laboratories and have not been extended to the production level.

The major industrial applications of microwave chemistry can be segmented as:

#### (1) Applications in Analytical Chemistry

The various applications of microwave radiation in analytical chemistry encompass the following process:

1. Ashing
2. Digestion
3. Extraction
4. Protein hydrolysis
5. Moisture/solids analysis
6. Spectroscopic analysis

#### (2) Applications in Chemical Synthesis

Application of microwave radiation in chemical synthesis encompasses its use in the acceleration of chemical synthesis. Microwave-enhanced synthesis allows organic chemists to work faster, generate higher yields, and increase product purity. In addition, due to the availability of high-capacity microwave apparatus, the yields of the experiments have now easily scaled up from milligrams to kilograms, without the need to alter reaction parameters.

## 2.3 Biodegradation [18]

### 2.3.1 Introduction

Biodegradation is a biochemical transformation of compounds in mineralization by microorganisms. Mineralization of organic compounds yields carbon dioxide and water under aerobic conditions, and methane and carbon dioxide under anaerobic conditions. According to ASTM standard D-5488-94d, biodegradation is defined as “process which is capable of decomposition of materials into carbon dioxide, methane, water, inorganic compounds, or biomass in which the predominant mechanism is the enzymatic action of microorganisms, that can be measured by standard tests, in a specified period of time, reflecting available disposal conditions”.

Biodegradability is also defined as the propensity of a material to get breakdown into its constituent molecules by natural processes (often microbial digestion). The metabolites released by degradation are also expected to be non-toxic to the environment and redistributed through the carbon, nitrogen and sulfur cycles.

Biodegradation can occur at different structural levels, i.e. molecular, macromolecular, microscopic, and macroscopic depending upon the mechanism. It has been argued that the phenomenon of degradation in vivo might not be equated with the term biodegradation, since biodegradation implies the active participation of biological entities such as enzymes or organisms in the degradation process.

### 2.3.2 Mechanism of biodegradation

The biodegradation of polymer is usually a heterogeneous process. Because of a lack of water-solubility and the size of the polymer molecules, microorganisms are unable to transport the polymeric material directly into the cells where most biochemical



processes take place; rather, they must first excrete extracellular enzymes which depolymerize the polymers outside the cells (Figure 2.9). As a consequence, if the molar mass of the polymers can be sufficiently reduced to generate water-soluble intermediates, these can be transported into the microorganisms and fed into the appropriate metabolic pathway(s). As a result, the end-products of these metabolic processes include water, carbon dioxide, and methane (in the case of anaerobic degradation), together with a new biomass. The extracellular enzymes are too large to penetrate deeply into the polymer material, and so act only on the polymer surface; consequently, the biodegradation of plastics is usually a surface erosion process.

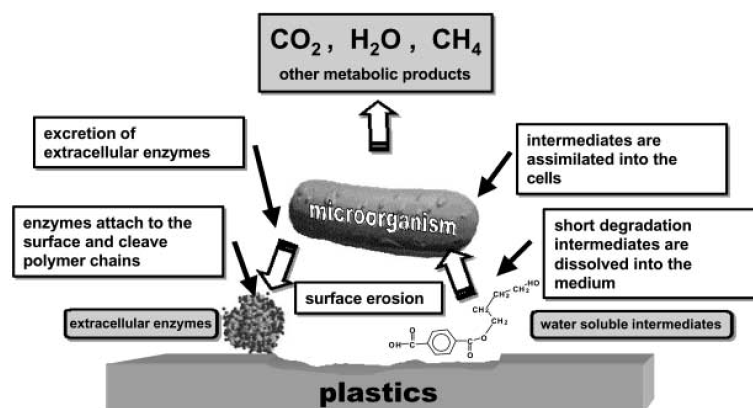


Figure 2.9 Mechanism of polymer biodegradation [5]

### 2.3.3 Factors Affecting Biodegradation

Biodegradation of polymer affected by various factors are given below:

#### (1) Mode of Microorganism

Microorganisms, e.g., bacteria and fungi, behave differently. Although they are commonly also quite specific with respect to the degradation of the substrate, many of them are, however, capable of adapting to the substrate. It is known that although a great number of microorganisms can produce a variety of enzymes, microorganisms usually specialize on the attack of only a single substrate and are, therefore, producing only one or a few enzymes. If the substrate is changed, the microorganisms start after a

few weeks or months the production of new enzyme capable of attacking the new substrate. The capability of microorganisms to adapt to new substrate is, of course, of great importance to the problem of the biodegradability of synthetic polymers.

### (2) Environmental Factor

Not only influence the polymer to be degraded, they also have a crucial influence on the microbial population and on the activity of the different microorganisms themselves. Parameters such as humidity, temperature, pH, salinity, the presence or absence of oxygen, and the supply of different nutrients have important effects on the microbial degradation of polymers, and so these conditions must be considered when the biodegradability of polymer is tested.

### (3) Chemical Structure of Polymer

In many cases polymer do not consist simply of only one chemical homogeneous component, but contain different polymers (blends) or low-molecular weight additives (e.g., plasticizers). Moreover, within one polymer itself different structural elements can be presented (copolymers), and these may either be distributed statistically along the polymer chains (random copolymers) or distributed alternately (alternating copolyesters); they may also be used to build longer blocks of each structure (block-copolymers). Another structural characteristic of a polymer is the possible branching of chains or the formation of networks (cross-linked polymers). These different structures of a polymer, despite having the same overall composition, can directly influence accessibility of the material to the enzyme-catalyzed polymer chain cleavage, and also have a crucial impact on higher-ordered structures of the polymers (crystals, crystallinity, and glass transition) which have been shown in the degradation behavior of polymers.

### 2.3.4 Methods for Biodegradation

The most important factor in determination of biodegradation is the proper selection of test procedure based on the nature of plastic and the climatic conditions of the study environment. There are wide varieties of methods currently available for measuring the biodegradability of polymeric materials.

#### 2.3.4.1 Soil Burial Method

Soil burial method is one of the frequently used methods for the determination of biodegradability of plastic. In this method, biodegradation test is performed under natural conditions or laboratory conditions. Sample with definite weight and dimension is buried in specific depth in the soil for different time intervals. From time to time, samples are withdrawn and analyzed for signs and quantitative characteristics of decomposition, such as weight loss, mechanical properties, or a microscopic (SEM) examination.

#### 2.3.4.2 Pure Culture Method

In pure culture method, specific bacteria and fungi can be applied for degradation of polymers. After that, isolated microorganism strain has been allowed for sufficient growth in different nutrient media. In pure culture method, pre-weighed disinfected films are aseptically added to sterilized culture medium and films in culture medium are incubated with shaking for 24 hours before inoculation to ensure asepsis. Culture medium is inoculated with spores from a specific microorganism and is incubated with shaking at 125 rpm for 4 weeks at optimal growth temperature for the selected microorganism. Four replicates are prepared for each different pretreated film. The sample is weighed after washing with 70% ethanol and drying at 45°C until equilibrated. Each of the different films is then compared with the corresponding uncultured material. The presence of microbes can be confirmed by using a microscope.

#### 2.3.4.3 Compost method

In this method, the definite weight of the polymer is subjected to the mixture of definite amount of mature compost and then incubated at 58°C with maintained moisture content at 65%. Biodegradation is measured based on the amount of material carbon converted to gaseous carbon dioxide. Nature of compost affects the degree of degradation. Mesophilic bacteria and mesophilic actinomycetes (the mesophilic microorganisms live at medium temperatures (20-45°C)) are fewer in number in the compost stored at 20°C than in the compost stored at the other two lower temperatures (i.e., -20°C and 4°C) contrary to expectation. Activity of the extracellular enzymes plausibly excreted by the microbes in the compost decreased as a result of the storage. Shape of the plastic sample and additives in the compost effect the polymer degradation in the compost. Vermiculite, a clay mineral, can be activated and used as a solid matrix in place of mature compost. The composting test method based on activated vermiculite is a comprehensive system for the assessment of the environmental impact of biodegradable polymer. Activated vermiculite affects neither the biodegradation rate nor the final biodegradation level. On the other hand, possible metabolic intermediates and polymeric residues left after biodegradation can be recovered more easily from activated vermiculite than from mature compost, a very complex organic matter. Therefore, at end of the test it has been possible to determine the carbon balance that is by taking into account both the evolved CO<sub>2</sub> and a polymeric residue extracted from vermiculite.

#### 2.3.4.4 Aerobic degradation in the presence of sewage sludge

Because of enriched environment of sewage sludge, the microbes present are more diverse in composition than other disposed methods encountered. In laboratory conditions, samples have been inoculated with sewage microbes. Gaseous CO<sub>2</sub> and CH<sub>4</sub> are monitored by headspace analysis using GC/MS.

### 2.3.5 Evaluation of Biodegradation

Biodegradation can be characterized as follow:

- Loss of weight
- Change in dimensions
- Change in tensile strength
- Carbon dioxide production
- Change in microorganisms population
- Change in molecular weight distribution
- Change in chemical and physical properties

## 2.4 Literature Review of Biodegradation

Currently, there are standard test methods that are designed for determining biodegradation of plastic materials in order to proper selecting for studying rate of biodegradation of various plastics both degradable and nondegradable plastics. Many researches have been studied on biodegradation of plastics by comparing the standard test methods and the type of plastics.

In 2005, Y. Rudeekit, T. Leejakpai, N. Euaphantasate, and K. Kongsuwan [19] compared the degradation of biodegradable plastic by aerobic microorganism using ASTM D5338-98(03) and ASTM D5988-03 as standard methods. They found that the biodegradation of cellulose as the positive control in testing soil for 89 days using ASTM D5338-98(03) was 4.06%. The LDPE/starch blends (11.51%) and starch foam (24.86%) were degraded approximately three and six times of filter paper, respectively. Whereas, the biodegradation of filter paper was 11.78% in testing soil for 89 days using ASTM D5988-03. Compared to that of filter paper, the biodegradation of LDPE/starch blends (31.87%), and starch foam (85.14%) was approximately three and seven times, respectively. This corresponded well with the results from ASTM D5338-98(03) and indicated that both standards gave the comparable result.

In addition, there are researches about biodegradation of modified cellulose and other polymer. For example, in 1997, M. Van Dee Zee, J. H. Stoutjesdijk, H. Feil, and J. Feijen [20] investigated the relevance of the modified Sturm test for predicting degradation of solid materials during a typical biological waste treatment process. To achieve this, aquatic biodegradability of the water insoluble polymeric material is compared with its mineralization under laboratory controlled composting conditions. Cellulose acetates with varying degrees of substitution (DS 1.5 to 3.0) have been chosen as representative substrates since they are well documented, chemically modified polymers, known to mineralize with different degradation rates under composting conditions. They reported that cellulose acetates with DS  $\leq$  2.5 were readily mineralized to CO<sub>2</sub> in the controlled composting test. The degradation rate was clearly affected by the degree of substitution (DS 1.5 > DS 2.5 > DS 3.0). Surprisingly, however, biodegradation of cellulose acetate materials was not observed in the aquatic Sturm test. Modifications of the pH and the inoculum source in an attempt to improve the activity of fungi and actinomycetes in the aquatic environment did not increase CO<sub>2</sub> evolution. It is concluded that the relevance of modified Sturm tests is limited for predicting complete biodegradation of polymeric materials during biological waste processing.

Also in 1997, E. Samios, R. K. Dart, and J. V. Dawkins [21] prepared and characterized the biodegradation on cellulose acetates with varying degrees of substitution (DS) between 0.7 and 1.7. The result showed that the biodegraded polymers follow the trends for the starting polymers, i.e. there is a drop in the molecular weight, becoming very marked with decreasing DS. The molecular weight drop in the DS 1.7 and DS 1.5 polymers is generally small, and can be attributed to the loss of acetate groups. The large subsequent drop in the DS 1.0 polymer, however, shows that depolymerization has also taken place.

In 2002, T. Ishigaki, W. Suganob, M. Ikek, and H.Taniguchid [22] investigated the effect of UV irradiation on enzymatic degradation of highly substituted cellulose acetate (CA). The results showed that the degradability of CA by cellulase decreased with increasing the degree of substitution (DS) of CA. Combination of the deacetylating enzyme (lipase or esterase) and cellulase did not promote the degradation of CA with DS 2.4. On the other hand, the UV-irradiated CAs that were suspended in the sterilized buffer and cellulase solution showed 23% and 60% of weight loss, respectively. UV irradiation resulted in the decrease of molecular weight of CA and did not affect DS. Observation by atomic force microscope confirmed that UV irradiation increased the surface area of CA film. Wash-out of depolymerized component from UV-irradiated CA film would increase the surface area and the contactability with cellulase. These results suggested that degradation of CA by cellulase would be positively influenced by UV irradiation under the natural environment.

Two year later, in 2004, T. Ishigaki, W. Sugano, A. Nakanishi, M.Tateda, M. Ike, and M. Fujita [23] investigated degradabilities of four kinds of commercial biodegradable plastics (BPs), polyhydroxybutyrate and hydroxyvalerate (PHBV) plastic, polycaprolactone plastic (PCL), blend of starch and polyvinyl alcohol (SPVA) plastic and cellulose acetate (CA) plastic in waste landfill model reactors that were operated as anaerobically and aerobically. They found that degradation behavior of BPs under the aerobic condition was completely different. PCL, a chemically synthesized BP, showed film breakage under the both conditions, which may have contributed to a reduction in the waste volume regardless of aerobic or anaerobic conditions. Effective degradation of PHBV plastic was observed in the aerobic condition, though insufficient degradation was observed in the anaerobic condition. But the aeration did not contribute much to accelerate the volume reduction of SPVA plastic and CA plastic. It could be said that the recalcitrant portions of the plastics such as polyvinyl alcohol in SPVA plastic and the highly substituted CA in CA plastic prevented the BP from degradation. These results indicated existence of the great variations in the degradability of BPs in aerobic and

anaerobic waste landfills, and suggest that suitable technologies for managing the waste landfill must be combined with utilization of BPs in order to enhance the reduction of waste volume in landfill sites.

In 2007, M.R. Calil, F. Gaboardi, C.G.F. Guedes, and D.S. Rosa [24] compared the biodegradation of poly( $\epsilon$ -caprolactone) (PCL), cellulose acetate (CA), and their blends using an aerobic biodegradation technique known as the Sturm test. Their biodegradation was assessed by their carbon dioxide (CO<sub>2</sub>) production and susceptibility to attack by a mixture of fungal strains in solid and liquid media in which samples of each blend were the only source of carbon. The extent of biodegradation was assessed by the loss of mass. The results show that the 40PCL/60CA blend showed faster biodegradation than the other blends because of its higher CO<sub>2</sub> production in aerobic medium (Sturm test). PCL was more susceptible to attack by a mixture of fungi on solid medium than was CA but showed a lower loss of mass (8.4%) than the latter polymer; the 60PCL/40CA blend showed the greatest loss of mass during the period of evaluation. In contrast, in liquid medium, PCL showed a greater loss of mass.



## CHAPTER III

### EXPERIMENTAL SECTION

#### 3.1 Materials and Chemicals

##### 3.1.1 Raw materials

In this work, pineapple leaf (Figure 3.1a), corn husk (Figure 3.1b), and waste cotton fabric (Figure 3.1c) were used as raw materials. Pineapple leaf and corn husk were obtained from local market. Waste cotton fabric was attained from a local textile factory.



Figure 3.1 (a) Pineapple leaf, (b) corn husk, and (c) waste cotton fabric

##### 3.1.2 Chemicals

- Sodium hydroxide (NaOH, analytical reagent 99.0%) was purchased from RCI Lab-Scan Asia Co., Ltd., Thailand.
- Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, analytical reagent 30%) was purchased from Merck Schuchardt OHG, Germany.
- Hydrochloric acid (HCl, analytical reagent 37%) was purchased from RCI Lab-Scan Asia Co., Ltd., Thailand.

- N,N-dimethylacetamide (DMAc, analytical reagent 99.5%) was purchased from RCI Lab-Scan Asia Co., Ltd., Thailand.
- Lithium chloride (LiCl, analytical reagent 99%) was purchased from Unilab (Ajax Finechem), Switzerland.
- N,N-dimethyl-4-aminopyridine (DMAP, analytical reagent  $\geq 98.0\%$ ) ( $C_7H_{10}N_2$ ) was purchased from Fluka Analytical (Sigma-Aldrich Germany).
- Lauroyl Chloride ( $CH_3(CH_2)_{10}CClO$ , analytical reagent  $\geq 97.5\%$ ) was purchased from Fluka Analytical (Sigma-Aldrich Germany).
- Ethanol ( $CH_3CH_2OH$ , analytical reagent 99.8%) was purchased from was purchased from RCI Lab-Scan Asia Co., Ltd., Thailand.
- Chloroform ( $CHCl_3$ , analytical reagent 99.8%) was purchased from RCI Lab-Scan Asia Co., Ltd., Thailand.

### 3.2 Instruments

Table 3.1 shows the instruments listed consecutively based on experimental procedure.

Table 3.1 Experimental instruments

| Instruments                                    | Model                       | Manufacturer             |
|--|-----------------------------|--------------------------|
| Hot plate                                      | MR Hei-Standard             | Heidolph                 |
| Microwave Oven                                 | MS2447BB                    | LG Electronic            |
| Fourier transform infrared spectroscopy        | NICOLET 6700                | Thermo Fisher Scientific |
| Proton nuclear magnetic resonance spectroscopy | Inova 500MHz                | Varian                   |
| Thermogravimetric analyzer                     | TGA/SDTA815 <sup>e</sup>    | METTLER TOLEDO           |
| Differential scanning calorimeter              | DSC1                        | METTLER TOLEDO           |
| Scanning electron microscope                   | JSM-6400                    | JEOL                     |
| Universal testing machine                      | LR 100k                     | LLOYD                    |
| Micrometer                                     | ERN469                      | Mitutoyo                 |
| Gloss Meter                                    | Micro-gloss 60 <sup>o</sup> | BYK-Gardner              |
| Contact Angle Meter                            | CAM-PLUS                    | Tantec                   |

### 3.3 Experimental Procedure

Flow chart of the whole manufacturing process is shown in Figure 3.2 and can be described in three main steps as follow:

#### 3.3.1 Preparation of cellulose powder

##### 3.3.1.1 Preparation of pineapple leaf and corn husk powder

Pineapple leaf and corn husk powder were prepared according to the following steps.

##### Delignification

Before delignification process, pineapple leaf and corn husk were soaked in distilled water at 80°C for 1 hour in order to remove water soluble hemicellulose. Next, they were soaked with 0.5 M NaOH solution at 100°C for 4 hours in order to remove lignin and remaining hemicellulose from pulp. After that, the pulp was filtered and washed with distilled water until the pH of washing water become neutral.

##### Bleaching

The delignified pineapple leaf pulp was bleached by 10% (V/V) H<sub>2</sub>O<sub>2</sub> in 0.5 M NaOH at 80°C for 2 hours; whereas the delignified corn husk pulp was bleached by 5% (V/V) H<sub>2</sub>O<sub>2</sub> in 0.5 M NaOH at the same condition of pineapple leaf pulp. The bleached pulp was washed with distilled water until the pH of washing water became neutral.

##### Hydrolysis and grinding

The pineapple leaf and corn husk bleached pulp were heated and stirred in boiling 2 N HCl for 4 hours. Then, the bleached pulp was filtered and washed with distilled water until its pH value become 7. The obtained pulp was then dried in an oven

at 60°C for 12 hours. Eventually, the pulp was ground with the agitator for three minutes to obtain cellulose powder.

### 3.3.1.2 Preparation of cotton powder

Cotton powder was prepared from waste cotton fabric by acid hydrolysis. First, the waste cotton fabric was cut into size 2x2 cm. Then, it was heated and stirred in boiling 2.5 N HCl for 2 hours. At the end of hydrolysis period, the sample powder was filtered and washed with distilled water until the washing water become neutral. The obtained sample powder was dried in an oven at 60°C for 12 hours.

### 3.3.2 Esterification of cellulose powder

The cellulose powder was dissolved in 8% (W/V) LiCl/DMAc solution. First, 4 g of LiCl was mixed with 50 ml of DMAc and stirred at 60°C until LiCl was completely dissolved in DMAc solvent. Then, 2 g of cellulose powder was added and maintained at that temperature for another 1 hour. After that, 4% of cellulose solution was cooled down to room temperature. Next, 0.9 equiv. of DMAP as a catalyst and 10 equiv. of lauroyl chloride as an esterifying agent were added into cellulose solution and the mixture was esterified in a domestic microwave oven (LG Electronic MS2447BB). The microwave power output and reaction time were varying from 80-400 watt and 30-180 second, respectively. At the end of esterification, the product was purified by precipitation and washing with ethanol and dried in an oven at 60°C for 12 hours.

### 3.3.3 Film casting

The esterified cellulose powder with different DS (degree of substitution) values was dissolved in chloroform. After that, the solution was spread on a glass plate at room temperature until the solvent was totally evaporated and the film was finally obtained.

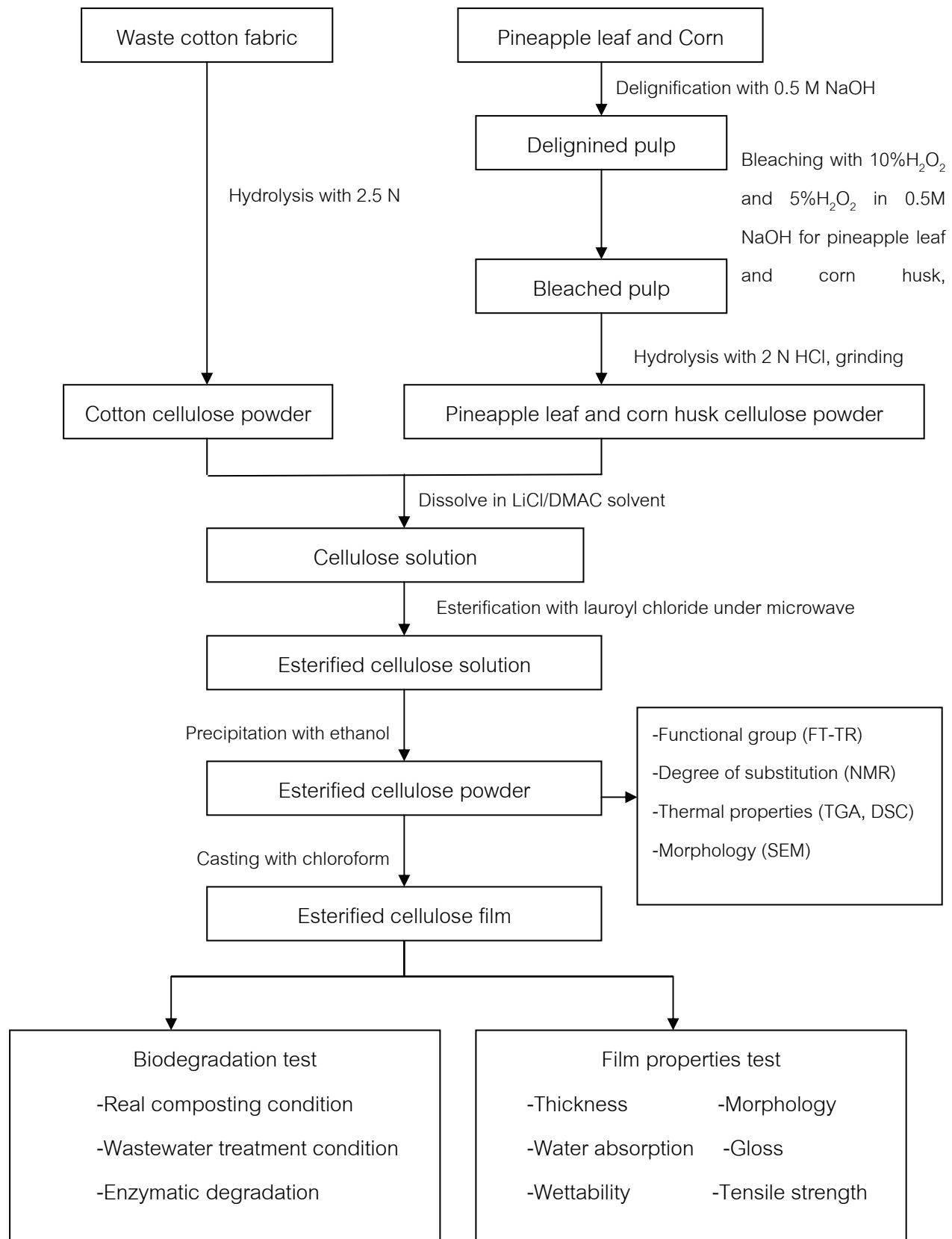


Figure 3.2 Flow chart of the entire experimented process

### 3.4 Characterization of Esterified Cellulose Powder

The unesterified and esterified cellulose powder samples were tested and characterized using various techniques as follow:

#### 3.4.1 Chemical Structure by FTIR Technique

Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize the functional group of unesterified and esterified cellulose powder. FTIR spectra were recorded on a NICOLET 6700 FTIR with 32 consecutive scans at a resolution of  $4\text{ cm}^{-1}$ . The samples were scanned at a frequency range of  $4000\text{-}400\text{ cm}^{-1}$ .

#### 3.4.2 Chemical Structure by $^1\text{H-NMR}$ Technique

The chemical structure was examined by Proton Nuclear Magnetic Resonance ( $^1\text{H-NMR}$ ) Spectroscopy in duterated chloroform ( $\text{CDCl}_3$ ). All of the chemical shifts were reported in parts per million (ppm) using tetramethylsilane (TMS) as an internal standard.

#### 3.4.3 Determination of the Degree of Substitution

The degree of substitution (DS) of esterified cellulose was evaluated by  $^1\text{H-NMR}$  with an integration of aliphatic chain protons and cellulosic sugar protons and calculated according to the following formula [25]:

$$\text{DS} = \frac{10 I_{\text{CH}_3}}{3I_{\text{sugar}} + I_{\text{CH}_3}} \quad (3.1)$$

Where  $I_{\text{CH}_3}$  is the integration for the methyl protons of aliphatic chain endgroup and  $I_{\text{sugar}}$  is the integration of glucosidic protons.

### 3.4.4 Thermal Properties

#### 3.4.4.1 Thermogravimetric Analysis (TGA)

TGA of approximately 7 mg of sample was carried out under nitrogen atmosphere from 30°C to 800°C with a heating rate of 10°C/min. Prior to do the experiment, the sample was dried in a vacuum oven at 60°C for 24 hours. The decomposition temperature ( $T_d$ ) was reported as the onset of weight loss of heated sample.

#### 3.4.4.2 Differential Scanning Calorimetry (DSC)

The sample size with an average weight of 6-10 mg encapsulated in a hermitically sealed aluminum pan was prepared for each sample. The same temperature profile was applied to all samples: first heating from -50°C up to 200°C in a nitrogen atmosphere with a heating rate of 10°C/min, followed by cooling the sample to -50°C with the same rate, and finally heating again to 200°C with the same condition as the first heating scan.

The melting temperature ( $T_m$ ) values were reported as the peak temperature of melting endotherms recorded on the second heating scan. The glass transition temperature ( $T_g$ ) values were reported as the midpoint of the heat capacity change in the glass transition region during the second heating scan.

### 3.4.5 Morphological Studies

Morphology of esterified-cellulose sample was characterized by a scanning electron microscopy. The scanning electron microscopy was operated at 15 kV. The



surface of the sample was sputter-coated with a thin layer of gold before being scanned to prevent surface charring under electron beam.

### 3.5 Characterization of Esterified Cellulose Film

The esterified cellulose films were tested and characterized using various techniques as follow:

#### 3.5.1 Film Thickness Measurement

The tensile properties of film samples are related to the thickness of film. Therefore, the film thickness measurement was conducted by using a micrometer. The average of five thickness values taken along the length of the film strip was used to calculate the tensile strength.

#### 3.5.2 Optical Properties

Gloss or specular reflectance is defined as the degree to which the finished surface of the materials approaches that of the theoretical specular gloss standard, or the perfect mirror, which is assigned a value of 1000. In practice, gloss measurements are made in comparison to a black tile with a refractive index of 1.567 and assigned an arbitrary value of 100 gloss units. The amount of specular reflectance of the black tile at given angle depends on the index of refraction of the gloss.

In this study, the gloss of film sample was determined by a micro-gloss 60° gloss meter at  $23 \pm 2^\circ\text{C}$  according to the ASTM D523 standard method. Calibrations of dark standard holder were 95.1 units. Five positions of each film sample were tested to obtain the average gloss values.

### 3.5.3 Surface Property Determination: Wettability

The contact angles of film sample were measured using a CAM-PLUS contact angle meter (Tantec, Inc.) according to Tantec's Half-Angle method. To calibrate the device, the height of the syringe was adjusted so that the needle tip image was at the lower border of the grid on the screen. The needle's image was then focused by moving the lens plate back and forth. The film specimen was placed onto the specimen holder under the syringe needle, and the knob was released clockwise to release the droplet of water. Bringing the specimen holder up slowly then down, one droplet of water was obtained, and was then focused. The line was then adjusted so that it was lined up with the left edge of the droplet. The line was moved till it cross the apex of the droplet, and the angle was measured on the protractor. A contact angle of zero results in wetting, while the angle between  $0^\circ$  and  $90^\circ$  results in spreading of the drop. The angle greater than  $90^\circ$  indicate that the liquid tends to bead or shrink away from the solid surface.

In this study, wettability of esterified-film sample was performed using a contact angle meter.  $10\ \mu\text{l}$  liquid droplets were placed at ten different sites on the surface of film sample. The contact angle at each position was measured and the average contact angle value and standard deviation were reported.

### 3.5.4 Water Absorption

The water absorption capacity of the esterified-films was measured according to the ASTM D570 standard test. The 20 mm x 30 mm film samples were dried in a vacuum oven at  $50^\circ\text{C}$  for 24 hours and then cooled in a dessicator before being weighed ( $W_1$ ). After that, the film samples were fully immersed in a container filled with distilled water at room temperature for 24 hours. Then, the films were taken off from the container, removed the surface water by wiping off with a dry cloth, and immediately

weighed ( $W_A$ ). The result of each film represents the average of five tests. The water absorption capacity (WAC) was calculated as [26]:

$$\text{WAC\%} = \frac{W_A - W_I}{W_I} \times 100 \quad (3.2)$$

Where:

$W_A$  = weight of sample at absorbing equilibrium (g)

$W_I$  = initial dry weight of sample (g)

### 3.5.5 Tensile Properties

Measurement of tensile properties such as tensile strength, tensile modulus, and percent elongation at break of film samples was carried out by Universal Testing Machine. Tensile tests were performed according to the ASTM D882 standard method, using a crosshead speed of 10 mm/min, a gauge length of 100 mm, and load cell of 50 N. The film samples with dimensions of 10 mm wide and 150 mm long were conditioned for 24 hours at 25°C before testing. For each sample, five specimens were tested and the results were averaged to obtain a mean value.

### 3.6 Biodegradation Procedure

In this work, biodegradability of the modified cellulose film was investigated under different natural conditions of waste water treatment system and composting condition. Additionally, the enzymatic degradation by cellulase enzyme was also performed.

#### 3.6.1 Real composting condition

A compost pile made of 50% *Samanea saman* leaf (*Samanea saman* (Jacq.) Merr.), 6.5% coconut husk, 6.5% chopped coconut fiber, 4.5% manure, 6.5% wood shaving, 6.5% rice husk ash, 6.5% surface soil, 6.5% sand, and 6.5% bio-fermented juice was prepared at Chulalongkorn University composting facility and used for assessing the biodegradability of the modified cellulose films. The compost consists of 0.79% nitrogen, 0.32 % phosphorus, 0.52% potassium, and 16.97% C/N ratio.

The biodegradation study was carried out for 3 months from June, 2009 to August, 2009. During an experiment, the environmental conditions including temperature, humidity, pH value, and the amount of microorganisms of compost pile was gathered and summarized in Table 3.2.

Table 3.2 Environmental conditions of compost pile during an experiment in 2009

| Month  | pH   | Temperature (°C) | Humidity of compost (%) | Population of microorganism* (CFU**/gram) |
|--------|------|------------------|-------------------------|---|
| June   | 8.01 | 26.5             | 51.95                   | $9.1 \times 10^7$                         |
| July   | 7.34 | 27.0             | 41.02                   | $13.0 \times 10^7$                        |
| August | 7.95 | 26.0             | 45.37                   | $1.2 \times 10^7$                         |

\*The population of microorganism was performed by the total plate count test.

\*\*CFU=Colony Forming Unit

The modified cellulose films were cut into the size of 2 cm x 2 cm and placed into the compost pile (1 m in width x 1.5 m in long x 0.1 m in height) at a depth of 5 cm from the surface, as shown in Figure 3.2. The samples were removed for testing their biodegradability at every 10 days. After removal, samples were washed with distilled water and dried under vacuum oven at 60°C for 24 hours before testing. The biodegradability of sample was followed by measuring the changes in percentage of weight loss and physical appearance.



Figure 3.3 Placement of modified cellulose films in the compost pile

### 3.6.2 Waste water treatment system condition

The modified cellulose films were prepared in square shape with the size of 2 cm x 2 cm, and placed into the cloth bag as shown in Figure 3.3. As seen, the bottom of the bag was filled with a number of gravels so that it can be vertically hanged or floated into the water during an experiment at a depth of 1 m from the surface.



Figure 3.4 The cloth bag containing modified cellulose film samples

After that, the films were soaked in the waste water treatment system of Rattanakosin Water Environment Control Plant (RHECP) in Bangkok for 3 months from May, 2009 to July, 2009. The films were removed from the waste water treatment system for inspecting at every 10 days. Before testing, the films were washed with distilled water and dried under vacuum oven at 60°C for 24 hours. Similar to composting test, the biodegradability of films was monitored by observing the changes in percentage of weight loss, and physical appearance.

The condition of waste water treatment system during the experiment including average of temperature, pH, and population of microorganism was measured at every 1 month and listed in Table 3.3.

Table 3.3 Environmental condition of waste water treatment system during an experiment in 2009

| Month | pH   | Temperature (°C) | Population of microorganism* (CFU**/ml) |
|-------|------|------------------|---|
| May   | 6.31 | 32.5             | $7.3 \times 10^4$                       |
| June  | 6.60 | 33.0             | $2.7 \times 10^5$                       |
| July  | 7.04 | 32.5             | $1.8 \times 10^7$                       |

\*The population of microorganism was performed by the total plate count test.

\*\*CFU=Colony Forming Unit

### 3.6.3 Enzymatic degradation

Modified cellulose films were cut into the size of 2 cm x 2 cm and weighed before being placed in 40 ml vial. Enzyme solution comprising 5.5 ml of 0.2 M acetate buffer pH 5.5 and 4.5 ml of cellulase solution was prepared. After adding the enzyme solution into the vial containing film samples, the vial was put into a water bath, with continuously shaking and heated at 55°C. Specimens were removed for testing at every

5 days for 20 days. After removal, specimens were washed with distilled water and dried under vacuum oven at 60°C for 24 hours to remove traces of moisture before testing. Samples were weighed to determine the percentage of weight loss. The evidence of enzymatic degradation was also confirmed by physical appearance.

### 3.7 Evaluation of Degradation

#### 3.7.1 Weight Loss

Weight loss of the film samples were measured by weighing the sample before and after biodegradation. The percentage weight loss of the film samples was calculated using the following equation:

$$\text{Weight loss (\%)} = \frac{W_i - W_f}{W_i} \times 100 \quad (3.3)$$

Where:

$W_i$  = initial weight of sample before degradation (g)

$W_f$  = final weight of sample after degradation (g)

#### 3.7.2 Physical Appearance

Electron micrographs were obtained from the film samples collected before and after biodegradation testing. Each sample was washed with distilled water and dried in a vacuum oven at 60°C for 24 hours. The scanning electron microscope was operated at 15 kV. The surface of films were coated with gold prior to investigation to avoid surface charging under electron beam.

## CHAPTER IV

### RESULTS AND DISCUSSION

In this study, pineapple leaf, corn husk, waste cotton fabrics were used as raw materials to prepare modified cellulose film in LiCl/DMAc solvent system with 0.9 equiv. of DMAP as a catalyst by using 10 equiv. of lauroyl chloride as an esterifying agent. The microwave energy was selected as a heating source for the esterification reaction to reduce time and energy use. By varying the microwave power and reaction time, modified cellulose with different degree of substitution (DS) values was achieved. The results were divided mainly into four parts as follows:

- Investigation of an optimum condition for the esterification reaction of cellulose powder
  - Characterization of esterified cellulose powder
  - Characterization of esterified cellulose film
  - Biodegradability of esterified cellulose film

#### 4.1 The Optimum Condition for Modification Reaction of Cellulose Powder with Different Degree of Substitution (DS) Values

The optimum condition for esterification reaction of cellulose powder in terms of microwave power and reaction time was investigated by measuring %weight increase and degree of substitution (DS) of esterified-cellulose. The results were divided into three parts based on the source of cellulose raw material.

The %weight increase of modified cellulose powder was evaluated by weighing the cellulose powder before and after modification reaction. The percentage weight increase of modified cellulose powder was calculated using the following equation:



$$\text{Weight increase (\%)} = \frac{W_f - W_i}{W_i} \times 100 \quad (4.1)$$

Where:

$W_f$  = final weight of sample after modification (g)

$W_i$  = initial weight of sample before modification (g)

The degree of substitution (DS) of modified cellulose powder was measured by  $^1\text{H-NMR}$  investigation of aliphatic chain protons and cellulosic sugar protons intensity and then calculated from the following equation [25]:

$$\text{DS} = \frac{10 I_{\text{CH}_3}}{3I_{\text{sugar}} + I_{\text{CH}_3}} \quad (3.1)$$

Where:

$I_{\text{CH}_3}$  = intensity of aliphatic chain protons

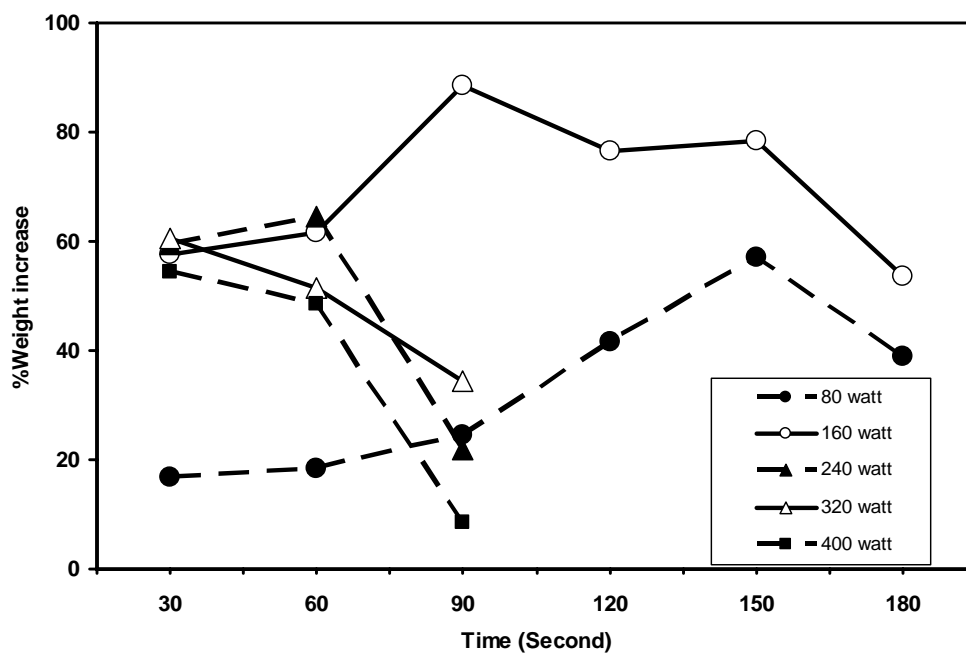
$I_{\text{sugar}}$  = intensity of cellulosic sugar protons

#### 4.1.1 Pineapple Leaf

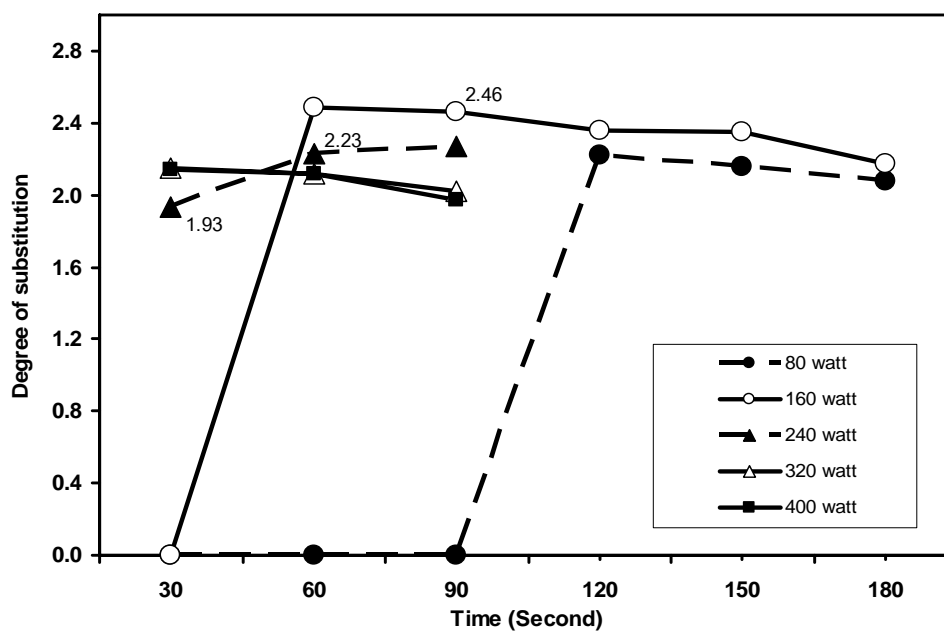
The effect of reaction time and microwave power on %weight increase and degree of substitution of pineapple leaf cellulose was shown in Figure 4.1 (a) and (b), respectively.

Figure 4.1 (a) displays the relationship between %weight increase and reaction time at different microwave power. The result revealed that at any modification microwave power, except at 320 watt and 400 watt, the longer reaction time applied, the higher % weight increase of pineapple leaf cellulose obtained. However, after it reached the optimum value, their %weight increase declined. This is because the excessive microwave power and reaction time attributed to an increase in the reaction temperature of the system, as a result, the degradation of pineapple leaf cellulose occurred. The highest %weight increase values for modification reaction at 80, 160, and 240 watt were 57.0%, 88.5%, and 64.5%, which were obtained at a reaction time of 150, 90, and 60 seconds, respectively.

At higher microwave power of 320 watt and 400 watt, the plot shows that when reaction time increased, the %weight increase of pineapple leaf cellulose was continuously decreased. The highest %weight increase values of 60.5% and 54.5% were attained at both 30 second reaction time which was the lowest reaction time utilized in the experimental. Although, it was believed that %weight increase would initially increase with reaction time applied between 0-30 second, but because of the limitation of microwave oven manufactured, similar trend with the plots of lower microwave power (80-240 watt) was not observed.



(a)



(b)

Figure 4.1 The relationship between (a) %weight increase and (b) degree of substitution of pineapple leaf cellulose and reaction time at different microwave power

Similar to the influence of microwave power, when we considered at the constant reaction time, it was found that %weight increase of pineapple leaf cellulose increased with increasing the microwave power up to the maximum value, and decreased afterwards. For example, at the reaction time of 90 second, %weight increase of pineapple leaf cellulose increased from 24.5% (at 80 watt) to 88.5% (at 160 watt) and then it was dropped to 22.0%, 34.5%, and 8.5% at the microwave power of 240, 320, and 400 watt, respectively. This is due to the excess microwave energy absorbed leading to the degradation of pineapple leaf cellulose.

The effect of microwave power and reaction time on degree of substitution of pineapple leaf cellulose was shown in Figure 4.2 (b). As seen, the degree of substitution of pineapple leaf cellulose increased significantly and then it slowly decreased at any microwave power. The highest values of degree of substitution for microwave power at 80, 160, 240, 320, and 400 watt were 2.22, 2.49, 2.27, 2.15, and 2.14 at reaction time of 120, 60, 60, 30, and 30 second, respectively.

Similar to %weight increase, at any reaction time, the result revealed that the higher microwave power applied, the greater degree of substitution of pineapple leaf cellulose obtained until it reached the optimum value. Beyond this point, their degree of substitution decreased. For example, at 90 second reaction time, the degree of substitution of pineapple leaf cellulose increased from 0 (at 80 watt) to 2.46 (at 160 watt) after that it decreased to 2.27, 2.02, and 1.97 at microwave power of 240, 320, and 400 watt, respectively.

In this study, to study the effect of degree of substitution (DS) values on the properties of modified pineapple leaf cellulose, three different conditions that yielded low, medium, and high degree of substitution (DS) values with reasonable %weight increase were selected. These conditions were 30 second 240 watt (DS 1.93), 60 second 240 watt (DS 2.23), and 90 second 160 watt (DS 2.46) which yielded the

%weight increase of modified pineapple leaf cellulose as 59.5%, 64.5%, 88.5%, and respectively.

#### 4.1.2 Corn Husk

Figure 4.2 demonstrates the relationship between (a) %weight increase and (b) degree of substitution of corn husk cellulose and reaction time at different microwave power, respectively. As shown in Figure 4.2 (a), at any microwave power, except 80 watt, %weight increase of corn husk cellulose enhanced with increasing reaction time until it reached the maximum value and then decreased. Similar to the pineapple leaf cellulose, the excess microwave power and reaction time caused the degradation of corn husk cellulose. The highest %weight increase values at the microwave power of 160, 240, 320, and 400 watt were 89.5%, 90.5%, 67.5%, and 71.0% at the reaction time of 150, 60, 90, and 60 second, respectively.

At 80 watt, as the reaction time increased, %weight increase of corn husk cellulose had a tendency to increase without reaching the optimum values. This is probably due to the lower microwave power and reaction time did not provide enough reaction temperature or energy for modification reaction in the system; as a result, %weight increase did not arrive the optimum value.

Similarly, when focusing at constant reaction time, %weight increase of corn husk cellulose increased up to its maximum values and then declined. Obviously, at 60 second of reaction time, %weight increase of corn husk cellulose increased from 17.5% (at 80 watt) to 50.5% (at 160 watt) and 90.5% (at 240 watt) and then it was dropped to 71.0% and 71.0% at 320 and 400 watt, respectively.

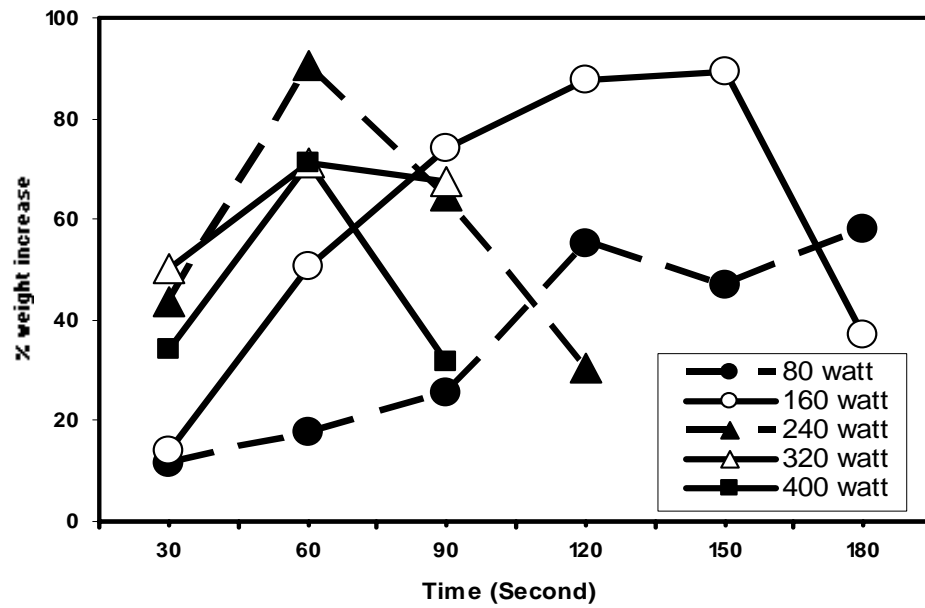
The influence of microwave power and reaction time on degree of substitution of corn husk cellulose was exhibited in Figure 4.2 (b). Various trends can be noticed. As

seen, at lowest microwave power of 80 watt, the degree of substitution of corn husk cellulose increased at the beginning state of 30-120 second reaction time and then the degree of substitution seemed to be unchanged. Similar to %weight increase at 80 watt, the obtained result is due to the insufficient reaction temperature resulted from lower microwave power and reaction time. So, the degree of substitution of corn husk cellulose did not approach the optimum value.

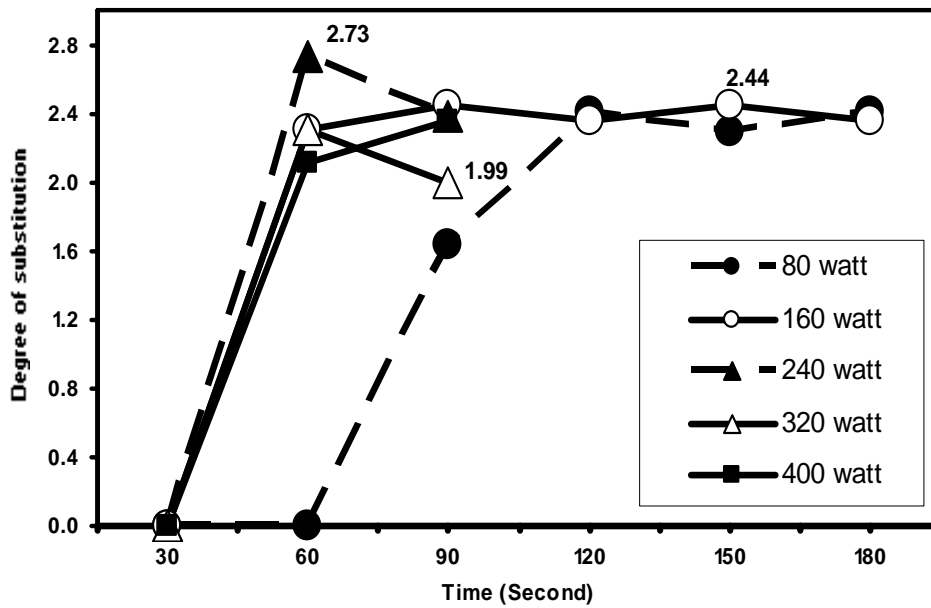
At higher microwave power of 160 watt, the degree of substitution of corn husk cellulose increased with the increasing of reaction time from 30 second to 90 second and then it seemed to be insignificantly changed. At the microwave power of 400 watt, the degree of substitution of corn husk cellulose was also increased with increasing of reaction time from 30 second to 90 second. The obtained results were believed that the degree of substitution of corn husk cellulose would decrease with higher reaction time more than 180 second and 90 second for the microwave power of 160 watt and 400 watt, respectively. The reason that we did not further conduct the reaction more than 180 and 90 second is because at these reaction times the corn husk cellulose was already degraded, as previously discussed.

For the microwave power of 240 watt and 320 watt, the highest degree of substitution was obtained at the reaction time of 60 second for both microwave power conditions and after that the degree of substitution decreased. As mentioned earlier, the decrease in the degree of substitution is due to the degradation of corn husk cellulose after it was exposed to the excess microwave power and reaction time.

Considering at the constant reaction time, it was found that the degree of substitution of corn husk cellulose was increased when increasing microwave power from 80 watt to 240 watt. After that, when the higher microwave power of 320 watt and 400 watt were applied, the degree of substitution decreased.



(a)



(b)

Figure 4.2 The relationship between (a) %weight increase and (b) degree of substitution of corn husk cellulose and reaction time at different microwave power

To further investigate the effect of DS values on the properties of modified corn husk cellulose, various modification reaction conditions of corn husk cellulose were selected as 60 second 240 watt (DS 2.73), 150 second 160 watt (DS 2.44), and 90 second 320 watt (DS 1.99), which represented high, medium, and low DS values with appropriate %weight increase of 90.5%, 89.5%, and 67.5%, respectively.

#### 4.1.3 Waste Cotton fabric

Figure 4.3 (a) shows the influence of microwave power and reaction time on %weight increase of cotton cellulose. The result exhibits that the %weight increase of cotton cellulose increased with increment of microwave power and reaction time until reaching the optimum value and then decreased due to the degradation of cellulose structure, except at 80 watt of microwave power.

For the microwave power of 80 watt, %weight increase of cotton cellulose increased at the initiate state of reaction time (30-90 second) and then after 90 second, %weight increase seemed to be slightly changed until the reaction time increased to 180 second. As discussed previously, the lower microwave power did not cause any degradation of cellulose structure even though the longer period of time was applied since the reaction temperature was not high enough to destruct the cellulose structure. Therefore, %weight increase of cotton cellulose might not reach the optimum value.

Figure 4.3 (b) presents the effect of reaction time and microwave power on degree of substitution of cotton cellulose. At lowest microwave power of 80 watt, the degree of substitution of cotton cellulose gradually increased with increasing of the reaction time. The highest DS value of 2.33 was found at 180 second of reaction time.

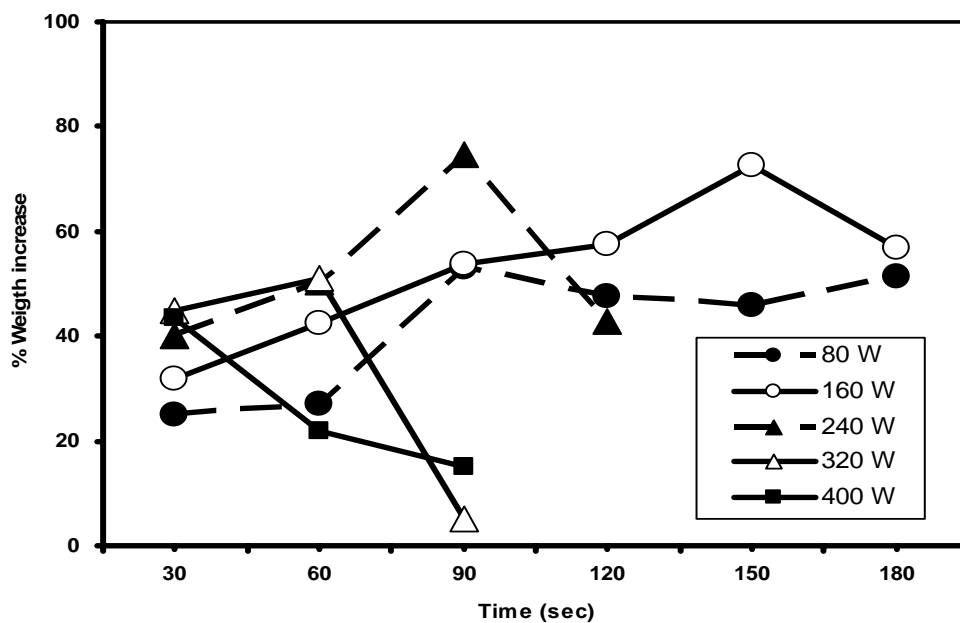


At higher microwave power of 160 watt and 240 watt, the degree of substitution of cotton cellulose continuously increased with increasing of reaction time until it reached the optimum value at 150 second and 90 second, respectively, and then dropped. The optimum DS values of cotton at these conditions were 2.44 and 2.48, respectively.

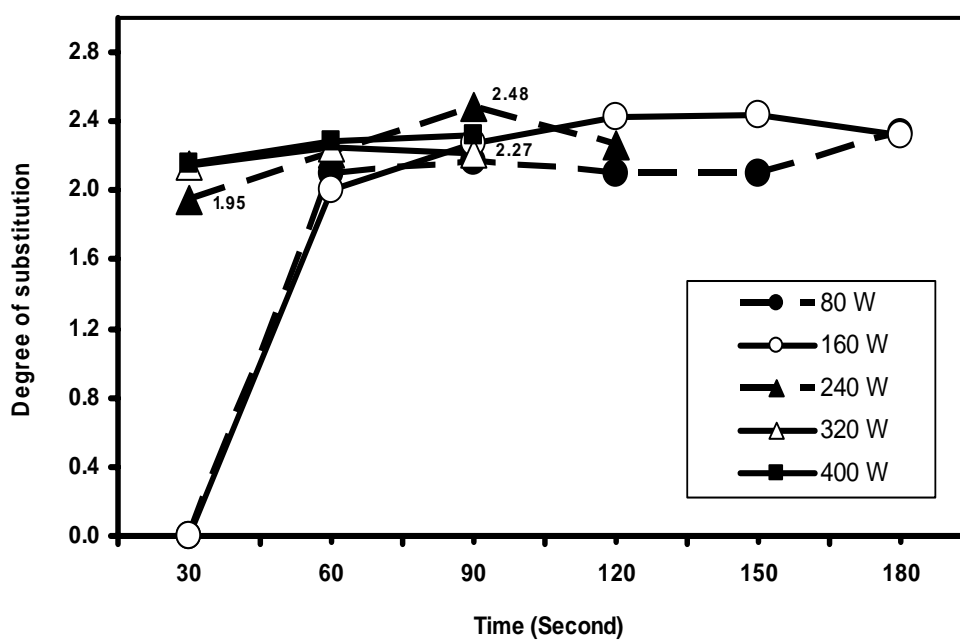
Different cases were found for the microwave power of 320 watt and 400 watt, although the degree of substitution of cotton cellulose increased with the increasing of reaction time from 30 second to 90 second, we did not continue the reaction beyond this point. Since it was believed that the degree of substitution of cotton cellulose would be decreased with higher reaction time more than 90 second. Due to the degradation of cellulose as evidenced by a very low amount of %weight increase of cotton cellulose presented in Figure 4.3 (a).

Similar to the other two cases, at constant reaction time, the degree of substitution of cotton cellulose increased with increasing of the microwave power applied until it reached the optimum value and then decreased. For example, at 90 second, the DS values of cotton cellulose increased as a microwave power increased from 80 to 160 and 240 watt. But when the microwave power was increased up to 320 watt and 400 watt, the DS values of cotton cellulose gradually decreased.

Three different conditions that yielded low, medium, and high degree of substitution (DS) values with reasonable %weight increase were selected and summarized in Table 4.1 along with those of pineapple leaf and corn husk.



(a)



(b)

Figure 4.3 The relationship between (a) %weight increase and (b) degree of substitution of waste cotton fabric cellulose and reaction time at different microwave power

Table 4.1 The optimum conditions for modification reaction of pineapple leaf, corn husk, and waste cotton fabric cellulose with the different degree of substitution (DS) values under microwave heating

| Source of Cellulose | The optimum condition |                  |      |      |
|---------------------|-----------------------|------------------|------|------|
|                     | Power<br>(watt)       | Time<br>(second) | %WI* | DS*  |
| Pineapple Leaf      | 160                   | 90               | 88.5 | 2.46 |
|                     | 240                   | 60               | 64.5 | 2.23 |
|                     | 240                   | 30               | 59.5 | 1.93 |
| Corn Husk           | 240                   | 60               | 90.5 | 2.73 |
|                     | 160                   | 150              | 89.5 | 2.44 |
|                     | 320                   | 90               | 67.5 | 1.99 |
| Waste Cotton Fabric | 240                   | 90               | 74.5 | 2.48 |
|                     | 160                   | 90               | 56.0 | 2.27 |
|                     | 240                   | 30               | 40.0 | 1.95 |

\*%WI = %weight increase, DS = degree of substitution

## 4.2 Characterization of Esterified Cellulose Powder

### 4.2.1 Chemical Structure by FTIR Technique

Functional groups of cellulose before and after esterification were characterized using FTIR technique. The IR vibrations of native cellulose and esterified cellulose are summarized in Table 4.2. The FTIR spectra of unmodified and esterified-cotton cellulose under microwave heating are presented in Figure 4.4. For unmodified cellulose, the principle strong broad band centered at  $3304\text{ cm}^{-1}$  is owing to O-H stretching vibration and the small peak at  $1647\text{ cm}^{-1}$  is associated with water hydration (H-O-H bending of absorbed water).

After modification, the spectrum obviously shows the efficiency of esterification with the decrease in the intensity of the characteristic band at about  $3300\text{ cm}^{-1}$ , assigned to the cellulose O-H vibration and the increasing in the intensity of the C-H stretching band around  $2854$  and  $2919\text{ cm}^{-1}$  arising from the aliphatic chain. This is due to the substitution of long chain aliphatic of lauroyl group at the hydroxyl group of cellulose molecules. Furthermore, the FTIR analysis also indicated the enhancement of the hydrophobic character of the esterified cellulose because the intensity of the band at  $1647\text{ cm}^{-1}$ , assigned to the absorbed water molecule, also decreased.

In addition, the IR spectrum of esterified cellulose displays different bands from the cellulose spectrum. It appeared a clear-cut confirmation of the evidences of esterification by showing the presence of two important ester bands at  $1735\text{-}1750\text{ cm}^{-1}$  (carbonyl C=O stretching of ester) and  $1255\text{ cm}^{-1}$  (-C-O- stretching). Moreover, the spectrum of esterified cellulose provides an evidence of esterification by showing the presence of three other prominent bands at  $1480\text{ cm}^{-1}$ ,  $1374\text{ cm}^{-1}$ , and  $1175\text{ cm}^{-1}$  which are attributed to  $\text{CH}_2$  bending and C-H bending in  $-\text{O}(\text{C}=\text{O})\text{-CH}_3$  group and C-C stretching, respectively.

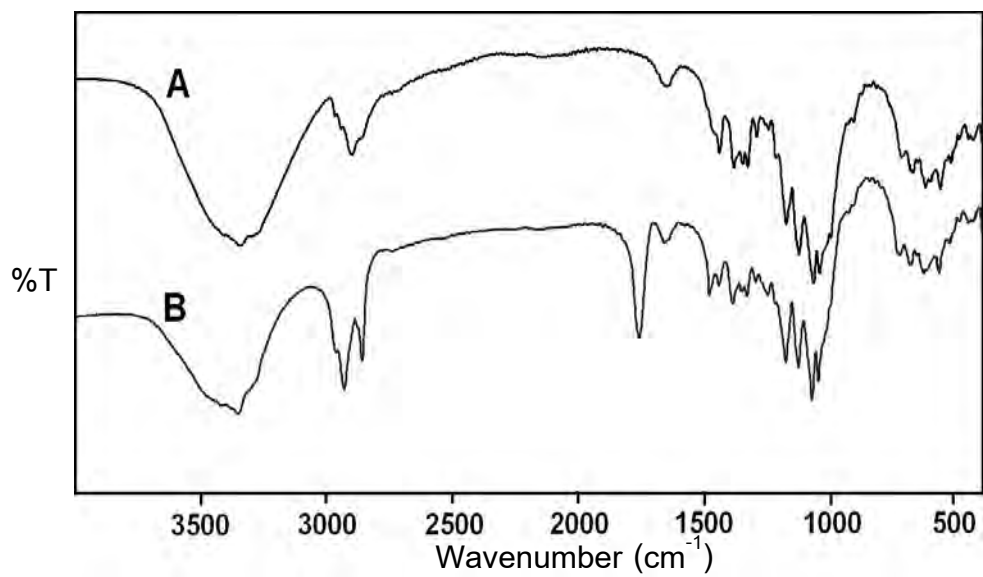


Figure 4.4 FTIR spectra of cellulose (A) and esterified cellulose (B)

Table 4.2 Infrared vibration and assignments for cellulose and esterified cellulose

| Major IR bands of component    |  |
|--------------------------------|--|
| Wavenumber (cm <sup>-1</sup> ) | Band Assignments   |
| Cellulose                      |  |
| 3304                           | OH stretching  |
| 2900                           | CH stretching of CH <sub>2</sub>                                   |
| 1647                           | H-O-H bending of absorbed water                                    |
| 1428                           | CH wagging (in-plane bending)                                      |
| 1370                           | CH bending (deformation stretch)                                   |
| 1335                           | OH in-plane bending  |
| 1316                           | CH wagging   |
| 1281                           | CH deformation stretch   |
| 1235                           | OH in plane bending  |
| 1203                           | OH in plane bending  |
| 1159                           | Anti-symatric bridge C-O-C stretching                              |
| 1109                           | Anti-symatric bridge C-O-C stretching                              |
| 1056                           | Anti-symatric in-plane ring stretch                                |
| 1034                           | C-O stretching   |
| 898, 706                       | Anti-symatric out-of-phase ring stretch: C1-O-C4;β-glucosidic bond |
| 665                            | O-H out of plane bending   |
| Cellulose laurate              |  |
| 3300                           | OH stretching  |
| 2854, 2919                     | CH stretching due to CH <sub>2</sub> and CH <sub>3</sub>           |
| 1742                           | C=O stretching of ester  |
| 1480, 1374                     | CH <sub>2</sub> bending, C-H bending                               |
| 1255                           | C-O stretching   |
| 1175                           | C-C stretching   |

#### 4.2.1.1 Effect of cellulose source

Figure 4.5 shows the FTIR spectra of pineapple leaf cellulose, corn husk cellulose, and cotton cellulose before and after modification reaction.

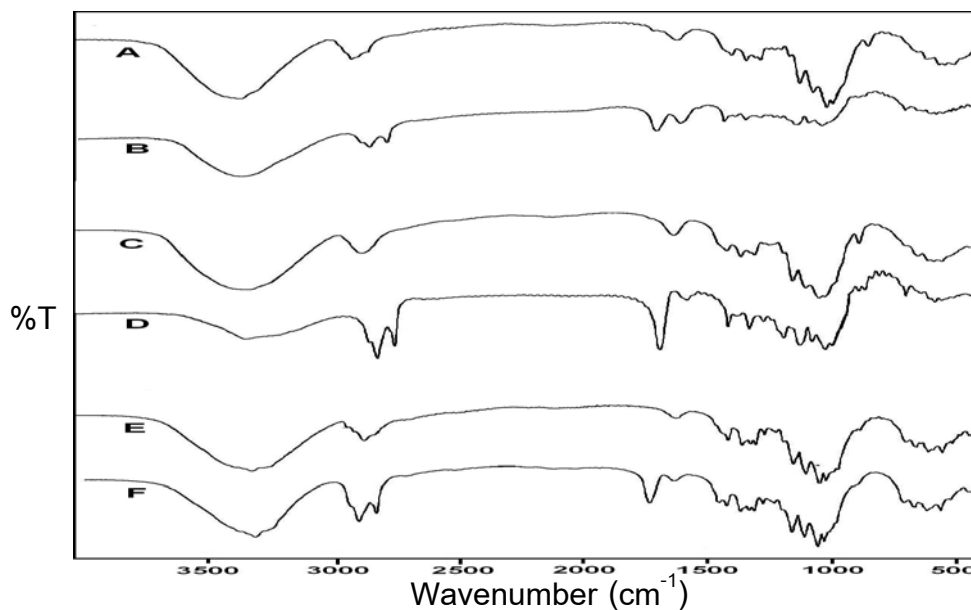


Figure 4.5 FTIR spectra of (A) pineapple leaf, (B) esterified pineapple leaf (high DS value), (C) corn husk, (D) esterified corn husk (high DS value), (E) cotton, and (F) esterified cotton (high DS value) cellulose

From the FTIR spectra of native pineapple leaf cellulose (spectrum A), native corn husk cellulose (spectrum C), and native cotton cellulose (spectrum E), it can be noticed that there was no difference in the chemical structure of those native cellulose. After esterification, the FTIR spectra of all esterified cellulose similarly showed the distinct carbonyl ester band around 1740 cm<sup>-1</sup>. They also indicated an increase in the intensity of the band around 2800-2900 cm<sup>-1</sup> corresponding to C-H stretching of lauroyl chain.

Comparing among the three esterified-cellulose spectra, the decreasing in the intensity of O-H stretching around  $3304\text{ cm}^{-1}$  of corn husk cellulose (spectrum D) was more pronounced than those of pineapple leaf cellulose (spectrum B) and cotton cellulose (spectrum F). Moreover, it was found that the esterified corn husk cellulose exhibited a significant increase in the intensity of the peak at  $1742\text{ cm}^{-1}$  which is corresponding to carbonyl C=O stretching of ester more obviously than the other two types of cellulose. These results indicated that the corn husk cellulose was successfully esterified more than the pineapple leaf and cotton cellulose, as evidenced by its greater DS values.

#### 4.2.1.2 Effect of degree of substitution

The FTIR spectra of pineapple leaf, corn husk, and cotton cellulose with variation of the DS value are shown in Figure 4.6, Figure 4.7, and Figure 4.8, respectively.

As seen, the FTIR spectra of each cellulose present similar characteristics that the transmittance intensity for the C=O ester moieties of the samples depended greatly on the DS value. As the DS value rises, the intensity of ester band becomes more intense. In case of a comparatively high DS value (every spectra D), the signal for ester band at  $1740\text{ cm}^{-1}$  was as strong as the band at  $2800\text{-}2900\text{ cm}^{-1}$  for C-H stretching associated with the lauroyl substituents, while the reverse trend appears in the case of a comparatively low DS value (every spectra C) and particularly in the samples with the lowest DS value (every spectra B). Conclusively, it was found that every spectra D showed the highest intense of carbonyl peak, and correspondingly weakest hydroxyl stretching band at  $3340\text{ cm}^{-1}$ , as expected for a high degree of esterification.



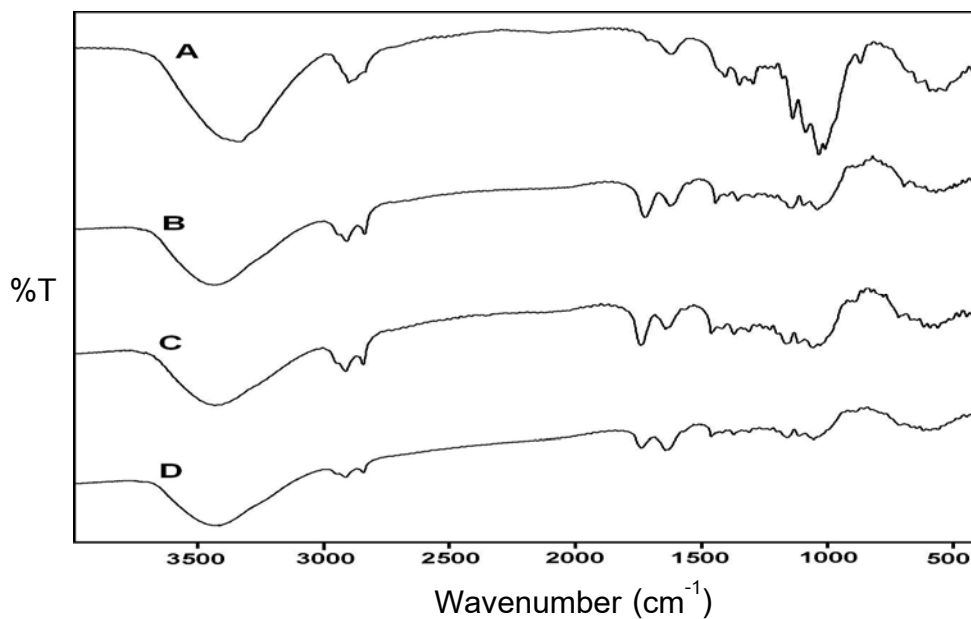


Figure 4.6 FTIR spectra of (A) unmodified pineapple leaf (DS=0), (B) modified pineapple leaf with DS=1.93 (low DS value), (C) modified pineapple leaf with DS=2.23 (medium DS value), and (D) modified pineapple leaf with DS=2.46 (high DS value)

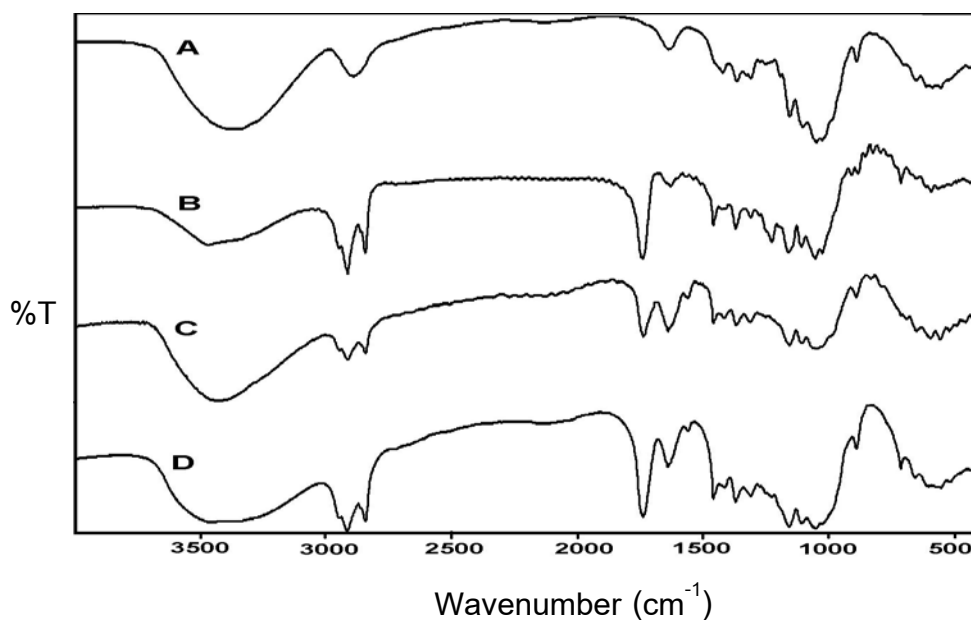


Figure 4.7 FTIR spectra of (A) unmodified corn husk (DS=0), (B) modified corn husk with DS=1.99 (low DS value), (C) modified corn husk with DS=2.44 (medium DS value), and (D) modified corn husk with DS=2.73 (high DS value)

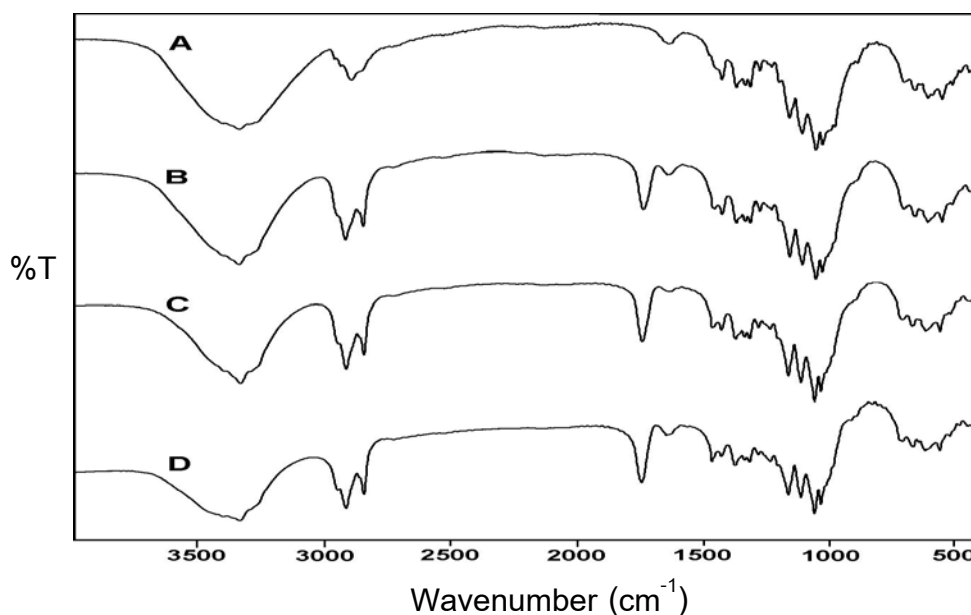


Figure 4.8 FTIR spectra of (A) unmodified cotton (DS=0), (B) modified cotton with DS=1.95 (low DS value), (C) modified cotton with DS=2.27 (medium DS value), and (D) modified cotton with DS=2.48 (high DS value)

#### 4.2.2 Chemical Structure by $^1\text{H-NMR}$ Technique

The chemical structure of esterified cellulose was also characterized by  $^1\text{H-NMR}$  spectroscopy in chloroform-*d* ( $\text{CDCl}_3$ ). The chemical shifts were evaluated in parts per million by using tetramethylsilane (TMS) as internal standard. Figure 4.9 illustrates the  $^1\text{H-NMR}$  spectrum and chemical structure of esterified cotton cellulose with lauroyl chloride as an esterifying agent. The signals observed in  $^1\text{H-NMR}$  spectroscopy of esterified cotton cellulose is presented in Table 4.3.

Modified cellulose with different degree of substitution values revealed the similar proton signals. The peak observed in modified cellulose within 3.46-5.06 ppm indicated the presence of the cellulose skeleton or anhydroglucose unit protons. The signals between 0.85-2.34 ppm were attributed to methyl protons of acyl substituent proton groups.

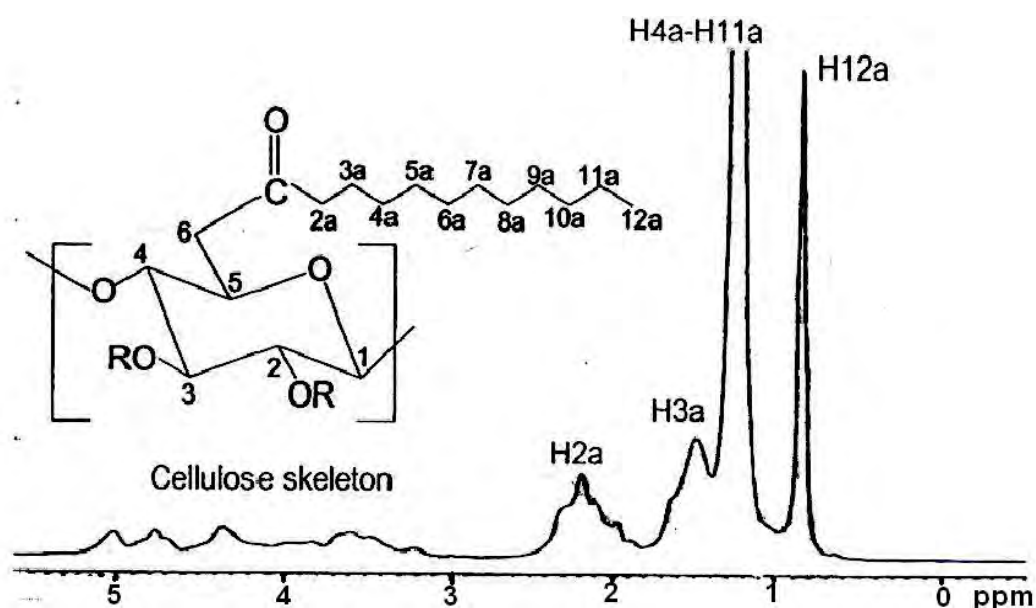


Figure 4.9  $^1\text{H-NMR}$  spectrum of esterified-cotton cellulose with lauroyl chloride as an esterifying agent

Table 4.3  $^1\text{H-NMR}$  signal of esterified-cotton cellulose with lauroyl chloride as an esterifying agent

| Cellulose Skeleton |                | Alkyl Chains               |                |
|--------------------|----------------|----------------------------|----------------|
| Position           | $\delta$ (ppm) | Position                   | $\delta$ (ppm) |
| Cellulose laurale  |                |                            |                |
| H-1                | 4.33           | H2a(CH <sub>2</sub> )      | 2.34           |
| H-2                | 4.82           | H3a(CH <sub>2</sub> )      | 1.59           |
| H-3                | 4.91           | H4a-H11a(CH <sub>2</sub> ) | 1.28           |
| H-4                | 3.63           | H12a(CH <sub>3</sub> )     | 0.91           |
| H-5                | 3.46           |                            |                |
| H-6                | 4.13           |                            |                |

### 4.2.3 Thermal Properties

#### 4.2.3.1 Thermogravimetric analysis (TGA)

Thermal stability of cellulose and esterified cellulose powder was analyzed by TGA. The decomposition temperature ( $T_d$ ) are important because they could imply the processing and manufacturing temperature without continuing or initiating a process of decomposition.

##### 4.2.3.1.1 Effect of cellulose source

Figure 4.10 presents TGA curves of pineapple leaf, corn husk, and cotton cellulose. As seen, the TGA curves of all cellulose appeared two steps of weight loss. The first step occurred around 70-90°C corresponding to the moisture decomposition in cellulose structure. The second step appearing at higher temperature around 317°C for pineapple leaf cellulose, 313°C for corn husk cellulose, and 320°C for cotton cellulose is attributed to the onset of decomposition temperature of cellulose structure. This result means that cotton cellulose has highest thermal stability since it starts to decompose at a higher temperature than pineapple leaf and corn husk cellulose. Besides, the total weight loss at the onset of decomposition temperature ( $T_d$  (onset)) of cotton is 14.8% which is lower than these of pineapple leaf (19.8%) and corn husk (18.8%).

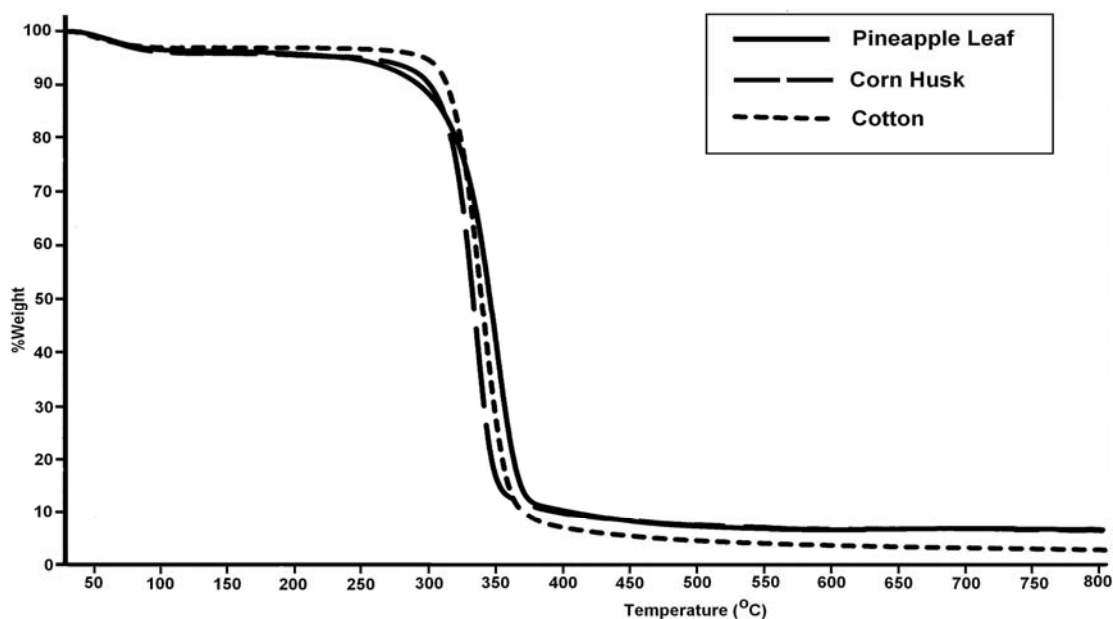


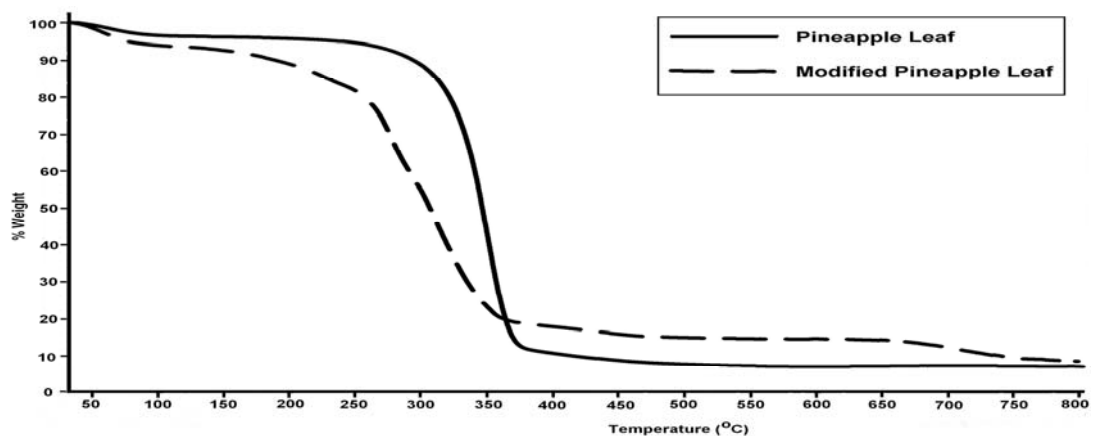
Figure 4.10 TGA thermogram of pineapple leaf, corn husk, and cotton cellulose

After modification reaction, TGA curves of modified pineapple leaf, modified corn husk, and modified cotton demonstrated differently from their counterparts as presented in Figure 4.11 (a), (b), and (c), respectively. TGA curve of modified pineapple leaf (Figure 4.11(a)) shows two stages of weight loss. The first stage in the range of 70-80°C with about 5.4% of total weight loss is due to the moisture decomposition in pineapple leaf cellulose. The second stage at about 256°C with 17.8% weight loss is due to the decomposition of cellulose itself. Similarly, modified corn husk (Figure 4.11(b)) exhibited two decomposition temperatures at 70°C and 192°C which represented the decomposition of moisture and corn husk cellulose, respectively.

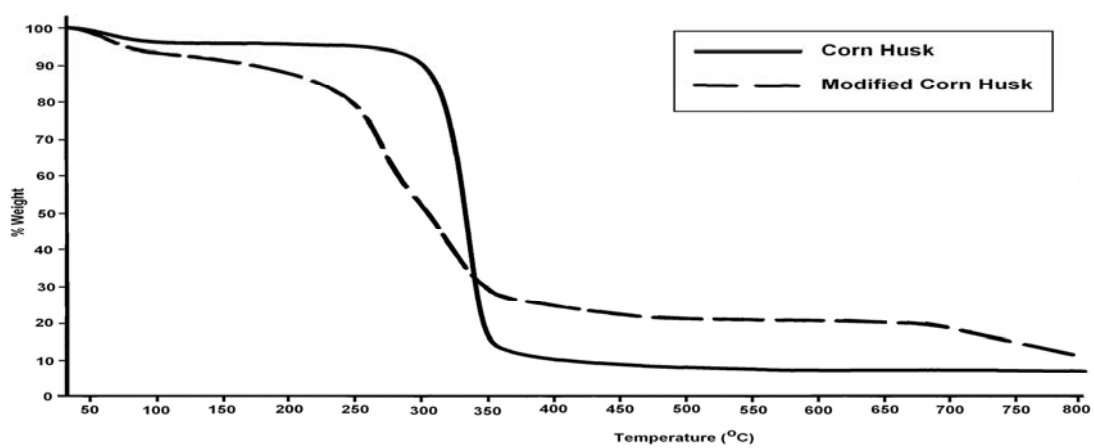
For modified cotton, Figure 4.11(c) displays that modified cotton cellulose has only one step shifted towards lower temperature at 273°C (Td onset). The decomposition step is the degradation of cotton cellulose which represented about 18.6% of total weight loss. Unlike corn husk and pineapple leaf, there was no decomposition step of absorbed moisture, implying that the hydroxyl groups in cellulose

were completely substituted by lauroyl chloride. As a result, esterified cotton was more hydrophobic than the cotton cellulose before modification.

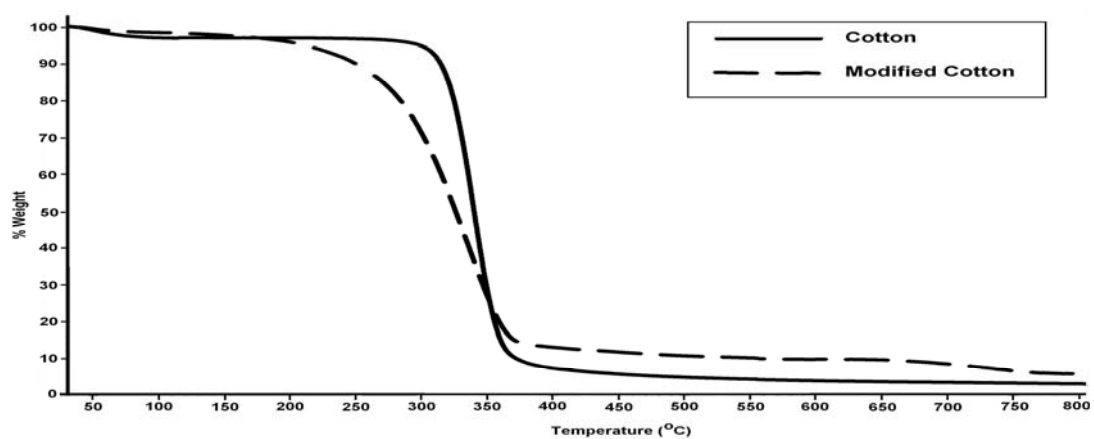
In conclusion, from Figure 4.11, it can be clearly observed that all of the modified cellulose began to decompose at a temperature substantially lower than the native cellulose. This behavior is according to the decrease in crystallinity associated with the substitution of lauric chain in cellulose structure.



(a)



(b)



(c)

Figure 4.11 TGA curves of (a) pineapple leaf, (b) corn husk, and (c) cotton cellulose before and after modification reaction with high DS values

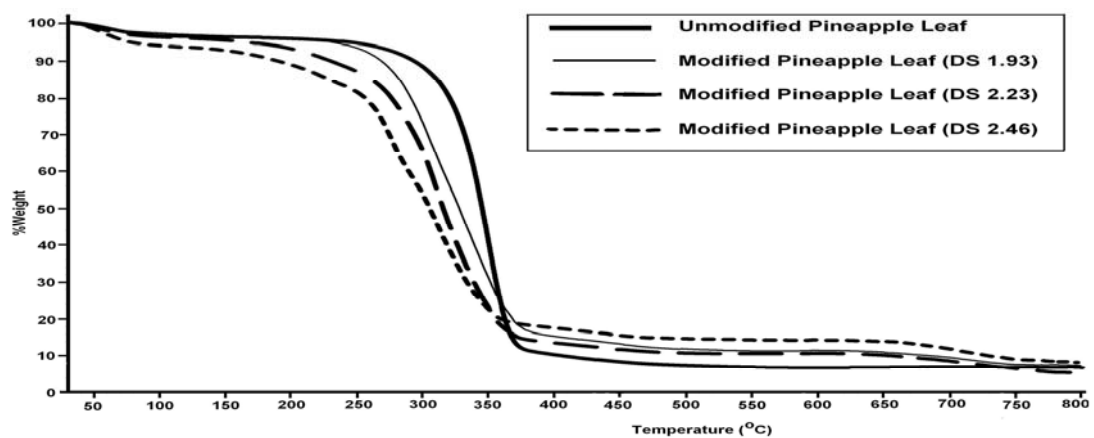
#### 4.2.3.1.2 Effect of degree of substitution

The influence of DS value on thermal stability of pineapple leaf, corn husk, and cotton cellulose is presented in Figure 4.12 (a), (b), and (c), respectively. The result revealed that the thermal stability of modified cellulose is affected by DS value. As seen in Figure 4.12, thermal stability of all modified cellulose decreased with the increasing of DS value. The Td onset of modified pineapple leaf cellulose with DS value of 1.93, 2.23, and 2.46 was 272°C, 266°C, and 256°C, respectively. For corn husk cellulose, Td onset with the DS value of 1.99, 2.44, and 2.73 was 275°C, 250°C, and 192°C, respectively. In addition, Td onset of modified cotton cellulose with the DS value of 1.95, 2.27, and 2.48 was 315°C, 302°C, and 273°C, respectively.

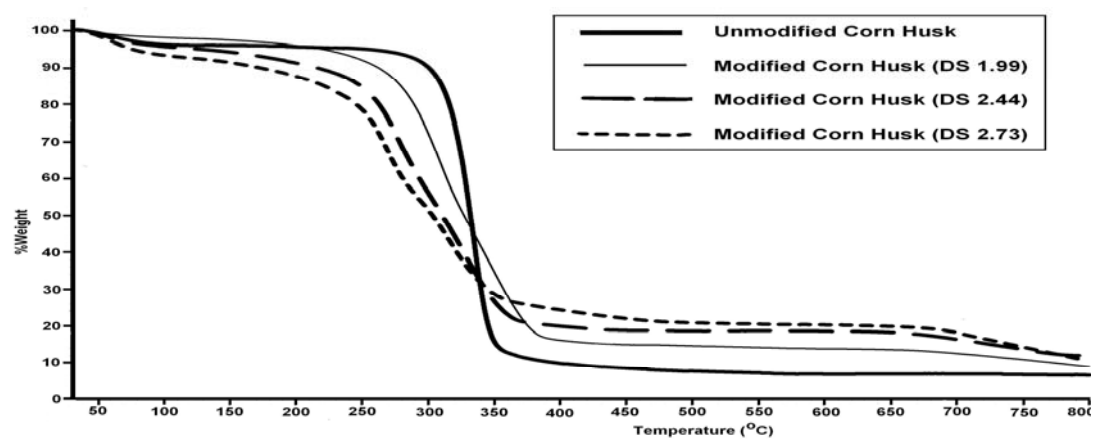
This result could be explained that the higher substitution (high DS value) of lauroyl chloride on hydroxyl group of cellulose structure reduced the inter- and intramolecular hydrogen bond and caused the decrement in crystallinity, as already mentioned earlier. Thus, the Td onset of modified cellulose decreased as the substitution of lauroyl chloride increased. Similar result can be observed in the literatures reported in 2000 by Jandura et al. [4x5] for long chain organic acid cellulose ester (11 or 13 carbon atoms) and in 2006 by Freire and co-worker [330]. They found that the thermal stability of cellulose fiber was affected by crystallinity, which decreased after substitution of cellulose hydroxyl with fatty acid chain. Therefore, the thermal stability of esterified cellulose decreased when cellulose was substituted by fatty acid.

The higher %weight residue at the temperature above 500°C of all modified cellulose comparing to the unmodified ones should be contributed from the lauric chain substituted on the hydroxyl group of cellulose. In fact, %weight residue was also increased with increasing the DS values confirming that the residue at high temperature was absolutely associated with the aliphatic chain substitution on the hydroxyl group of cellulose.

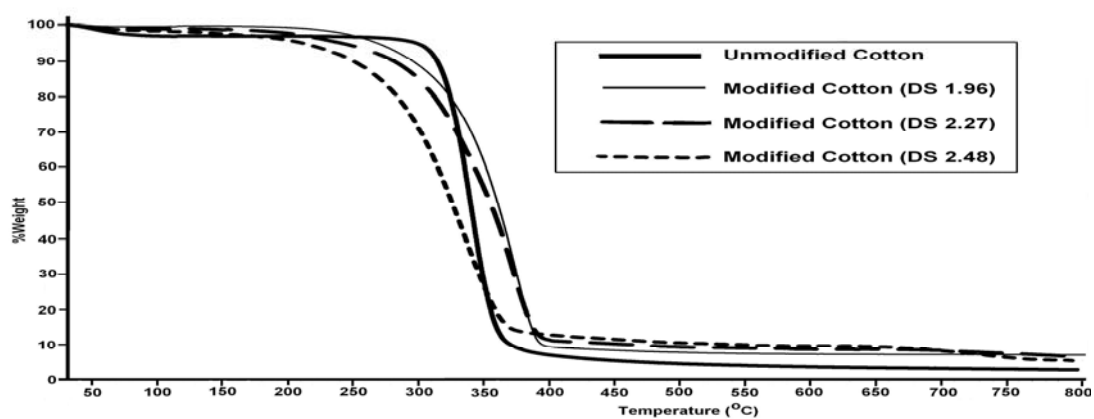




(a)



(b)



(c)

Figure 4.12 TGA curves of (a) pineapple leaf, (b) corn husk, and (c) cotton cellulose with different DS values

#### 4.2.3.2 Differential scanning calorimetry (DSC)

Thermal transition temperature was characterized by a differential scanning calorimetry (DSC). The melting temperature ( $T_m$ ) of esterified cellulose was reported as the peak temperature of melting endotherms recorded on the second heating scan.

##### 4.2.3.2.1 Effect of cellulose source

According to TGA thermograms, the thermal decomposition temperatures of esterified cellulose were in the range of  $300^{\circ}\text{C}$  to  $320^{\circ}\text{C}$ . Therefore, DSC scans were limited to the maximum temperature of  $200^{\circ}\text{C}$  to avoid sample decomposition.

Figure 4.13 illustrates the second heating scan of the DSC thermograms for pineapple leaf, corn husk, and cotton cellulose as raw materials before esterification reaction. As seen, thermograms of all celluloses did not show any significant transition temperature.

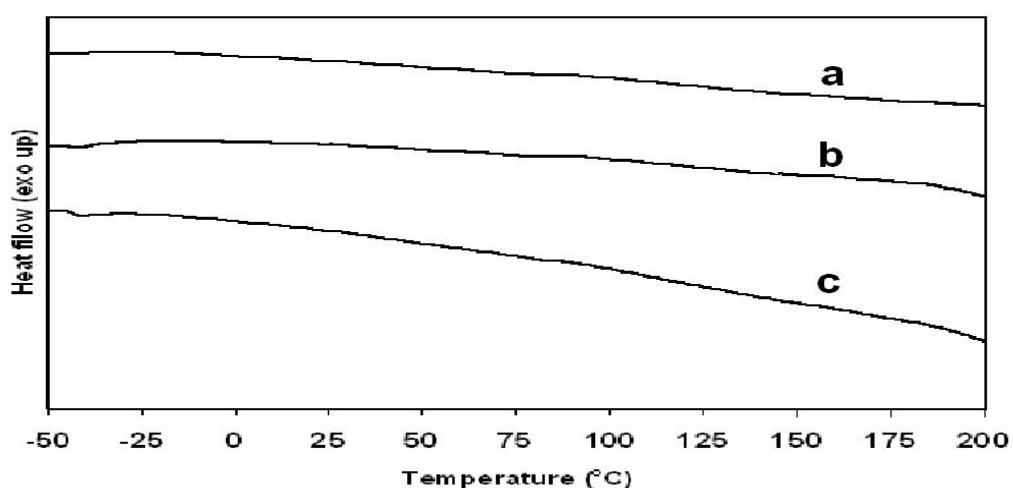


Figure 4.13 DSC thermograms (second heating scan) of (a) pineapple leaf, (b) corn husk, and (c) cotton

Cellulose is a linear high polymer having glucose as a repeating unit, and it has an opportunity of forming significant hydrogen bonding. The resulting high intermolecular forces, in addition to the regular structure of polymer resulted in its high degree of crystallinity. Hence, no melting transition of cellulose can be observed or occurred at temperatures that its melting point nears its decomposition temperature so it can be degraded prior to pyrolysis. In this sense, the cellulose crystallinity in pineapple leaf, corn husk, and cotton cellulose prevent them from presenting thermoplasticity up to melting. Moreover, pineapple leaf, corn husk, and cotton did not show the glass transition temperature owing to their high crystalline structure.

The second heating scan for the DSC thermograms of pineapple leaf, corn husk, and cotton after esterification reaction are presented in Figure 4.14. The DSC thermogram of esterified cotton displayed the second-order transition at  $87.98^{\circ}\text{C}$ , while the second order-transition of esterified pineapple leaf and corn husk were hardly noticed at about  $88^{\circ}\text{C}$  and  $95^{\circ}\text{C}$ , respectively. As shown, there were no significant differences in  $T_g$  among different cellulose source. Obviously, no melting peak was observed indicating that the substitution of lauroyl chloride on the hydroxyl group of cellulose was unable to completely disrupt all the intermolecular hydrogen bondings within the cellulose structure. The esterified-cellulose still possessed high intermolecular forces and high degree of crystallinity.

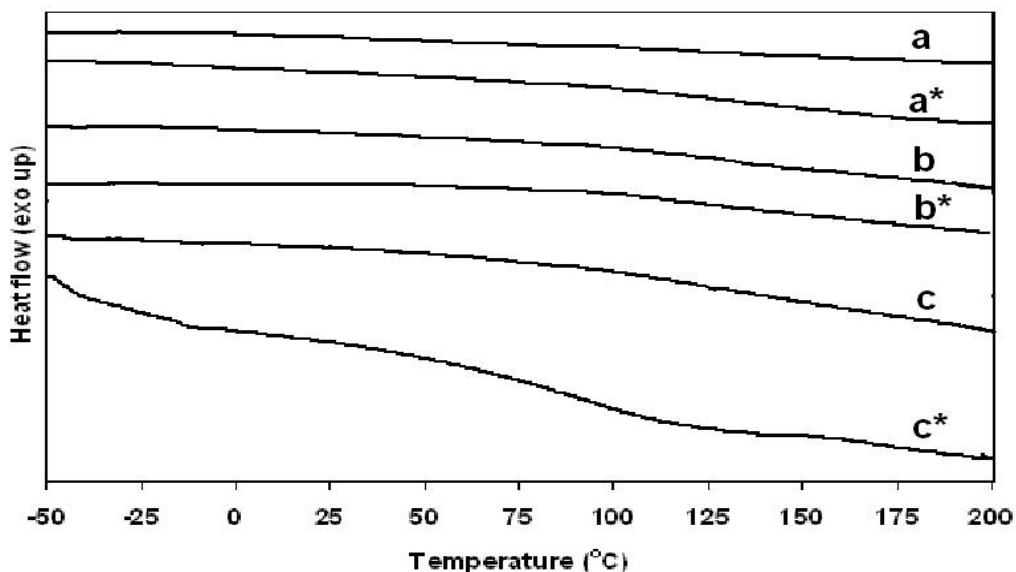


Figure 4.14 DSC thermograms (second heating scan) of (a) pineapple leaf, (a\*) esterified pineapple leaf, (b) corn husk, (b\*) esterified corn husk, (c) cotton and (c\*) esterified cotton

#### 4.2.3.2.2 Effect of degree of substitution

The influence of DS value on thermal transition of pineapple leaf, corn husk, and cotton after esterification is shown in Figure 4.15, 4.16, and 4.17, respectively. The results show that the esterified cellulose with acyl substituent is their majority amorphous materials with a measurable  $T_g$ . This is due to the loss of crystallinity of the cellulose as demonstrated in prior section. The glass transition temperature slightly decreased with the increasing of DS value. The glass transition of esterified pineapple leaf with the lowest DS value was  $97.42^\circ\text{C}$ , when the DS value of esterified pineapple leaf increased, the  $T_g$  shifted towards lower temperature of  $90.86^\circ\text{C}$  and  $88^\circ\text{C}$  at medium and high DS value, respectively. For esterified corn husk, its  $T_g$  appeared at  $125^\circ\text{C}$ ,  $113.91^\circ\text{C}$ , and  $95^\circ\text{C}$  for low, medium, and high DS values, respectively. The esterified cotton with low and medium DS value did not show  $T_g$ , whereas at high DS value the esterified cotton showed  $T_g$  at  $87.98^\circ\text{C}$ .

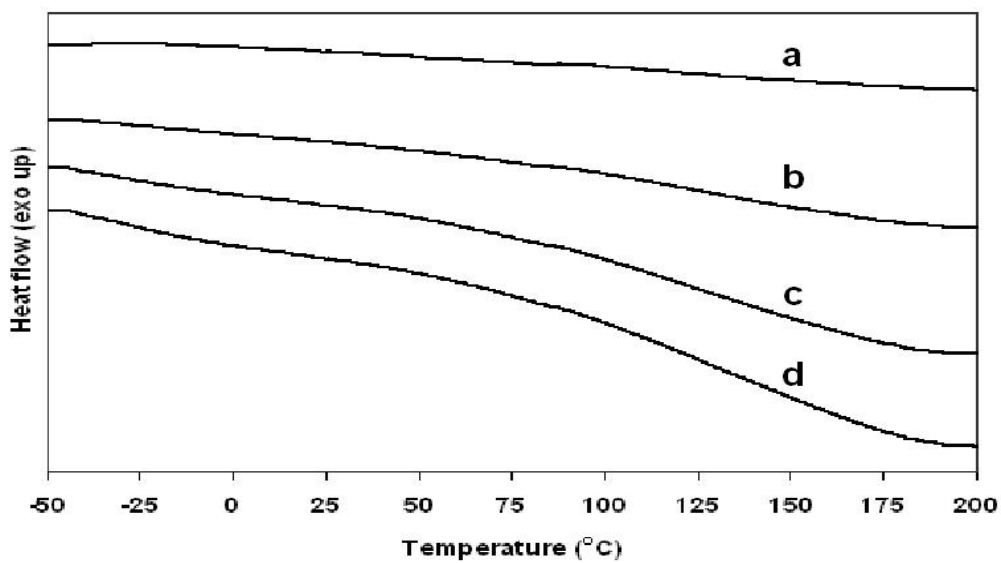


Figure 4.15 DSC thermograms (second heating scan) of (a) pineapple leaf and esterified pineapple leaf with (b) low, (c) medium, and (d) high DS values

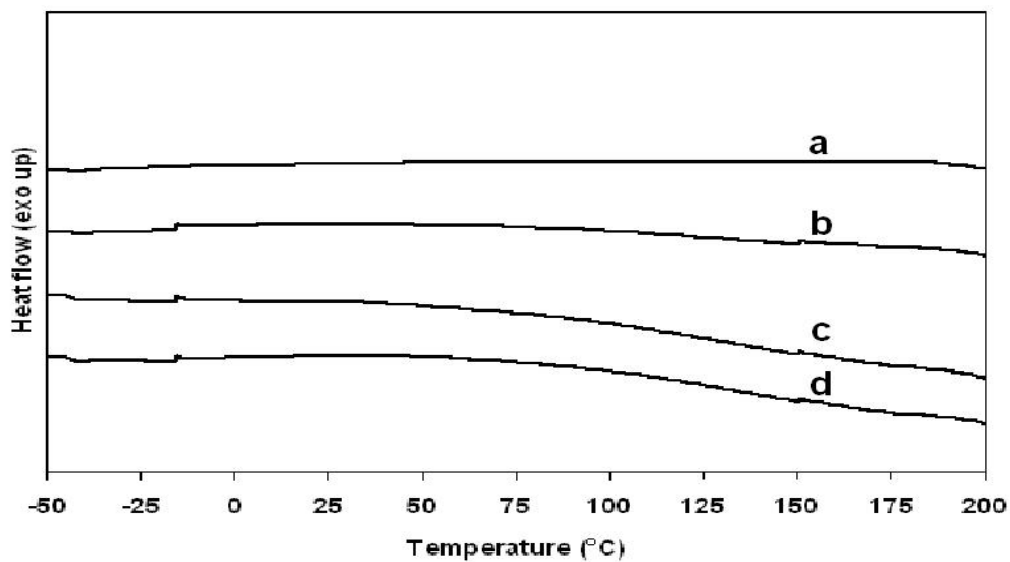


Figure 4.16 DSC thermograms (second heating scan) of (a) corn husk and esterified corn husk with (b) low, (c) medium, and (d) high DS values

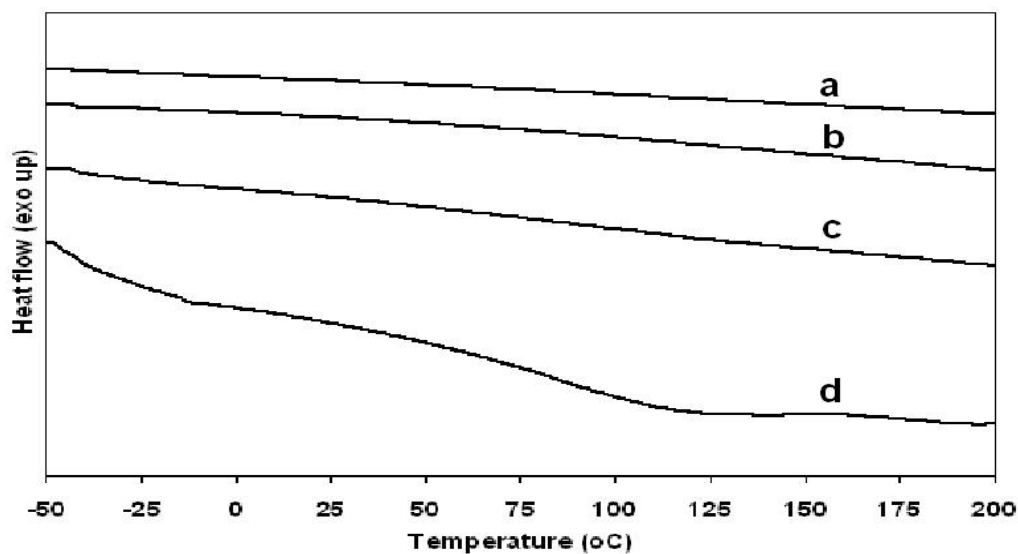


Figure 4.17 DSC thermograms (second heating scan) of (a) cotton and esterified cotton with (b) low, (c) medium, and (d) high DS values

#### 4.2.4 Morphological Studies

Before esterification, pineapple leaf cellulose, corn husk cellulose, and cotton cellulose can be seen as white powder by naked eyes. However, the morphological characteristics of unmodified pineapple leaf, corn husk, and cotton cellulose were observed differently under a scanning electron microscope.

The SEM micrographs of unmodified and modified pineapple leaf cellulose are exhibited in Figure 4.18. The unmodified pineapple leaf cellulose showed a smooth surface of a fragment, flatted, fibril or a flake shape with approximately 10-60  $\mu\text{m}$  in its length. After modification reaction, pineapple leaf cellulose presented the rough surface with larger dimension or particle size. The particle size of modified pineapple leaf cellulose was slightly increased with increasing DS value. As seen, its size was increased from approximately 200  $\mu\text{m}$  of low DS value to around 250 and 320  $\mu\text{m}$  of

medium and high DS values, respectively. This result indicated that lauroyl chloride as an esterifying agent was successfully substituted on the hydroxyl group of native pineapple leaf cellulose and aggregated on its surface resulting in the large dimension of esterified cellulose.

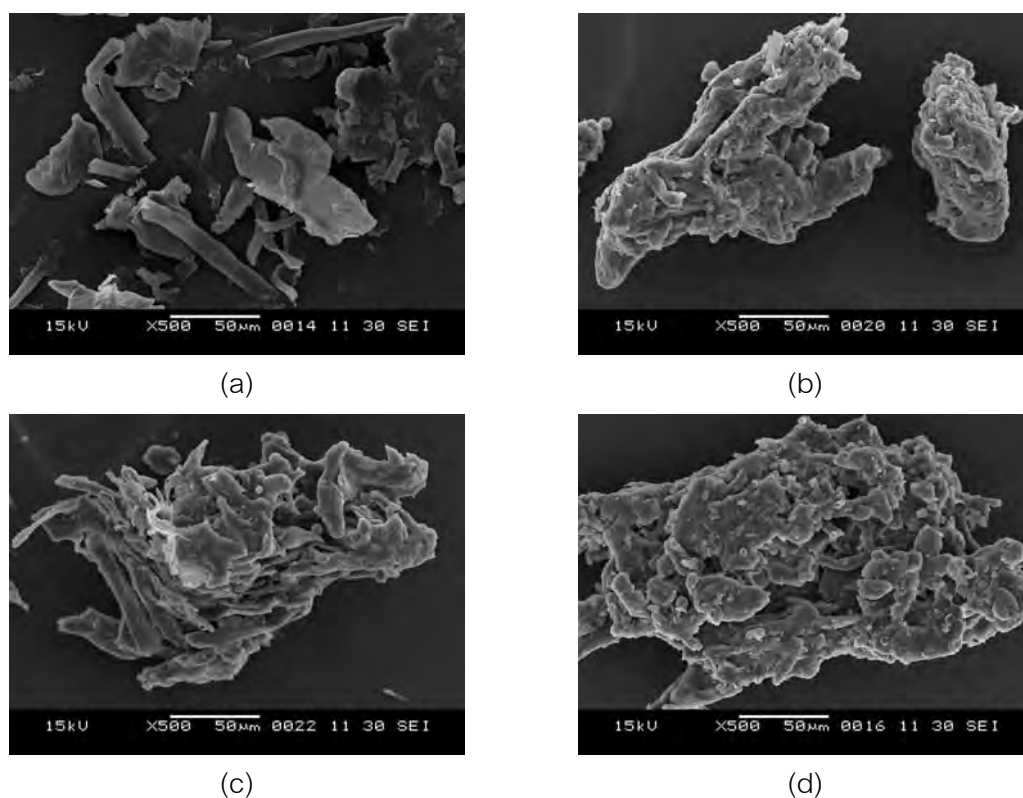


Figure 4.18 SEM micrographs of unmodified pineapple leaf cellulose (a) and modified pineapple leaf with (b) low, (c) medium, and (d) high DS values

Similarly, Figure 4.19 shows that the unmodified corn husk cellulose presented the flattened fibril or the flake shape with relatively smooth surface. The particle size of unmodified corn husk cellulose was in the range of 10-100  $\mu\text{m}$  (Figure 4.19 (a)). Whereas the modified corn husk cellulose exhibited larger particle size with rough surface (Figure 4.19 (b), (c), and (d)). The particle size of modified corn husk cellulose increased with increasing DS value from 110  $\mu\text{m}$  (low DS value) to 300  $\mu\text{m}$  (medium DS

value) and 700  $\mu\text{m}$  (high DS value). The different morphologies between the unmodified and modified corn husk cellulose were resulted from lauroyl chloride substitution on the hydroxyl groups of corn husk cellulose leading to an aggregation of lauroyl chloride on its surface, which then makes its particle size enlarged.

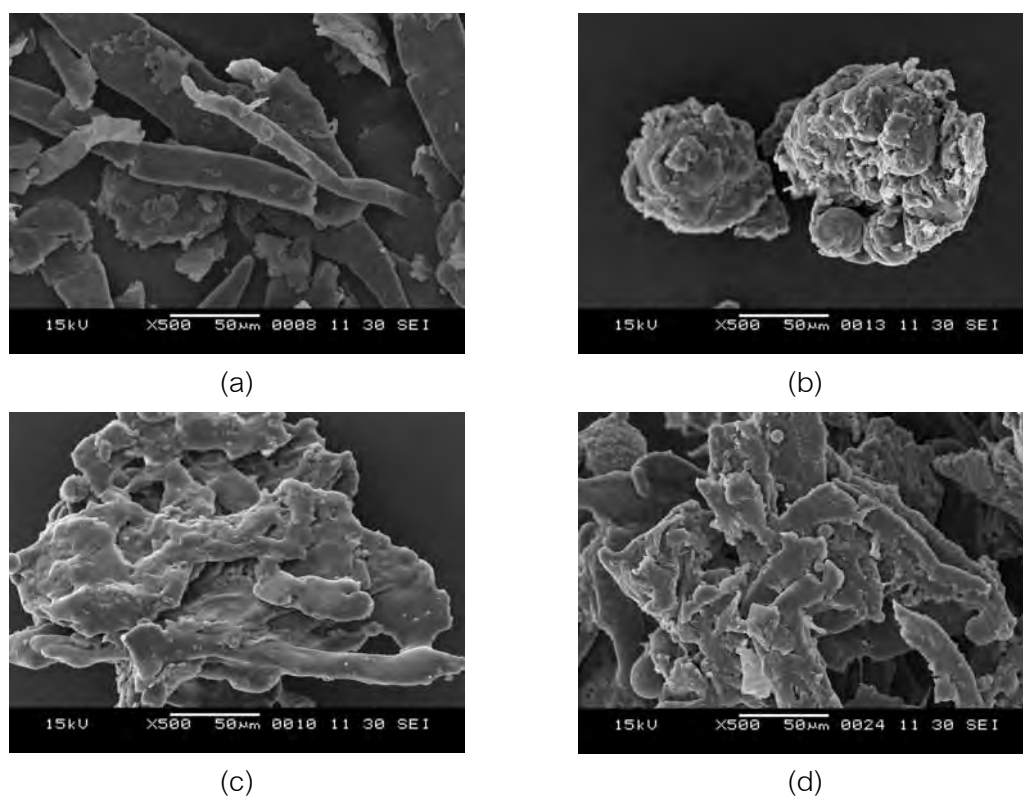


Figure 4.19 SEM micrographs of unmodified corn husk cellulose (a) and modified corn husk with (b) low, (c) medium, and (d) high DS values

The SEM micrographs of unmodified and modified cotton cellulose are presented in Figure 4.20. The morphology of unmodified cotton cellulose revealed the short fiber shape having smooth surface with approximately 10  $\mu\text{m}$  in dimension (Figure 4.20 (a)). After modification reaction, the surface morphology of modified cotton



cellulose was different from unmodified cotton cellulose in that it showed rough surface and larger particle size (Figure 4.20 (b), (c), and (d)). As seen, the particle size of modified cotton cellulose was increased as a function of DS value from 120  $\mu\text{m}$  of low DS value to 150  $\mu\text{m}$  (medium DS value) and 220  $\mu\text{m}$  (high DS value). These results implied the aggregation of acyl substitution of lauroyl chloride on the cotton cellulose surface.

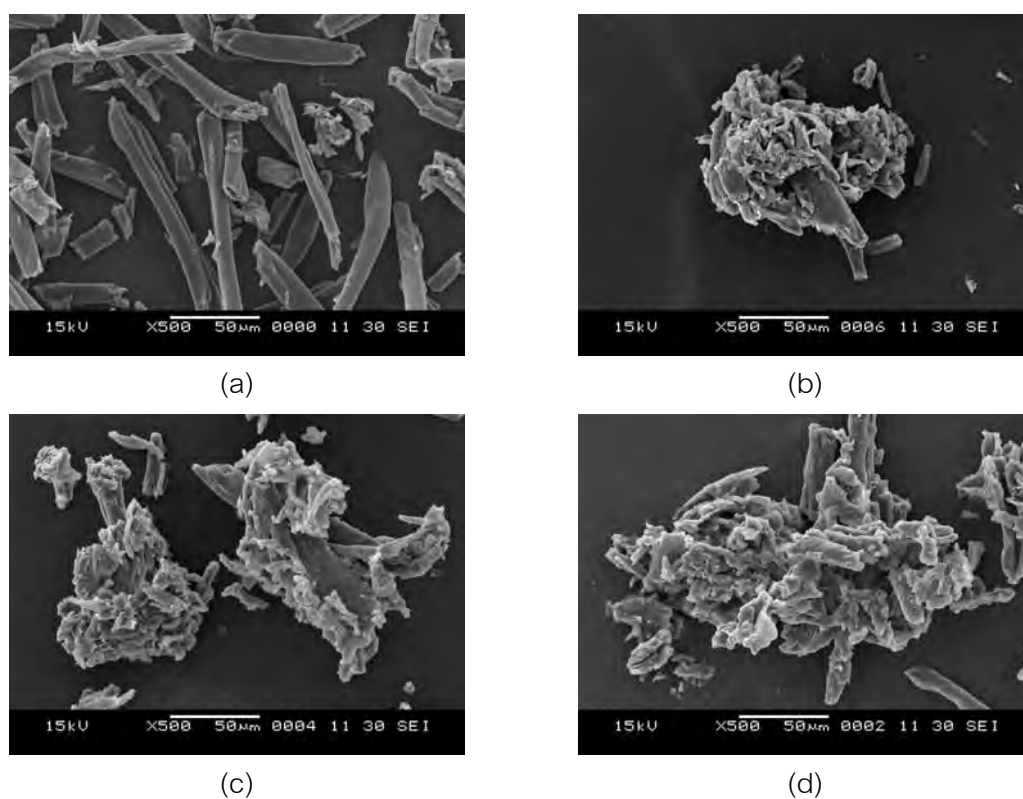


Figure 4.20 SEM micrographs of unmodified cotton cellulose (a) and modified cotton with (b) low, (c) medium, and (d) high DS values

### 4.3 Characterization of Esterified Cellulose Film

Esterified cellulose films were prepared by a casting method with chloroform and the thickness of film samples was approximately 250-300  $\mu\text{m}$ . Gloss, wettability, water absorption, and tensile properties of modified cellulose film from pineapple leaf, corn husk, and cotton with different DS values were evaluated.

#### 4.3.1 Gloss

The physical appearance of modified cellulose films in term of surface properties was determined by gloss measurement. The gloss values of modified cellulose films are summarized in Table 4.4.

Table 4.4 Gloss values of modified pineapple leaf, corn husk, and cotton films at different DS values

|                | Gloss*(unit)     |                   |                  |
|----------------|------------------|-------------------|------------------|
|                | High DS          | Medium DS         | Low DS           |
| Pineapple Leaf | 21.76 $\pm$ 8.67 | 19.60 $\pm$ 4.13  | 14.63 $\pm$ 9.63 |
| Corn Husk      | 23.14 $\pm$ 1.66 | 16.56 $\pm$ 3.22  | 6.72 $\pm$ 1.47  |
| Cotton         | 43.76 $\pm$ 6.41 | 27.14 $\pm$ 11.78 | 4.84 $\pm$ 1.50  |

\*Gloss of standard black calibration = 95.1 units

The data shown that gloss values of all modified cellulose films increased with increasing DS values. This result can be explained that since the gloss of materials relates to the smoothness of the material surface, thus the smoother surface yields the greater gloss value. In other words, increasing of DS values resulted in the smooth surface of modified cellulose film. This is because increasing of DS values means increasing of acyl substitution in cellulose structure leading to an increase in the

solubility of modified cellulose in chloroform. As a result, the modified cellulose film with higher DS value obtained the greater gloss value.

Considering at medium and high DS values, the result showed that modified cotton film possessed higher gloss value than the other modified cellulose films. This behavior is due to the fact that modified cotton film had more whiteness and greater smooth surface than modified pineapple leaf and modified corn husk films. The whiteness results in the gloss value in term of light reflection. After esterification, the esterified cotton had white color; whereas, the other two types of cellulose exhibited slight yellowness. Thus, the modified cotton film had greater gloss value although the DS value of esterified cotton film was less than that of esterified pineapple leaf and corn husk films at high and medium DS values.

#### 4.3.2 Wettability

The wettability of film surface determined by contact angle measurement revealed the hydrophobicity of the surface as indicated by an increase in contact angle values. The contact angle values of modified cellulose films with different DS values are summarized in Table 4.5.

As seen, the contact angle values of all modified cellulose films, increased when the DS values increased, which means that the wettability of all modified cellulose films decreased with increasing DS values. This result can be explained in terms of the change in hydrophobicity of cellulose surface upon esterification reaction. In general, the nature celluloses are less or inconsiderably hydrophobic than the modified celluloses. The decreasing hydroxyl groups or increasing acyl groups in cellulose structure upon esterification reaction leads to the increase in hydrophobicity of modified cellulose. As a result, water droplet is more difficult to be absorbed on the cellulose surface.

Table 4.5 Contact angle values of modified pineapple leaf, corn husk, and cotton films at different DS values

|                | Contact Angle (Degree) |            |           |
|----------------|------------------------|------------|-----------|
|                | High DS                | Medium DS  | Low DS    |
| Pineapple Leaf | 114.1 ±6.3             | 100.2 ±4.1 | 88.7 ±9.1 |
| Corn Husk      | 121.2 ±3.7             | 94.0 ±7.8  | 92.4± 9.3 |
| Cotton         | 108.8±7.8              | 99.5±9.5   | 94.8±11.9 |

#### 4.3.3 Water Absorption

The water absorption of modified pineapple leaf, corn husk, and cotton films was evaluated by measurement of %weight increase after immersing the films in water at room temperature for 24 hours. The effect of DS values on water absorption of modified cellulose films is shown in Table 4.6.

It can be observed that water absorption of all modified cellulose films significantly decreased with an increasing of the DS values. Similar to gloss values and wettability, the obtained result is due to a decreasing of hydroxyl groups and an increasing of hydrophobicity of modified cellulose. In other words, the increasing of DS value resulted in high acyl substitution of cellulose structure leading to the high hydrophobicity of modified cellulose.

When we consider the effect of cellulose source at low DS values on water absorption, it was found that the modified cotton film had lower water absorption values comparing to the other cellulose sources. This results, similar to wettability, implied that the esterified cotton films perform higher hydrophobicity, and it have the decreasing ability of wellability and water absorption.

Table 4.6 Water absorption of modified pineapple leaf, corn husk, and cotton films at different DS values

|                | Water Absorption (%) |              |              |
|----------------|----------------------|--------------|--------------|
|                | High DS              | Medium DS    | Low DS       |
| Pineapple Leaf | 21.56 ± 2.12         | 25.71 ± 1.71 | 51.97 ± 5.17 |
| Corn Husk      | 20.25 ± 4.17         | 22.95 ± 1.89 | 63.70 ± 4.95 |
| Cotton         | 4.28 ± 0.38          | 5.01 ± 1.87  | 17.35 ± 5.78 |

#### 4.3.4 Tensile Properties

The tensile properties of all modified cellulose films are summarized in Table 4.7. The effect of DS values of modified cellulose films on tensile strength, tensile modulus, and %elongation at break are illustrated in Figure 4.21 (a), (b), and (c), respectively.

When we focus on the effect of DS values, it was found that the tensile strength (Figure 4.21 (a)), tensile modulus (Figure 4.21 (b)), and elongation at break (Figure 4.21 (c)) of all modified cellulose films increased with increasing of DS values. This result is possibly owing to (1) the increasing of long-chain substituent may be attributed to the partial crystallization and overlepping of C<sub>12</sub> side chains in lauroyl chloride as esterifying agent, and (2) the occurrence of chain entanglement of long-chain substitution of lauroyl chloride. As a result, all tensile properties were improved. According to Sealey and co-workers [27], the increasing of degree of substitution of lauroyl chain caused an increase in side chain crystal thickness resulted in increasing of the tensile strength and tensile modulus. The increase of elongation at break with increasing DS values may be referred to the internal plasticization provided by non-alignment part of long-chain fatty acid groups leading to an enhancement in the mobility between chains.

In case of cellulose source, clearly at high DS value (DS pineapple leaf=2.46, DS corn husk=2.73, and DS cotton=2.48), modified corn husk film exhibited the highest tensile properties followed by modified pineapple leaf film and modified cotton film, respectively. The superior tensile properties of modified corn husk film may be assigned to the influence of its DS value which was greater than those of the other two modified cellulose films. Hence, modified corn husk film with the highest DS value (DS=2.73) shown the maximum in tensile properties.

Table 4.7 Tensile properties of modified pineapple leaf, corn husk, and cotton films at different DS values

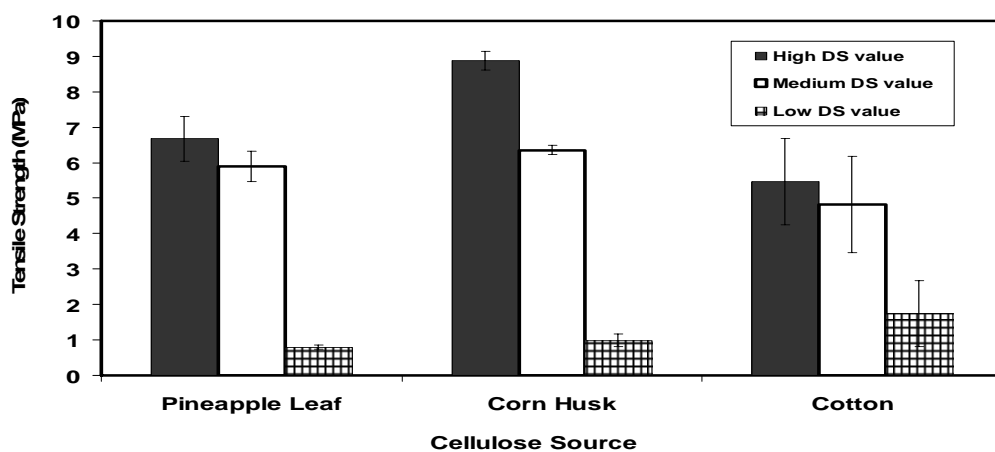
|                | Tensile Strength (MPa) |           |            |
|----------------|------------------------|-----------|------------|
|                | High DS                | Medium DS | Low DS     |
| Pineapple Leaf | 6.68 ± 0.63            | 5.89±0.43 | 0.79±0.06  |
| Corn Husk      | 8.87±0.26              | 6.35±0.13 | 0.98 ±0.18 |
| Cotton         | 5.47±1.22              | 4.82±1.35 | 1.75±0.93  |

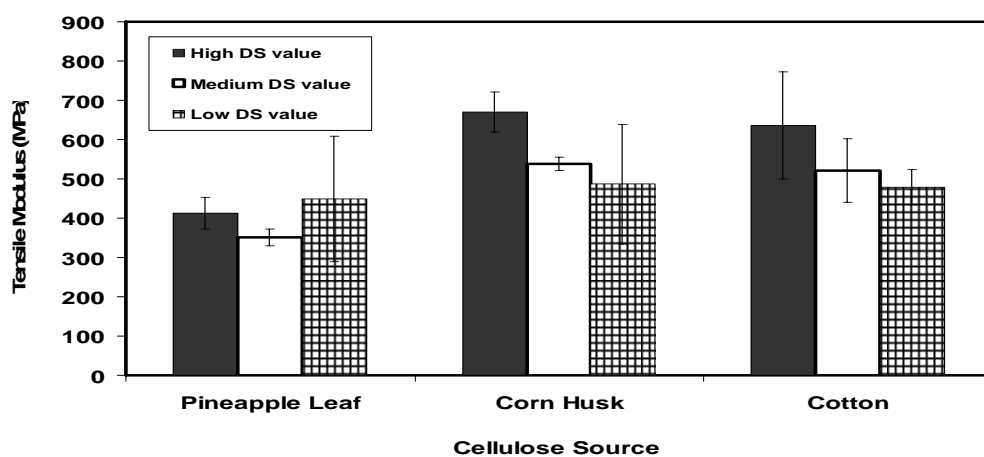
|                | Tensile Modulus (MPa) |               |               |
|----------------|-----------------------|---------------|---------------|
|                | High DS               | Medium DS     | Low DS        |
| Pineapple Leaf | 413.36± 40.03         | 350.86 ±21.63 | 448.40±159.70 |
| Corn Husk      | 670.40±50.39          | 537.91±16.71  | 486.26±151.67 |
| Cotton         | 635.72±135.99         | 521.65±80.40  | 479.23±44.41  |

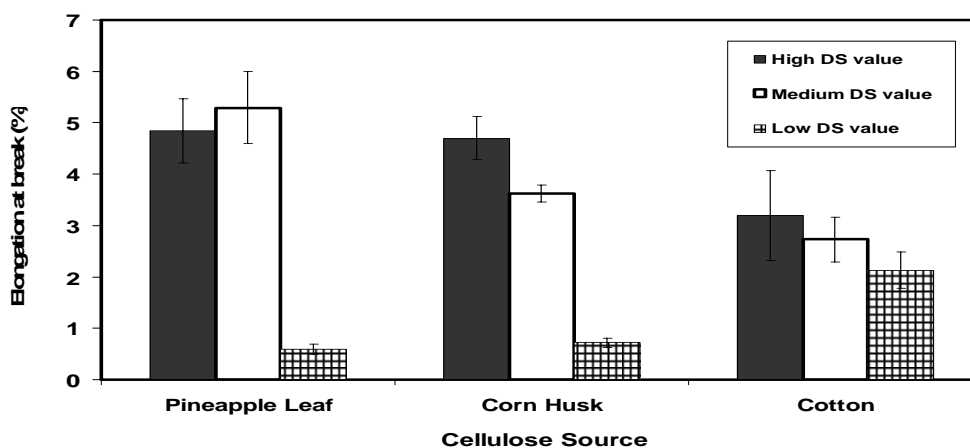
|                | Elongation at break (%) |            |            |
|----------------|-------------------------|------------|------------|
|                | High DS                 | Medium DS  | Low DS     |
| Pineapple Leaf | 4.84±0.63               | 5.29 ±0.70 | 0.60±0.10  |
| Corn Husk      | 4.70±0.42               | 3.62±0.16  | 0.72 ±0.09 |
| Cotton         | 3.20±0.87               | 2.73±0.44  | 2.13±0.35  |



(a)



(b)



(c)

Figure 4.21 Effect of DS value on tensile strength (a), tensile modulus (b), and elongation at break (c) of modified pineapple leaf, corn husk, and cotton films

#### 4.4 Biodegradability of Esterified Cellulose Film

Biodegradability of esterified cellulose films was carried out by real composting condition, waste water treatment system condition, and enzymatic degradation. The biodegradability of esterified cellulose films was followed periodically by determining the change in %weight loss and physical appearance of the film surface.

##### 4.4.1 Effect of Degree of Substitution

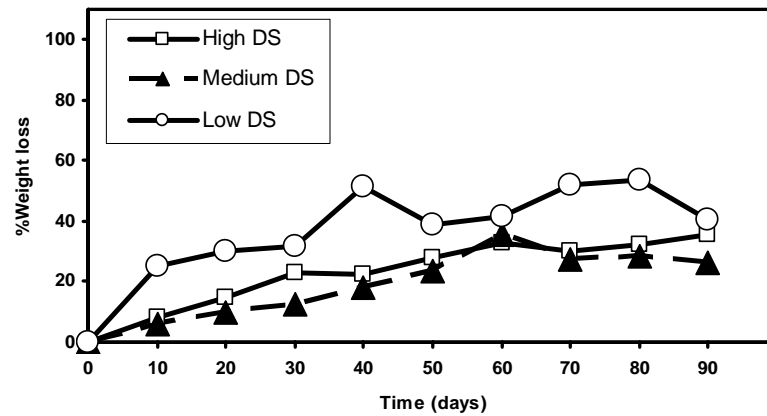
Figure 4.22, 4.23, and 4.24 illustrate %weight loss of esterified cellulose films with different DS values under real composting condition, waste water treatment system condition, and enzymatic degradation, respectively. As seen in Figure 4.22, upon increasing of exposure time in real composting condition, %weight loss of all types of films regardless of DS value or cellulose sources continuously increased especially for the esterified corn husk that it can be almost completely degraded within three months. Similar trends were also found when these films were tested in waste water treatment system. The effect of biodegradability conditions will be compared and discussed shortly. The degradation or %weight loss of cellulose film is resulted from consumption of microorganisms. Microorganisms such as bacteria and fungi can degrade cellulose ester by producing enzymes to digest the carbon molecules of cellulose backbone and ingest them in their digestive system. Cellulases are enzymes catalyzing the hydrolysis of cellulose, as a result, cellulose occurs degradation by appearing holes, increasing %weight loss, shorter molecular chain, etc. Regarding the effect of degree of substitution, obviously, in all conditions, the lower degree of substitution resulted in the esterified cellulose films with greater biodegradability. Esterified pineapple leaf, corn husk, and cotton films with low degree of substitution had the greatest biodegradation rate. For example, under waste water treatment system (Figure 4.23 (c)), the esterified cotton film with low DS values had considerable highest %weight loss as high as 100%



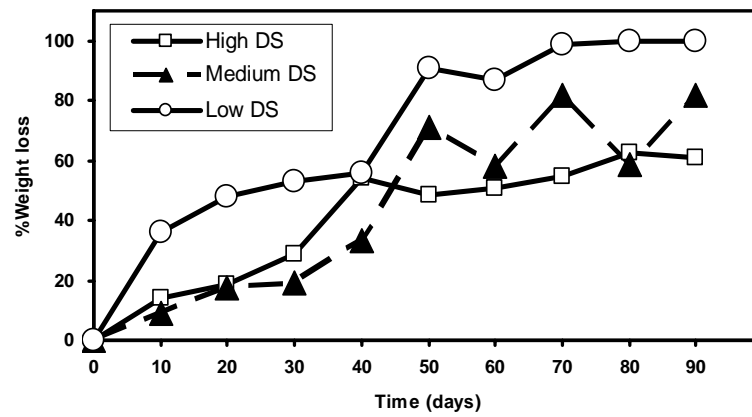
upon exposed in waste water for 90 days; whereas the film at high DS values had only 13.71% weight loss.

The decreasing of biodegradability with the increasing of degree of substitution may be due to the ester side chains inhibit the working of enzymes to attack cellulose itself. Thus, the higher DS value, the lower unsubstituted residues; as a result, enzymes can not work efficiently. In addition, considering water absorption of esterified cellulose films, it was found that all esterified cellulose films with low DS value had higher water absorption than the esterified cellulose films with higher DS value. This result implies that the esterified films with low DS value can be hydrolyzed easier than the other films with higher DS values, as a result, these films exhibited greater biodegradability.

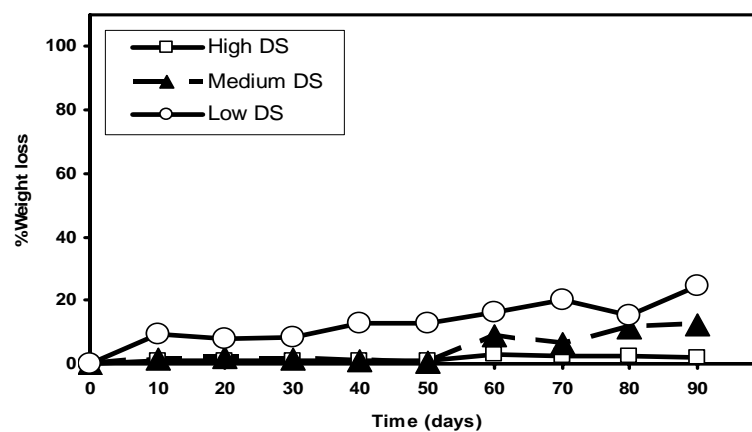
The influence of degree of substitution is more clearly illustrated in Figure 4.25, 4.26, and 4.27 which those Figures show the appearance of pineapple leaf, corn husk, and cotton films with different DS values in real composting condition, waste water treatment system condition and enzymatic degradation, respectively. Clearly, the esterified cellulose films with low DS value exhibits the greater biodegradability than those films with higher DS value in particular when comparing with the film before biodegradation. From visual observation, after biodegradation significant changes can be noticed such as roughening of the surface, formation of holes or cracks, de-fragmentation, changes in color, and even formation of bio-films on surface. This result can be confirmed by SEM micrographs. The esterified pineapple leaf films with low DS value (Figure 4.28 (d)) presents the distinct degradation of the film as evidenced by the existing of various and larger holes, while the esterified pineapple leaf films with higher DS value (Figure 4.28 (b), (c)) show lower amount of small cavities. Similar results were also found for the esterified corn husk and cotton films as presented in Figure 4.29 and 4.30, respectively.



(a)

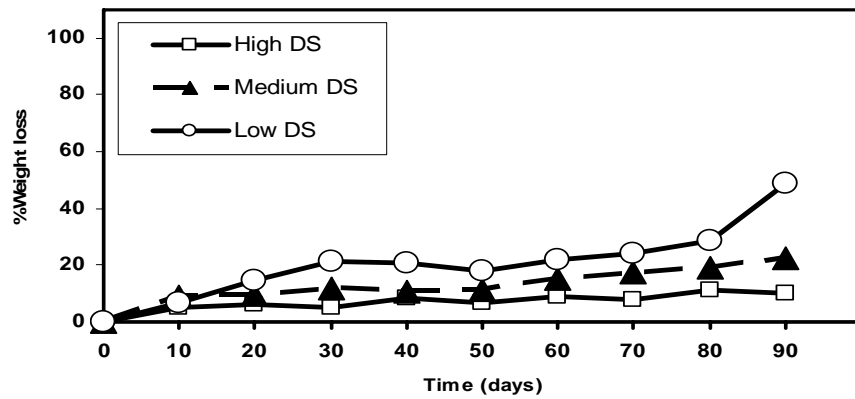


(b)

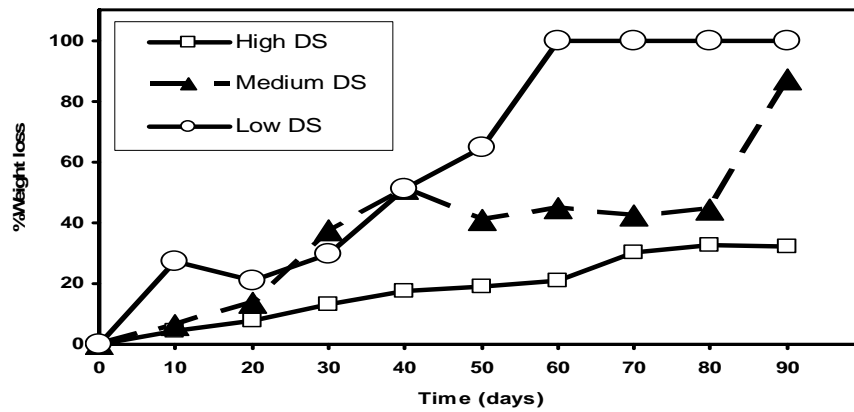


(c)

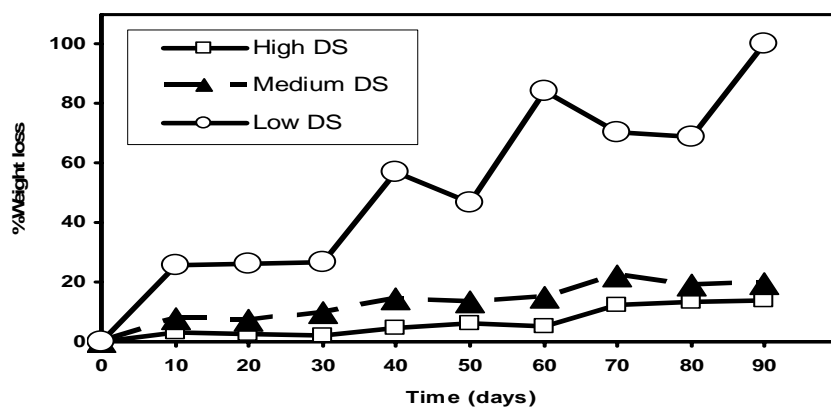
Figure 4.22 Effect of degree of substitution on %weight loss of (a) pineapple leaf, (b) corn husk, and (c) cotton cellulose films in real composting condition



(a)

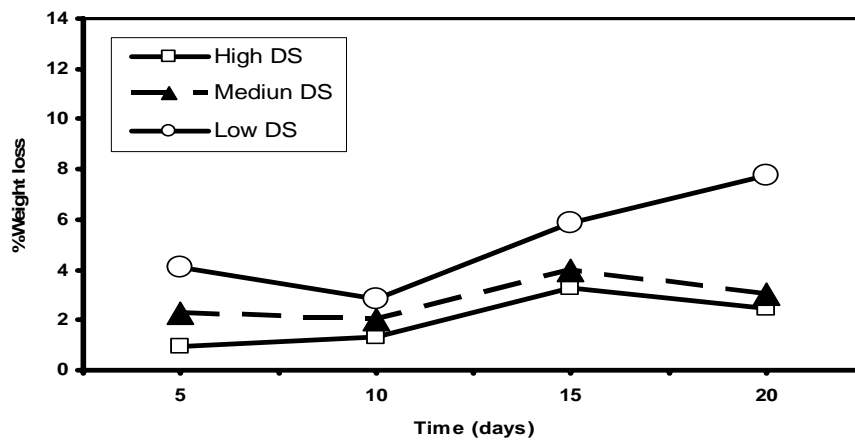


(b)

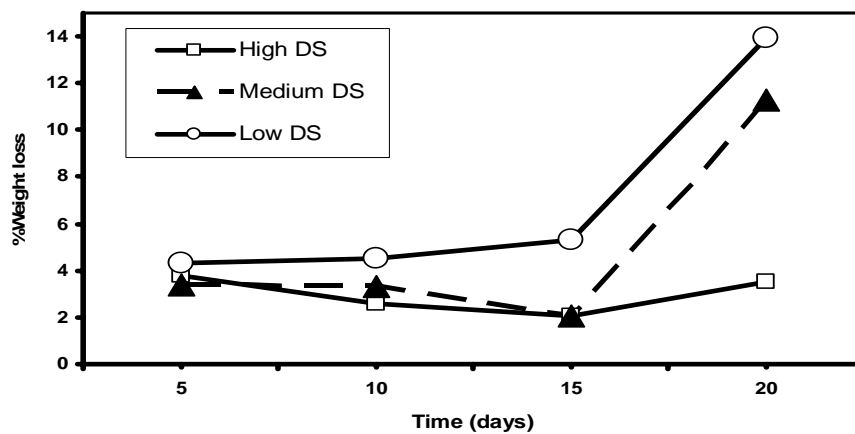


(c)

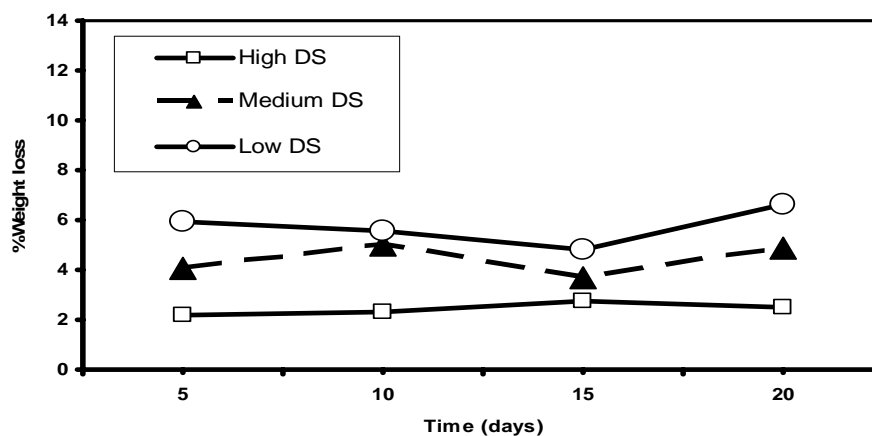
Figure 4.23 Effect of degree of substitution on %weight loss of (a) pineapple leaf, (b) corn husk, and (c) cotton cellulose films in waste water treatment system condition



(a)



(b)



(c)

Figure 4.24 Effect of degree of substitution on %weight loss of (a) pineapple leaf, (b) corn husk, and (c) cotton cellulose films in enzymatic degradation

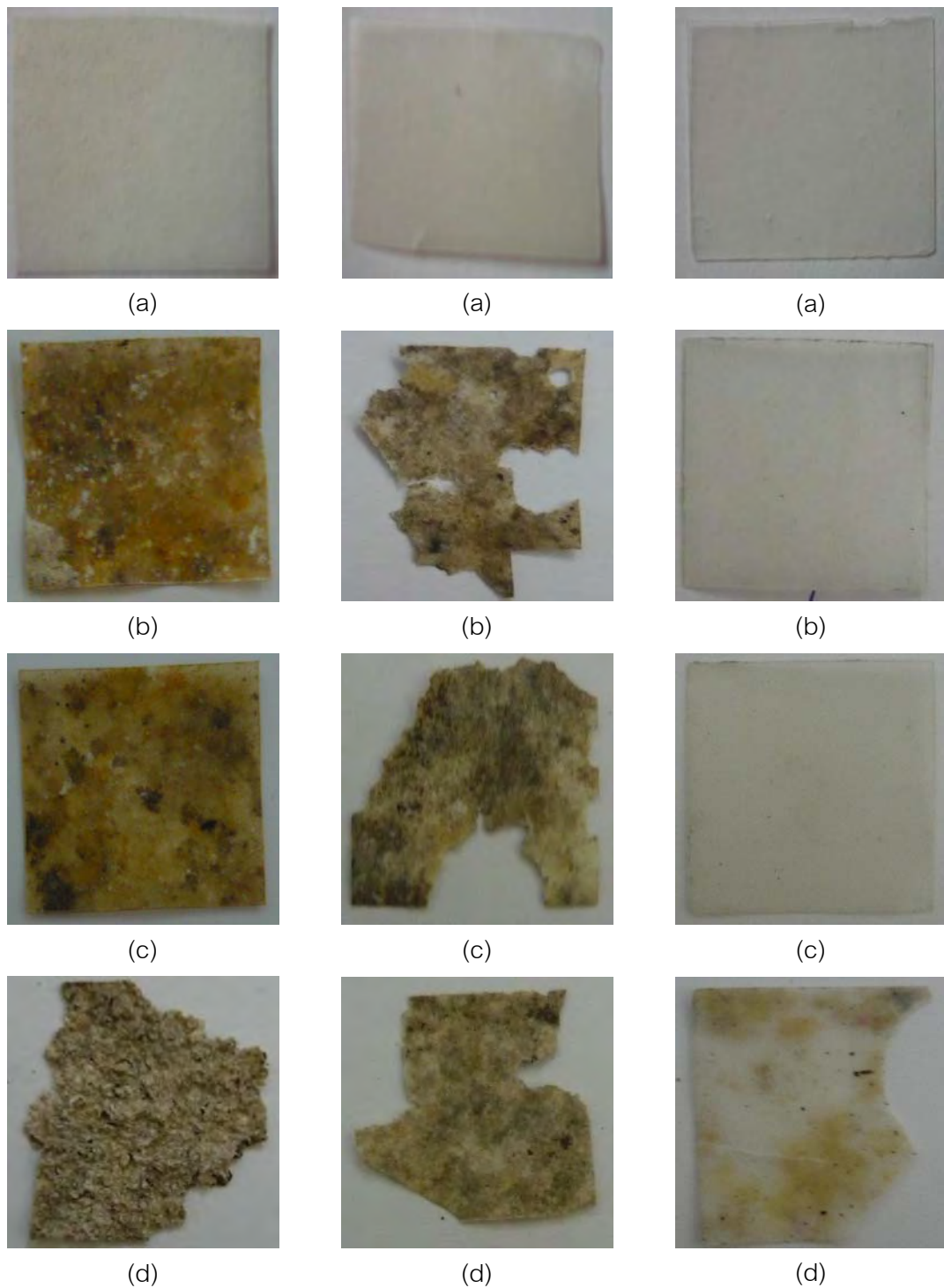


Figure 4.25 Appearance of esterified pineapple leaf (left), corn husk (middle), and cotton (right) before (a) and after biodegradation testing under real composting condition for 90 days with high DS (b), medium DS (c), and low DS (d) values

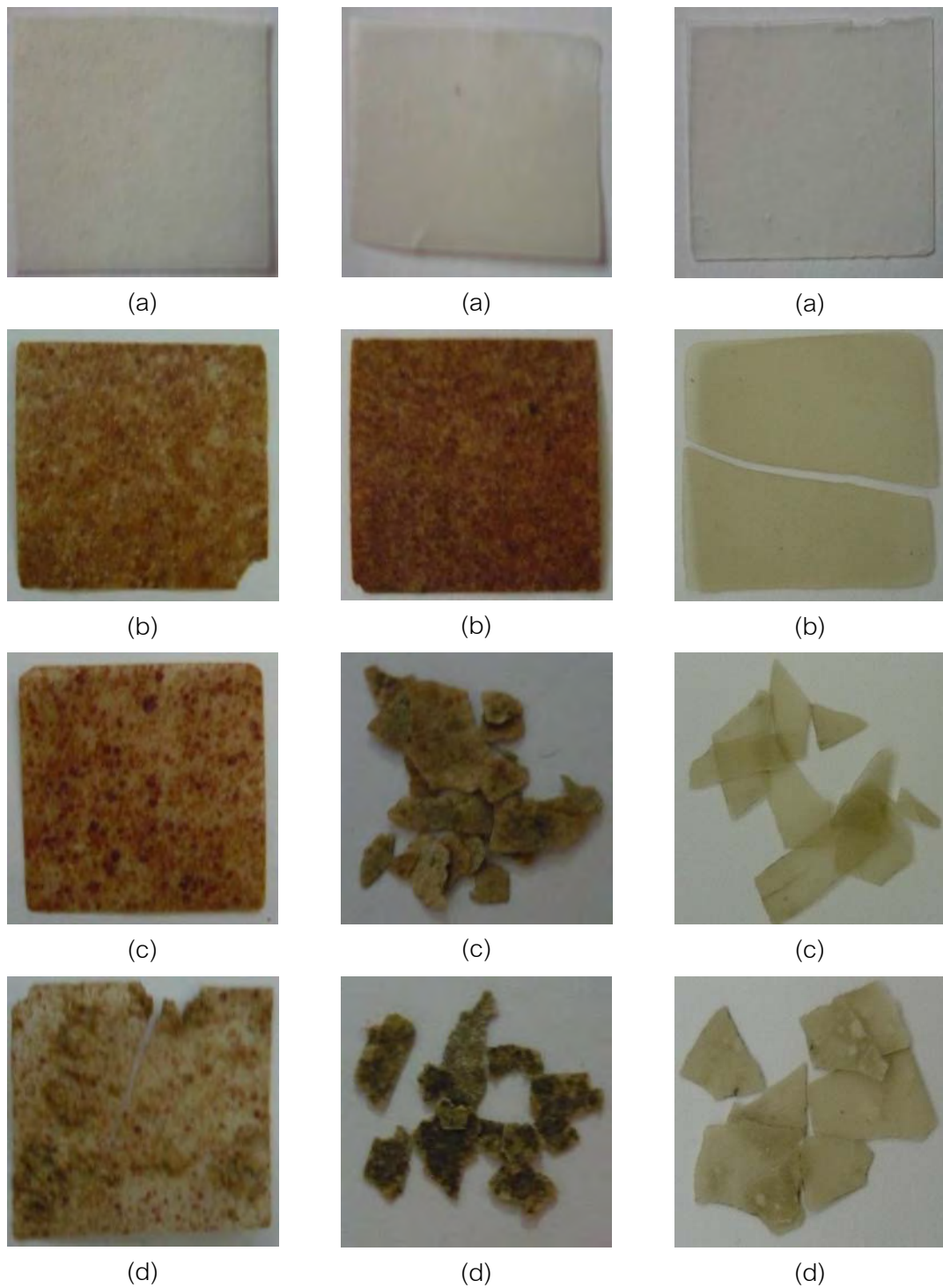


Figure 4.26 Appearance of esterified pineapple leaf (left), corn husk (middle), and cotton (right) before (a) and after biodegradation testing in waste water treatment condition for 50 days with high DS (b), medium DS (c), and low DS (d) values

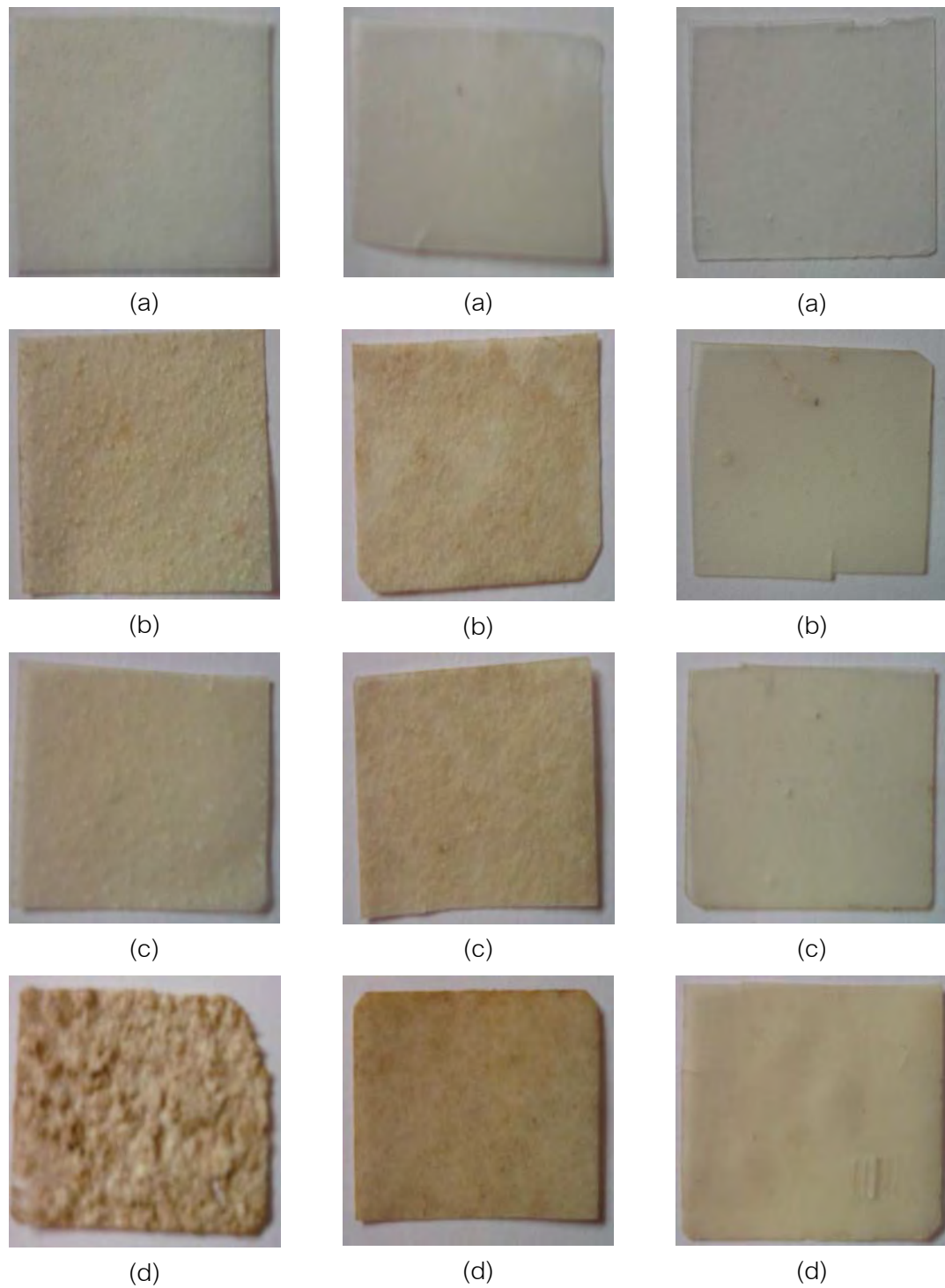


Figure 4.27 Appearance of esterified pineapple leaf (left), corn husk (middle), and cotton (right) before (a) and after biodegradation testing under enzymatic degradation for 20 days with high DS (b), medium DS (c), and low DS (d) values

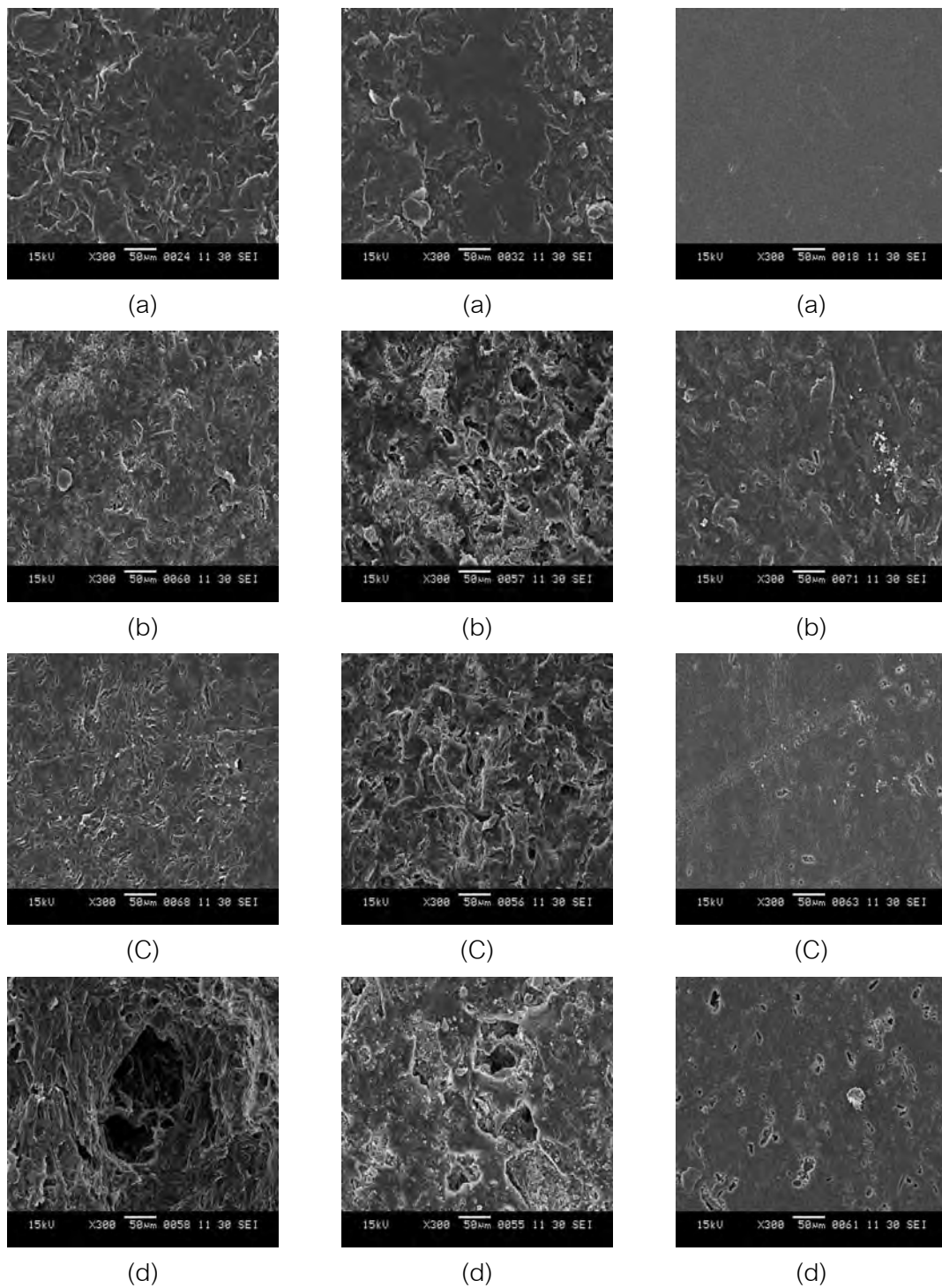


Figure 4.28 SEM micrographs of esterified pineapple leaf (left), corn husk (middle), and cotton (right) before (a) and after biodegradation testing under real composting condition for 90 days with high DS (b), medium DS (c), and low DS (d) values



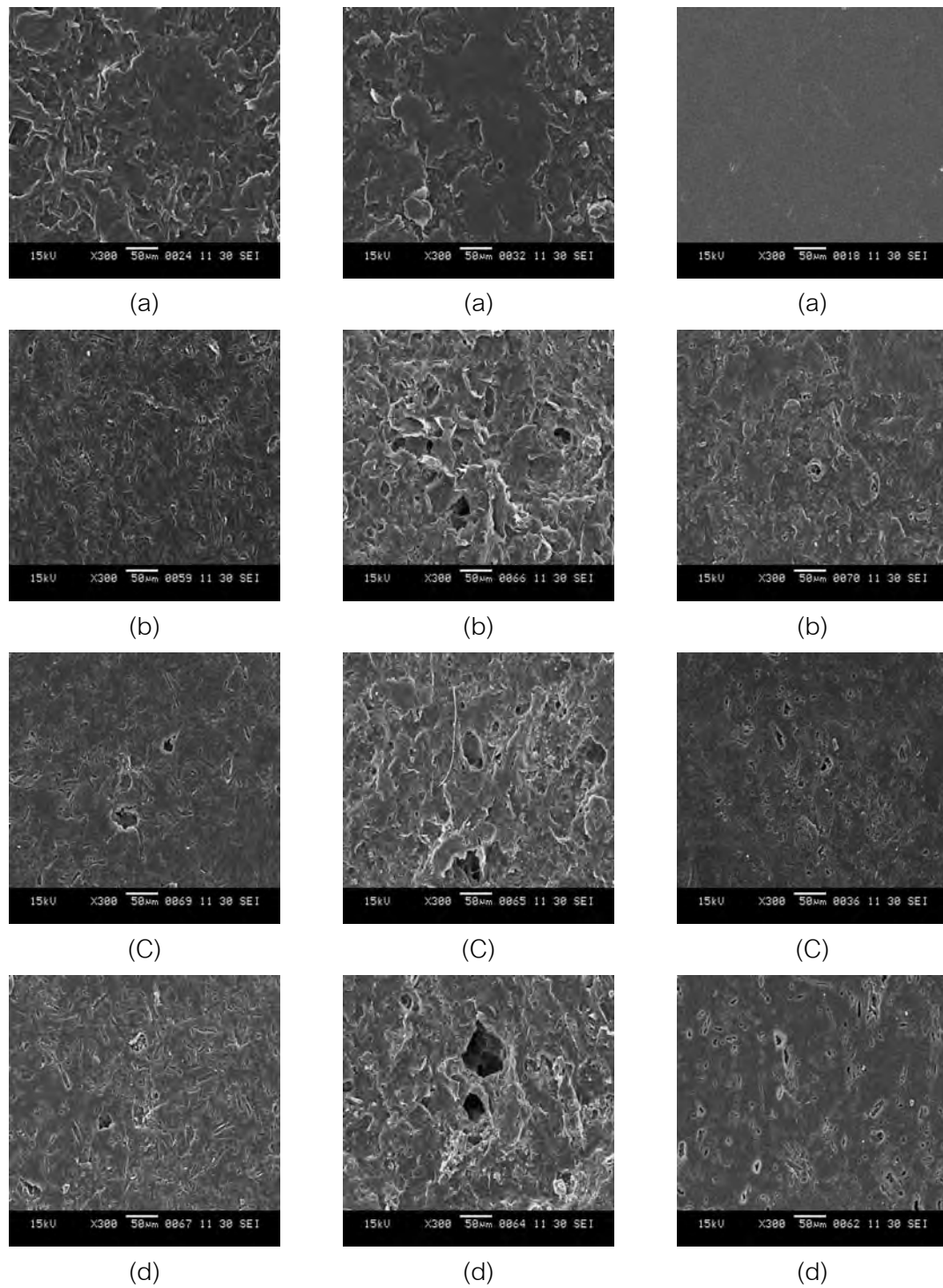


Figure 4.29 SEM micrographs of esterified pineapple leaf (left), corn husk (middle), and cotton (right) before (a) and after biodegradation testing under waste water treatment system condition for 90 days with high DS (b), medium DS (c), and low DS (d) values

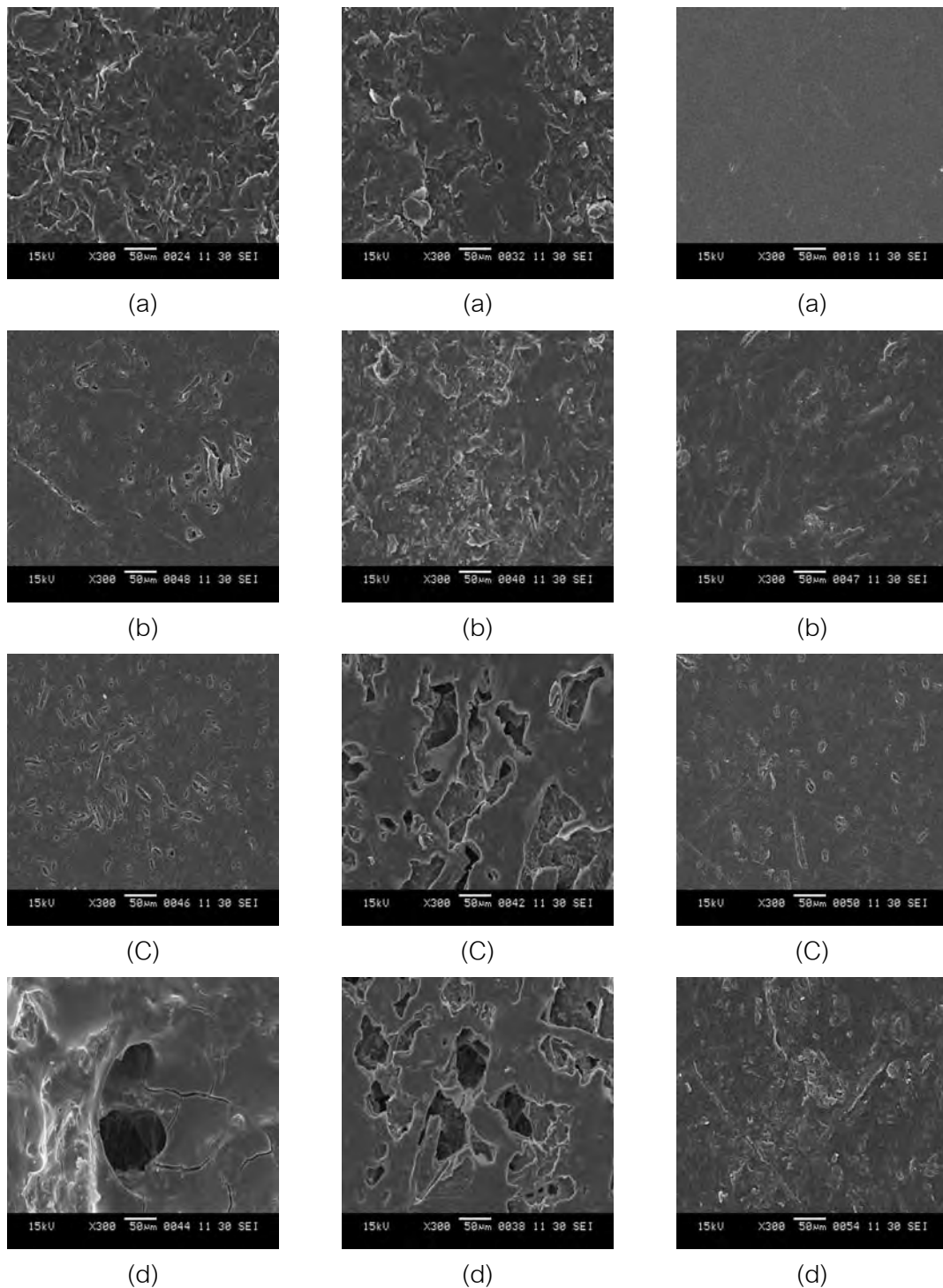


Figure 4.30 SEM micrographs of esterified pineapple leaf (left), corn husk (middle), and cotton (right) before (a) and after biodegradation testing under enzymatic degradation for 20 days with high DS (b), medium DS (c), and low DS (d) values

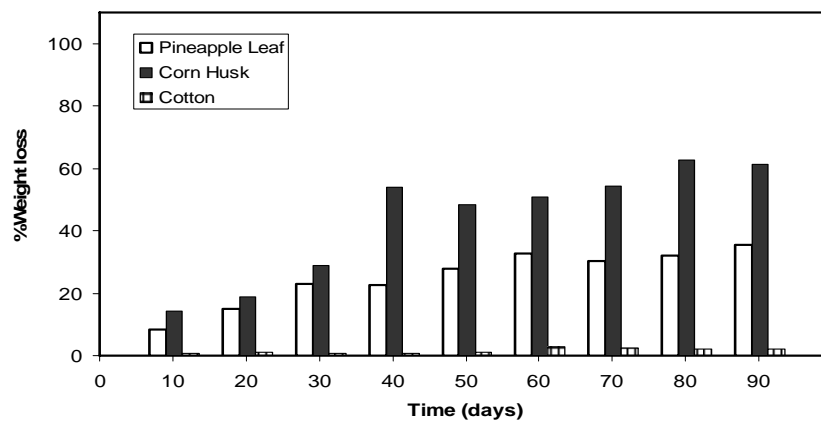
#### 4.4.2 Effect of cellulose source

Influence of cellulose source on biodegradability of esterified pineapple leaf, corn husk, and cotton films under real composting condition, waste water treatment system condition, and enzymatic degradation is displayed in Figure 4.31, 4.32, and 4.33, respectively. As shown, %weight loss of all esterified cellulose films increased with duration time of all biodegradation tests.

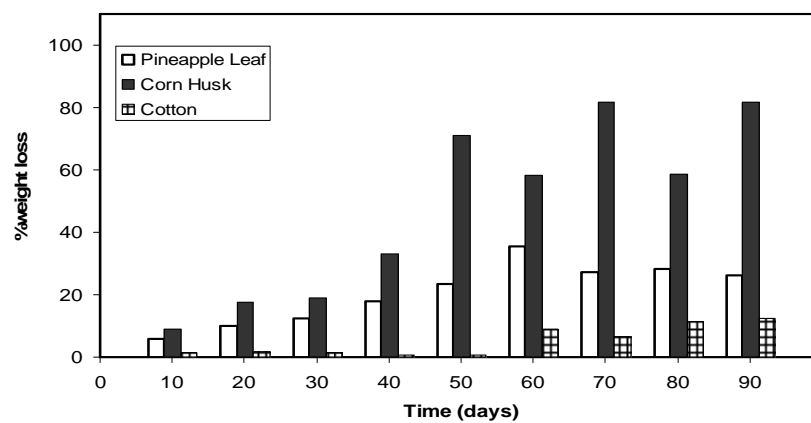
When comparing %weight loss of different raw materials at the same duration time of biodegradation tests, it was found that %weight loss of esterified cellulose film from corn husk was higher than the other two cellulose sources (i.e., pineapple leaf and cotton) under both real composting condition and waste water treatment system condition. This result can be confirmed with an appearance and SEM micrographs in Figure 4.25, 4.26, 4.27, 4.28, 2.29, and 4.30, respectively. As seen, the esterified cellulose films from corn husk under real composting and waste water treatment system condition exhibited various and larger holes more than the esterified cellulose films from pineapple leaf and cotton. In addition, it can be seen that the physical appearance changes in these films were varied differently and particularly differed from before biodegradation. Obviously, the esterified cotton films were changed from clear and transparent films into white and opaque; whereas the esterified pineapple and corn husk films were become darker and rougher. These results suggest that different celluloses behave and respond differently regardless on the biodegradation condition. The greater in biodegradability of the esterified corn husk indicated by %weight loss was resulted from its water absorption value. As discussed earlier in section 4.3.3, the water absorption values of esterified corn husk, pineapple leaf, and cotton (at low DS values) were 63.70%, 51.97%, and 17.35%, respectively. This highest amount of water absorption of esterified corn husk film significantly facilitates the biodegradation mechanism by microorganisms (i.e. hydrolysis process) resulting in the greatest biodegradability. The differences in color changes after biodegradation of each film are probably due to the interaction between microorganisms and cellulose. Similar result

was also reported by Rudeekit et al. [28] that after two months of soil burial test (landfill condition) the PLA film was changed from clear and transparent to be opaque and brittle. Although they suggested that this result was attributed from an increment of degree of crystallinity of the film. This explanation is still in doubt and need to be further clarified since generally after biodegradation, the degraded film should possess lower degree of crystallinity or have an amorphous structure instead. Another possible explanation is that after an initial degradation, crystalline spherulites appear on the surface; that can be explained by a preferential degradation of the amorphous polymer fraction, etching the slower-degrading crystalline parts out of the material [29].

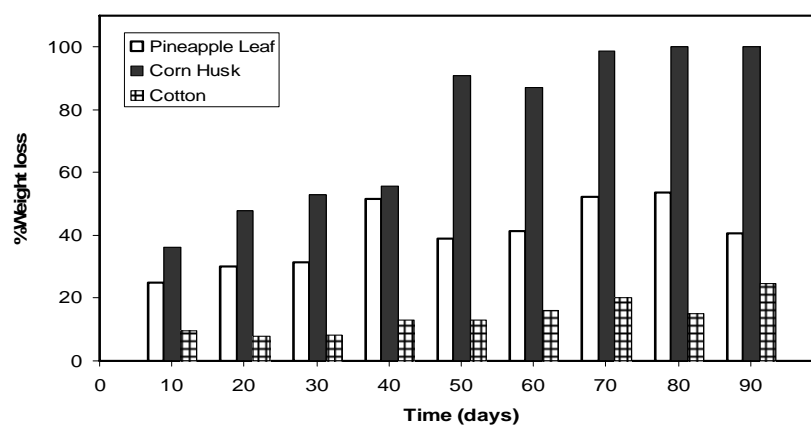
For enzymatic degradation, at high DS value (Figure 4.33 (a)), %weight loss of esterified cellulose film from all cellulose sources were insignificantly different. However, at medium DS value (Figure 4.33 (b)) and low DS value (Figure 4.33 (c)), esterified cellulose film from corn husk showed higher %weight loss than the other two cellulose sources after 20 days of exposure in enzyme solution. Although lower amount of weight loss can be noticed comparing to the other two biodegradation condition, similar trend was also found that esterified corn husk film had higher potential to be degraded by enzyme cellulose condition. From the obtained results, it can be concluded that the esterified cellulose films from corn husk had greater biodegradability than the esterified cellulose films from pineapple leaf and cotton under every biodegradable conditions.



(a)

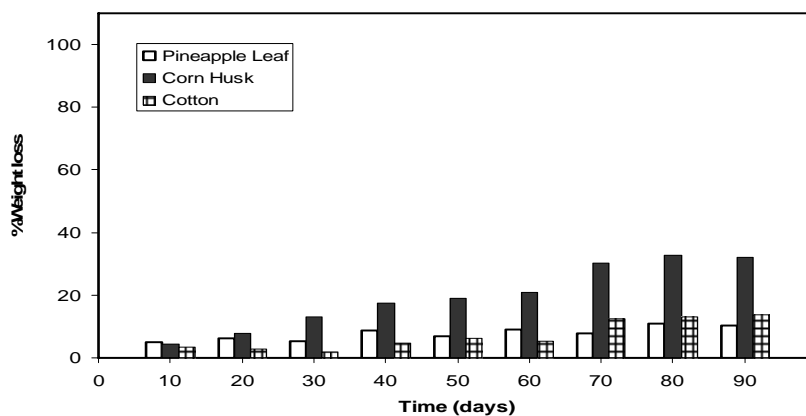


(b)

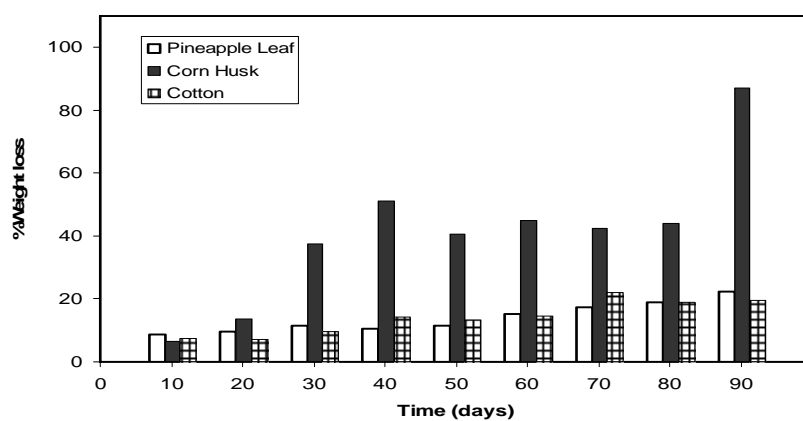


(c)

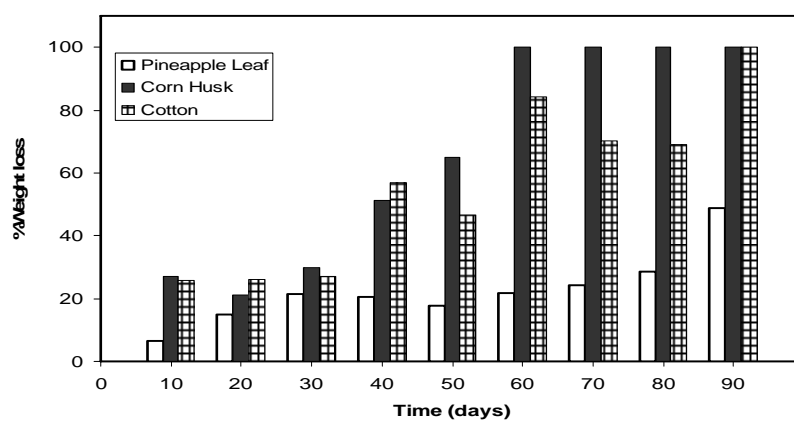
Figure 4.31 Effect of cellulose source on %weight loss of esterified cellulose films with (a) high DS value, (b) medium DS value, and (c) low DS values under real composting condition



(a)

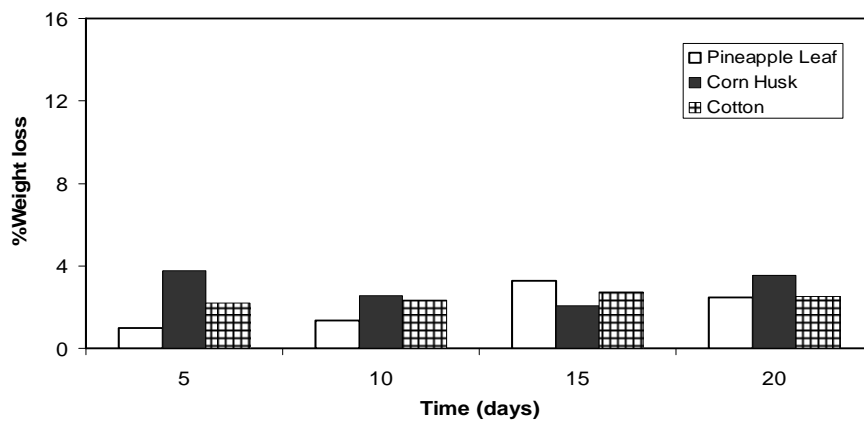


(b)

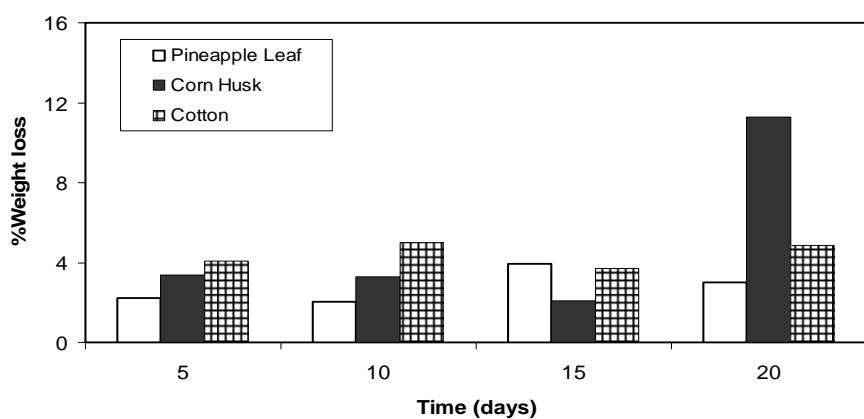


(c)

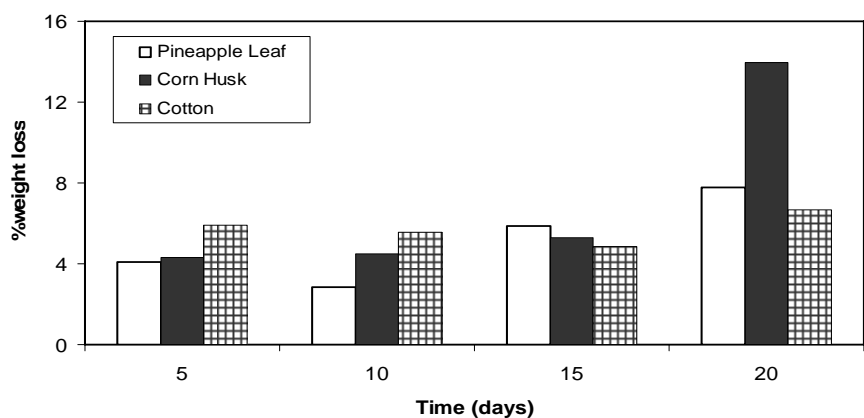
Figure 4.32 Effect of cellulose source on %weight loss of esterified cellulose films with (a) high DS value, (b) medium DS value, and (c) low DS values under waste water treatment system condition



(a)



(b)



(c)

Figure 4.33 Effect of cellulose source on %weight loss of esterified cellulose films with (a) high DS value, (b) medium DS value, and (c) low DS values under enzymatic degradation

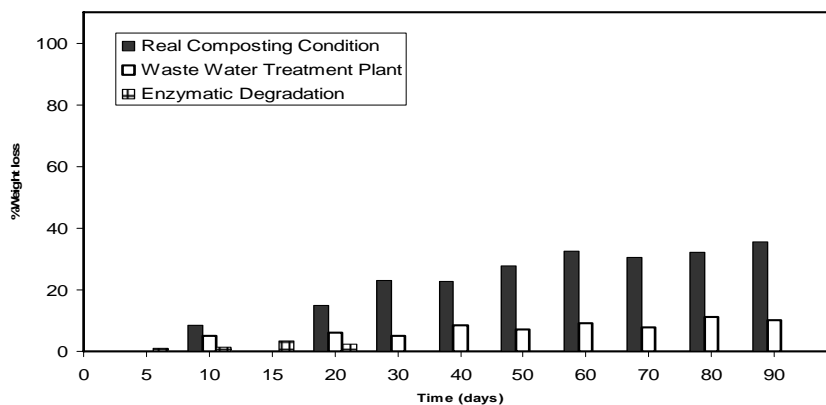
#### 4.4.3 Effect of biodegradation condition

Since the biodegradability and rate of biodegradation of biodegradable plastics are dependent on the disposal environment and its conditions as humidity, temperature, pH, salinity, the presence or absence of oxygen, and the supply of different nutrients, etc. In this work, the biodegradability of esterified cellulose films under different disposal environments was evaluated. The effect of biodegradation condition on %weight loss of esterified cellulose films from pineapple leaf, corn husk, and cotton is presented in Figure 4.34, 4.35, and 4.36, respectively.

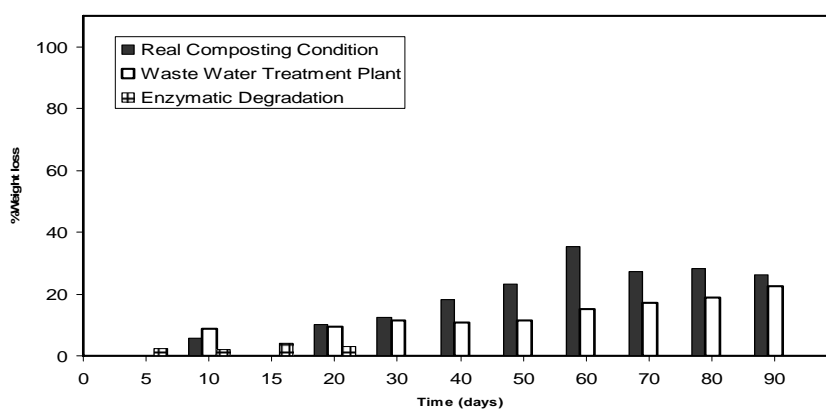
When considering %weight loss of esterified cellulose films from pineapple leaf and corn husk at the same duration time and DS value, it was found that the real composting condition resulted in higher %weight loss of the films than the waste water treatment system condition and enzymatic degradation. Obviously, from visual inspection (Figure 4.25-4.27) and SEM analysis (Figure 4.28- 4.30), esterified cellulose films from pineapple leaf and corn husk under real composting condition had rougher surface with larger and higher amount of holes than those films under waste water treatment system condition and enzymatic degradation. In addition, some de-fragmentation, cracks, and changes in color were also observed. In contrast, slight changes can be noticed for any films exposed to enzymatic degradation. This is due to the fact that the real composting condition had higher amount of microorganisms and pH value (as previously presented in Table 3.3 in chapter III) than the waste water treatment system condition and enzymatic degradation; as a result, the esterified pineapple leaf and corn husk films can be degraded significantly better. The higher amount or population of microorganism found in our composting condition is believed due to the appropriate compost formulation which yielded about 16.97% C/N ratio. Besides, the proper environmental conditions as temperature, humidity of compost, pH value are all key factor to effectively promote the biodegradation mechanism of microorganisms. For enzymatic degradation, surprisingly, all the esterified cellulose films were degraded vary slowly with approximately less than 15% weight loss after 20



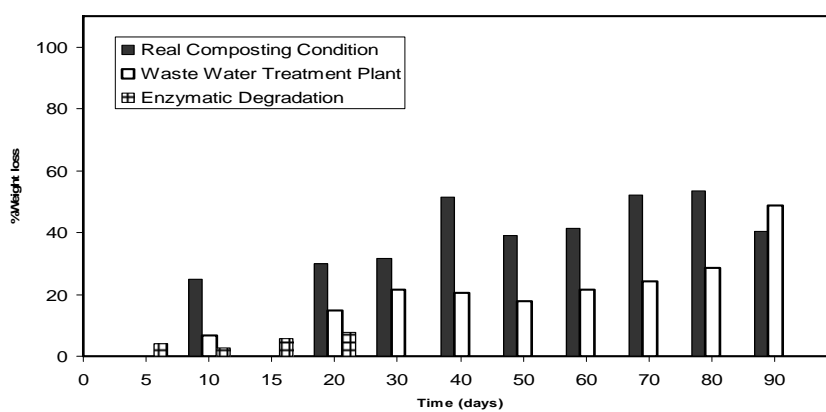
days of exposure in enzymatic solution. This is probably because the biodegradation of the films are still in the first or initial step of degradation called hydrolysis, after passing through this step the depolymerization and mineralization processes should be occurred. Some synthetic polymers like polylactic acids and their copolymers also showed this hydrolysis period within about 10 days before the real biodegradation mechanisms set in. For esterified cellulose film from cotton, it showed higher biodegradability in waste water treatment system condition than the other two conditions (Figure 4.36). This is due to the bulk property of cotton film which was quite compared to brittle the other two types of the films. Once the esterified cotton film was exposed into waste water treatment system, physical from circulating water can cause mechanism damage such as the cracking of the film into small pieces. This initial breakdown of a polymer from its brittleness was then making it favorable for microbial to attack around these several newly created surfaces. Another possible explanation is that the small and tiny pieces of broken films were escaped from the net of cloth bag; this problem can arise when the material disintegrates excessively; resulting in higher amount of weight loss of the test specimens. These results are confirmed by an appearance changes and SEM micrographs in Figure 4.25-4.27 and 4.28-4.30.



(a)

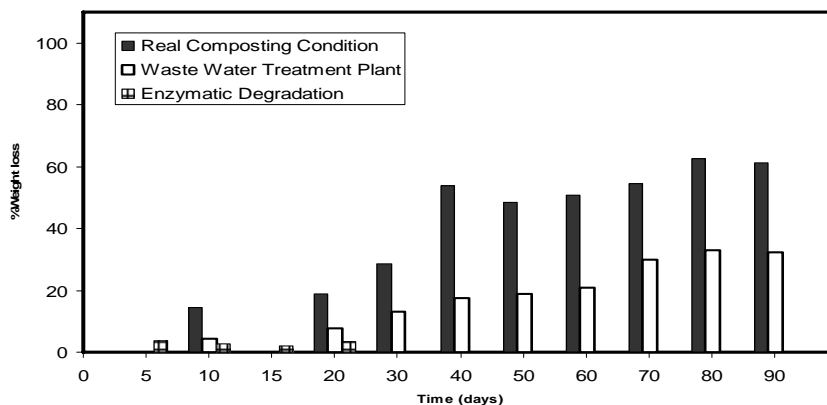


(b)

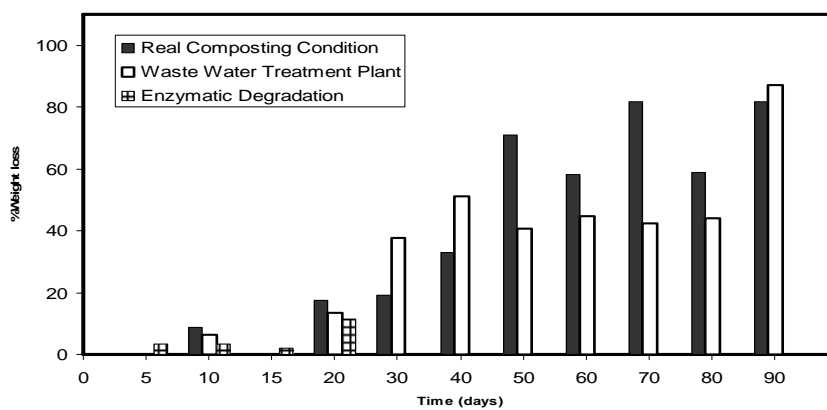


(c)

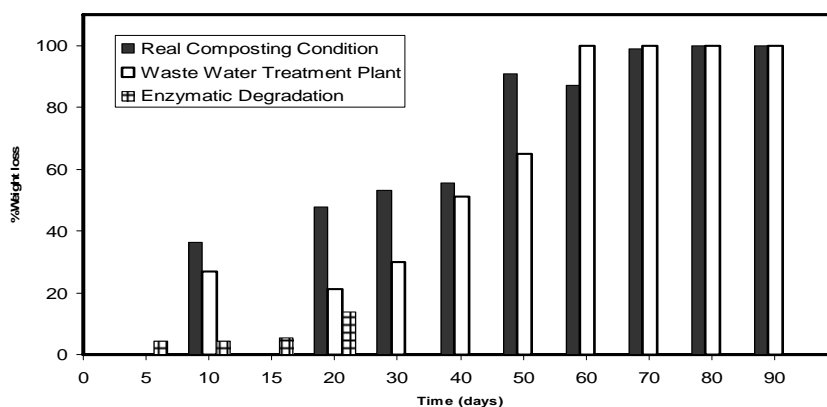
Figure 4.34 %Weight loss of esterified cellulose films from pineapple leaf with (a) high DS value, (b) medium DS value, and (c) low DS value under different biodegradation tests



(a)

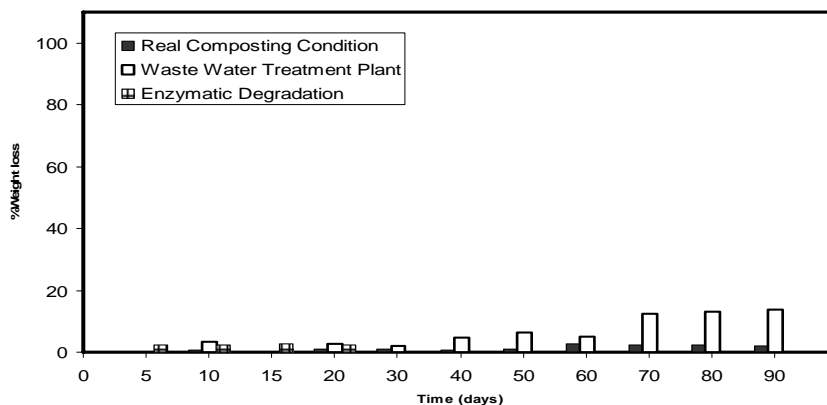


(b)

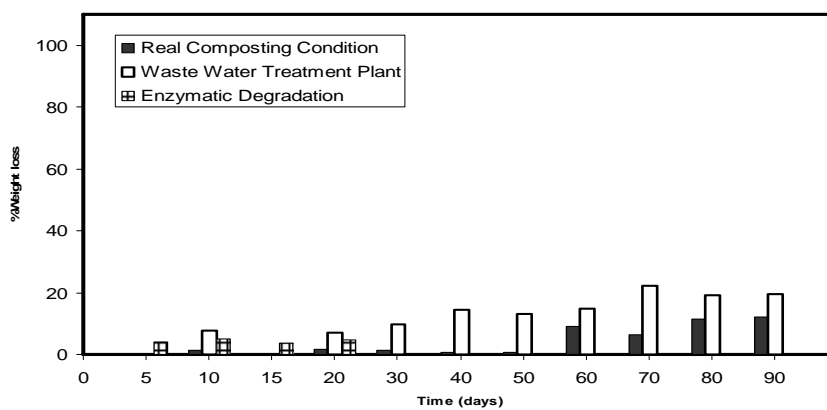


(c)

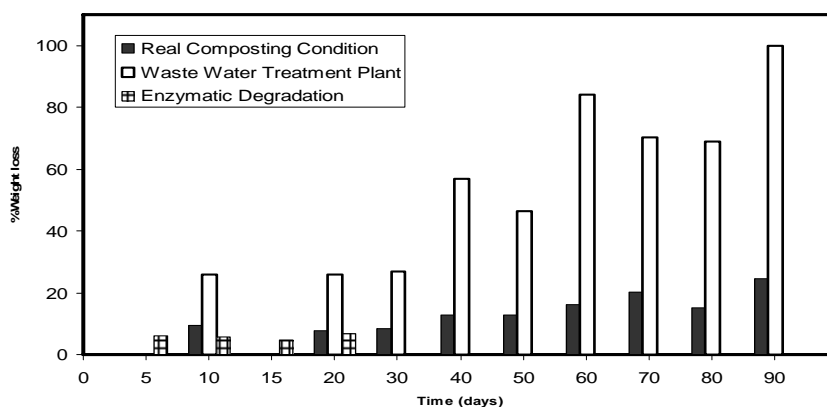
Figure 4.35 %Weight loss of esterified cellulose films from corn husk with (a) high DS value, (b) medium DS value, and (c) low DS value under different biodegradation tests



(a)



(b)



(c)

Figure 4.36 %Weight loss of esterified cellulose films from cotton with (a) high DS value, (b) medium DS value, and (c) low DS value under different biodegradation tests

## CHAPTER V

### CONCLUSIONS

Modified cellulose films from pineapple leaf, corn husk, and waste cotton fabrics were prepared in LiCl/DMAc solvent system by esterification reaction under microwave energy using lauroyl chloride and DMAP as an esterifying agent and a catalyst, respectively. By varying the microwave power and reaction time, modified cellulose with different degree of substitution (DS) values was obtained. Finally, the effects of cellulose source and degree of substitution on the physical, mechanical, and biodegradable properties of esterified cellulose films were investigated. The results are summarized as follow:

1. The optimum conditions for modification of pineapple leaf, corn husk, and waste cotton fabric that yield low, medium, and high degree of substitution (DS) values with reasonable %weight increase under microwave heating are concluded in Table 5.1.

2. From FTIR analysis, modified cellulose from all cellulose sources exhibited evidence of esterification by showing three important: the presence of ester bands at  $1735-1750\text{ cm}^{-1}$  (carbonyl C=O stretching of ester), the increasing in the intensity of alkyl chain absorption (C-H stretching) at  $2854-2919\text{ cm}^{-1}$ , and the decreasing in the intensity of O-H band at  $3300\text{ cm}^{-1}$ .

3. The esterification reaction was successfully confirmed by the  $^1\text{H-NMR}$  technique. The  $^1\text{H-NMR}$  spectra showed peaks between 0.85-2.34 ppm, corresponding to alkyl groups of fatty acid chain, and other peaks between 3.46-5.06 ppm were attributed to the cellulose skeleton or anhydroglucose unit protons.

Table 5.1 The optimum conditions for modification reaction of pineapple leaf, corn husk, and waste cotton fabric cellulose with the different degree of substitution (DS) values under microwave heating

| Source of Cellulose | The optimum condition |                  |      |      |
|---------------------|-----------------------|------------------|------|------|
|                     | Power<br>(watt)       | Time<br>(second) | %WI* | DS*  |
| Pineapple Leaf      | 160                   | 90               | 88.5 | 2.46 |
|                     | 240                   | 60               | 64.5 | 2.23 |
|                     | 240                   | 30               | 59.5 | 1.93 |
| Corn Husk           | 240                   | 60               | 90.5 | 2.73 |
|                     | 160                   | 150              | 89.5 | 2.44 |
|                     | 320                   | 90               | 67.5 | 1.99 |
| Waste Cotton Fabric | 240                   | 90               | 74.5 | 2.48 |
|                     | 160                   | 90               | 56.0 | 2.27 |
|                     | 240                   | 30               | 40.0 | 1.95 |

\*%WI = %weight increase, DS = degree of substitution

4. From TGA analysis, the result showed that esterified cellulose started to decompose at a lower temperature ( $T_d$  onset=190-300°C) than unmodified cellulose ( $T_d$  onset=310-320°C). This behavior is due to the decrease in crystallinity associated with the substitution of acyl side chain in cellulose structure. The thermal stability of esterified cellulose was dependent on the DS value; the thermal stability decreased with the increasing of DS value. At the constant DS value, esterified cotton showed the higher thermal stability than esterified pineapple leaf and esterified corn husk, respectively.

5. The DSC thermograms of pineapple leaf, corn husk, and cotton did not show any significant transition temperature ( $T_g$ ,  $T_m$ ). After esterification, there were no

significant differences in  $T_g$  among different types of cellulose source. Esterified cotton presented the second order-transition at 87-98°C, while the  $T_g$  of pineapple leaf and corn husk were 88°C and 95°C, respectively. In addition, the  $T_g$  slightly decreased with the increasing of DS value. However, there was no sign of the  $T_m$  for the esterified cellulose within the range of heating scans.

6. SEM micrograph of pineapple leaf and corn husk cellulose exhibited a smooth surface of a fragment, fattened fibril, or a flake shape while cotton cellulose showed the short fiber shape with smooth surface. After esterification, all celluloses revealed aggregation of fatty acid side chain groups on the surface thus resulted in rough surface and larger dimension.

7. The gloss values of all esterified cellulose films increased with increasing DS values because of the gloss value of material related to the smoothness of the material surface, thus increasing of DS values means increasing of acyl substitution in cellulose structure leading to an increasing in the solubility of modified cellulose in chloroform, as a result, the smooth surface of esterified cellulose films can be obtained.

8. Wettability and water absorption of all esterified cellulose films decreased with increasing DS values, which means that these films were more hydrophobic than unmodified cellulose films.

9. The results on mechanical properties showed that the tensile properties of all esterified cellulose films were dependent on degree of substitution. The increasing of tensile strength, tensile modulus, and elongation at break as an increasing of the degree of substitution value is due to (1) the increasing of long-chain substituent may be attributed to the partial crystallization and overlepping of  $C_{12}$  side chains in lauroyl chloride as esterifying agent, and (2) the occurrence of chain entanglement of long-chain substitution of lauroyl chloride so it had the greater tensile properties. In addition,

the obtained results were found that the esterified corn husk film had the greater tensile properties than the esterified pineapple leaf and cotton films.

10. The esterified cellulose films from all cellulose source exhibited considerable biodegradability particularly for esterified corn husk film as evidenced by the appearance of numerous tiny holes caused by microorganism consumption and an increasing of %weight loss.

The biodegradability of all esterified cellulose films decreased with the increasing of DS value. This decreasing of biodegradation rate may be due to the ester side chain inhibited the working of enzymes to attack cellulose itself. The biodegradability of esterified cellulose films from corn husk was higher than the esterified cellulose films from pineapple leaf and waste cotton fabrics.

When considering the effect of biodegradation condition, the result showed the biodegradability of esterified pineapple leaf and corn husk films under real composting condition was higher than that under waste water treatment system condition and enzymatic degradation. Whilst, the esterified cotton film had the highest biodegradability under waste water treatment system condition.



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## APPENDIX

### A : Esterification of Pineapple Leaf Cellulose

A1 The weight increase (%) of pineapple leaf cellulose esterified with lauroyl chloride under microwave energy

| Time<br>(second) | Microwave Power (Watt) |      |      |      |      |
|------------------|------------------------|------|------|------|------|
|                  | 80                     | 160  | 240  | 320  | 400  |
| 30               | 16.7                   | 57.5 | 59.5 | 60.5 | 54.5 |
| 60               | 18.5                   | 61.5 | 64.5 | 51.5 | 48.5 |
| 90               | 24.5                   | 88.5 | 22.0 | 34.5 | 8.5  |
| 120              | 41.5                   | 76.5 | -    | -    | -    |
| 150              | 57.0                   | 78.5 | -    | -    | -    |
| 180              | 39.0                   | 53.5 | -    | -    | -    |

A2 The degree of substitution of pineapple leaf cellulose esterified with lauroyl chloride under microwave energy

| Time<br>(second) | Microwave Power (Watt) |      |      |      |      |
|------------------|------------------------|------|------|------|------|
|                  | 80                     | 160  | 240  | 320  | 400  |
| 30               | 0                      | 0    | 1.93 | 2.15 | 2.14 |
| 60               | 0                      | 2.49 | 2.23 | 2.12 | 2.12 |
| 90               | 0                      | 2.46 | 2.27 | 2.02 | 1.97 |
| 120              | 2.22                   | 2.36 | -    | -    | -    |
| 150              | 2.16                   | 2.35 | -    | -    | -    |
| 180              | 2.08                   | 2.17 | -    | -    | -    |

### B : Esterification of Corn Husk Cellulose

B1 The weight increase (%) of corn husk cellulose esterified with lauroyl chloride under microwave energy

| Time<br>(second) | Microwave Power (Watt) |      |      |      |      |
|------------------|------------------------|------|------|------|------|
|                  | 80                     | 160  | 240  | 320  | 400  |
| 30               | 11.5                   | 14.0 | 43.5 | 50.0 | 34.0 |
| 60               | 17.5                   | 50.5 | 90.5 | 71.0 | 71.0 |
| 90               | 25.5                   | 74.0 | 64.5 | 67.5 | 31.5 |
| 120              | 55.0                   | 87.5 | 30.5 | -    | -    |
| 150              | 47.0                   | 89.5 | -    | -    | -    |
| 180              | 58.0                   | 37.0 | -    | -    | -    |

B2 The degree of substitution of corn husk cellulose esterified with lauroyl chloride under microwave energy

| Time<br>(second) | Microwave Power (Watt) |      |      |      |      |
|------------------|------------------------|------|------|------|------|
|                  | 80                     | 160  | 240  | 320  | 400  |
| 30               | 0                      | 0    | 0    | 0    | 0    |
| 60               | 0                      | 2.30 | 2.73 | 2.30 | 2.11 |
| 90               | 1.63                   | 2.45 | 2.38 | 1.99 | 2.36 |
| 120              | 2.41                   | 2.35 | -    | -    | -    |
| 150              | 2.29                   | 2.44 | -    | -    | -    |
| 180              | 2.41                   | 2.35 | -    | -    | -    |

### C : Esterification of Cotton Cellulose

C1 The weight increase (%) of cotton cellulose esterified with lauroyl chloride under microwave energy

| Time<br>(second) | Microwave Power (Watt) |      |      |      |      |
|------------------|------------------------|------|------|------|------|
|                  | 80                     | 160  | 240  | 320  | 400  |
| 30               | 25                     | 32   | 40   | 45   | 43.5 |
| 60               | 27                     | 42.5 | 50.3 | 51.0 | 22.0 |
| 90               | 53.0                   | 53.8 | 74.5 | 5.0  | 15.0 |
| 120              | 47.5                   | 57.5 | 42.8 | -    | -    |
| 150              | 45.8                   | 72.5 | -    | -    | -    |
| 180              | 51.5                   | 56.8 | -    | -    | -    |

C2 The degree of substitution of cotton cellulose esterified with lauroyl chloride under microwave energy

| Time<br>(second) | Microwave Power (Watt) |      |      |      |      |
|------------------|------------------------|------|------|------|------|
|                  | 80                     | 160  | 240  | 320  | 400  |
| 30               | 0                      | 0    | 1.95 | 2.15 | 2.16 |
| 60               | 2.10                   | 2.00 | 2.22 | 2.25 | 2.28 |
| 90               | 2.17                   | 2.27 | 2.48 | 2.22 | 2.32 |
| 120              | 2.10                   | 2.42 | 2.26 | -    | -    |
| 150              | 2.10                   | 2.44 | -    | -    | -    |
| 180              | 2.33                   | 2.32 | -    | -    | -    |

## D : Properties of Pineapple Leaf Cellulose Film

### D1 Gloss values of modified pineapple leaf films at different DS values

| Sample No. | Gloss* (Unit) |           |        |
|------------|---------------|-----------|--------|
|            | High DS       | Medium DS | Low DS |
| 1          | 28.8          | 20.5      | 10.3   |
| 2          | 31.0          | 21.6      | 12.0   |
| 3          | 23.5          | 21.4      | 9.4    |
| 4          | 12.9          | 12.3      | 31.1   |
| 5          | 12.6          | 22.2      | 7.7    |
| Average    | 21.76         | 19.6      | 14.1   |
| SD         | 8.67          | 4.13      | 9.63   |

\*Gloss of standard black calibration = 95.1 units

### D2 Contact angle values of modified pineapple leaf films at different DS values

| Position | Contact Angle (degree) |          |          |           |          |          |          |          |          |
|----------|------------------------|----------|----------|-----------|----------|----------|----------|----------|----------|
|          | High DS                |          |          | Medium DS |          |          | Low DS   |          |          |
|          | Sample 1               | Sample 2 | Sample 3 | Sample 1  | Sample 2 | Sample 3 | Sample 1 | Sample 2 | Sample 3 |
| 1        | 106                    | 122      | 124      | 98        | 99       | 95       | 80       | 86       | 84       |
| 2        | 112                    | 112      | 118      | 101       | 93       | 100      | 71       | 79       | 82       |
| 3        | 110                    | 100      | 118      | 101       | 90       | 105      | 69       | 79       | 85       |
| 4        | 112                    | 106      | 112      | 102       | 101      | 100      | 105      | 78       | 89       |
| 5        | 104                    | 111      | 112      | 102       | 94       | 100      | 98       | 91       | 87       |
| 6        | 114                    | 118      | 114      | 103       | 97       | 104      | 91       | 85       | 88       |
| 7        | 114                    | 119      | 110      | 100       | 100      | 108      | 96       | 88       | 95       |
| 8        | 118                    | 121      | 110      | 99        | 93       | 103      | 102      | 89       | 92       |
| 9        | 114                    | 130      | 112      | 104       | 104      | 102      | 106      | 86       | 98       |
| 10       | 115                    | 124      | 112      | 104       | 106      | 98       | 92       | 89       | 102      |
| Average  | 114.1                  |          |          | 100.2     |          |          | 88.7     |          |          |
| sd.      | 6.3                    |          |          | 4.1       |          |          | 9.1      |          |          |



### D3 Water absorption of modified pineapple leaf films at different DS values

| No.<br>Sample | High DS    |            |       | Medium DS  |            |       | Low DS     |            |       |
|---------------|------------|------------|-------|------------|------------|-------|------------|------------|-------|
|               | dry weight | wet weight | % WA* | dry weight | wet weight | % WA* | dry weight | wet weight | % WA* |
| 1             | 89.0       | 111.5      | 25.28 | 65.6       | 81.9       | 24.85 | 106.8      | 169.2      | 58.43 |
| 2             | 85.3       | 103.4      | 21.22 | 72.4       | 91.7       | 26.66 | 92.7       | 145.3      | 56.74 |
| 3             | 83.8       | 101.2      | 20.76 | 107.8      | 138.1      | 28.11 | 59.1       | 87.7       | 48.39 |
| 4             | 81.0       | 97.3       | 20.12 | 69.3       | 86.8       | 25.25 | 63.6       | 94.0       | 47.80 |
| 5             | 76.4       | 92.0       | 20.42 | 82.3       | 101.8      | 23.69 | 65.2       | 96.8       | 48.47 |
|               | Average    |            | 21.56 | Average    |            | 25.71 | Average    |            | 51.97 |
|               | sd         |            | 2.12  | sd         |            | 1.71  | sd         |            | 5.17  |

%WA\*=%Water Absorption

### D4 Tensile properties of modified pineapple leaf films at different DS values

| No. Sample | High DS          |                 |                     |
|------------|------------------|-----------------|---------------------|
|            | Tensile Strength | Tensile Modulus | Elongation at break |
| 1          | 6.1564           | 456.29          | 3.9413              |
| 2          | 6.8333           | 393.00          | 4.4806              |
| 3          | 7.0033           | 354.87          | 5.1732              |
| 4          | 5.9262           | 424.81          | 5.0795              |
| 5          | 7.4649           | 437.85          | 5.5227              |
| Average    | 6.68             | 413.36          | 4.84                |
| sd.        | 0.63             | 40.03           | 0.63                |
| No. Sample | Medium DS        |                 |                     |
|            | Tensile Strength | Tensile Modulus | Elongation at break |
| 1          | 5.1480           | 361.87          | 4.134               |
| 2          | 6.0046           | 323.15          | 5.746               |
| 3          | 6.2550           | 335.97          | 5.8808              |
| 4          | 5.8912           | 378.10          | 5.1621              |
| 5          | 6.1325           | 355.22          | 5.5359              |
| Average    | 5.89             | 350.86          | 5.29                |
| sd.        | 0.43             | 21.63           | 0.70                |
| No. Sample | Low DS           |                 |                     |
|            | Tensile Strength | Tensile Modulus | Elongation at break |
| 1          | 0.80829          | 625.01          | 0.55764             |
| 2          | 0.87686          | 229.04          | 0.65873             |
| 3          | 0.75786          | 582.28          | 0.53217             |
| 4          | 0.70792          | 420.57          | 0.49298             |
| 5          | 0.78466          | 385.08          | 0.73985             |
| Average    | 0.79             | 448.40          | 0.60                |
| sd.        | 0.06             | 159.70          | 0.10                |

## E : Properties of Corn Husk Cellulose Film

## E1 Gloss values of modified corn husk films at different DS values

| Sample No. | Gloss* (Unit) |           |        |
|------------|---------------|-----------|--------|
|            | High DS       | Medium DS | Low DS |
| 1          | 21.4          | 18.7      | 5.4    |
| 2          | 25.0          | 14.7      | 6.3    |
| 3          | 24.5          | 19.8      | 9.2    |
| 4          | 21.5          | 11.9      | 6.0    |
| 5          | 23.3          | 17.7      | 6.7    |
| Average    | 23.14         | 16.56     | 6.72   |
| SD         | 1.66          | 3.22      | 1.47   |

\*Gloss of standard black calibration = 95.1 units

## E2 Contact angle values of modified corn husk films at different DS values

| Position | Contact Angle (degree) |          |          |           |          |          |          |          |          |
|----------|------------------------|----------|----------|-----------|----------|----------|----------|----------|----------|
|          | High DS                |          |          | Medium DS |          |          | Low DS   |          |          |
|          | Sample 1               | Sample 2 | Sample 3 | Sample 1  | Sample 2 | Sample 3 | Sample 1 | Sample 2 | Sample 3 |
| 1        | 122                    | 115      | 126      | 92        | 81       | 90       | 99       | 84       | 92       |
| 2        | 122                    | 124      | 129      | 89        | 85       | 97       | 92       | 84       | 102      |
| 3        | 120                    | 123      | 118      | 86        | 93       | 99       | 90       | 86       | 105      |
| 4        | 123                    | 120      | 123      | 82        | 95       | 100      | 88       | 82       | 112      |
| 5        | 120                    | 115      | 116      | 88        | 90       | 103      | 95       | 92       | 104      |
| 6        | 122                    | 120      | 122      | 90        | 87       | 108      | 89       | 95       | 105      |
| 7        | 121                    | 130      | 117      | 84        | 88       | 100      | 85       | 90       | 113      |
| 8        | 118                    | 126      | 118      | 90        | 96       | 107      | 95       | 83       | 90       |
| 9        | 122                    | 120      | 118      | 97        | 94       | 108      | 88       | 73       | 94       |
| 10       | 126                    | 120      | 120      | 96        | 95       | 109      | 80       | 88       | 98       |
| Average  | 121.2                  |          |          | 94.0      |          |          | 92.4     |          |          |
| sd.      | 3.7                    |          |          | 7.8       |          |          | 9.3      |          |          |

## E3 Water absorption of modified corn husk films at different DS values

| No.<br>Sample | High DS    |            |       | Medium DS  |            |       | Low DS     |            |       |
|---------------|------------|------------|-------|------------|------------|-------|------------|------------|-------|
|               | dry weight | wet weight | % WA* | dry weight | wet weight | % WA* | dry weight | wet weight | % WA* |
| 1             | 91.8       | 115.5      | 25.82 | 48.1       | 58.0       | 20.58 | 97.9       | 152.5      | 55.77 |
| 2             | 96.8       | 112.6      | 16.32 | 84.9       | 106.1      | 24.97 | 117.7      | 198.1      | 68.31 |
| 3             | 87.6       | 108.0      | 23.29 | 69.9       | 86.3       | 23.46 | 113.3      | 189.7      | 67.43 |
| 4             | 103.4      | 123.2      | 19.15 | 48.6       | 59.0       | 21.40 | 111.1      | 181.8      | 63.64 |
| 5             | 106.2      | 123.9      | 16.67 | 80.5       | 100.1      | 24.35 | 108.0      | 176.4      | 63.33 |
|               | Average    |            | 20.25 | Average    |            | 22.95 | Average    |            | 63.70 |
|               | sd         |            | 4.17  | sd         |            | 1.89  | sd         |            | 4.95  |

%WA\*=%Water Absorption

## E4 Tensile properties of modified corn husk films at different DS values

| No. Sample | High DS          |                 |                     |
|------------|------------------|-----------------|---------------------|
|            | Tensile Strength | Tensile Modulus | Elongation at break |
| 1          | 9.044            | 610.29          | 4.5219              |
| 2          | 8.6653           | 740.37          | 4.2492              |
| 3          | 8.5303           | 659.83          | 4.4629              |
| 4          | 8.9993           | 643.06          | 5.265               |
| 5          | 9.1319           | 698.45          | 4.9983              |
| Average    | 8.87             | 670.40          | 4.70                |
| sd.        | 0.26             | 50.39           | 0.42                |
| No. Sample | Medium DS        |                 |                     |
|            | Tensile Strength | Tensile Modulus | Elongation at break |
| 1          | 6.3185           | 511.58          | 3.5487              |
| 2          | 6.2305           | 545.04          | 3.566 5             |
| 3          | 6.3269           | 531.62          | 3.7336              |
| 4          | 6.5826           | 552.71          | 3.7549              |
| 5          | 6.2954           | 548.61          | 3.4249              |
| Average    | 6.35             | 537.91          | 3.62                |
| sd.        | 0.13             | 16.71           | 0.16                |
| No. Sample | Low DS           |                 |                     |
|            | Tensile Strength | Tensile Modulus | Elongation at break |
| 1          | 1.1353           | 707.39          | 0.75529             |
| 2          | 1.1326           | 456.69          | 0.83586             |
| 3          | 0.69437          | 318.39          | 0.61822             |
| 4          | 1.0047           | 391.4           | 0.75291             |
| 5          | 0.94123          | 557.41          | 0.64283             |
| Average    | 0.98             | 486.26          | 0.72                |
| sd.        | 0.18             | 151.67          | 0.09                |

## F : Properties of Cotton Cellulose Film

### F1 Gloss values of modified cotton films at different DS values

| Sample No. | Gloss* (Unit) |           |        |
|------------|---------------|-----------|--------|
|            | High DS       | Medium DS | Low DS |
| 1          | 46.9          | 29.4      | 6.9    |
| 2          | 41.2          | 14.3      | 5.0    |
| 3          | 33.7          | 24.5      | 2.9    |
| 4          | 49.4          | 45.8      | 5.4    |
| 5          | 47.6          | 21.7      | 4.0    |
| Adverage   | 43.76         | 27.14     | 4.84   |
| Stdev.     | 6.41          | 11.78     | 1.50   |

\*Gloss of standard black calibration = 95.1 units

### F2 Contact angle values of modified cotton films at different DS values

| Position | Contact Angle (degree) |          |          |           |          |          |          |          |          |
|----------|------------------------|----------|----------|-----------|----------|----------|----------|----------|----------|
|          | High DS                |          |          | Medium DS |          |          | Low DS   |          |          |
|          | Sample 1               | Sample 2 | Sample 3 | Sample 1  | Sample 2 | Sample 3 | Sample 1 | Sample 2 | Sample 3 |
| 1        | 79                     | 108      | 112      | 93        | 102      | 106      | 88       | 100      | 103      |
| 2        | 102                    | 108      | 108      | 93        | 95       | 107      | 90       | 94       | 102      |
| 3        | 103                    | 113      | 113      | 94        | 102      | 110      | 96       | 97       | 94       |
| 4        | 106                    | 117      | 119      | 98        | 102      | 110      | 84       | 104      | 98       |
| 5        | 112                    | 117      | 114      | 95        | 98       | 100      | 63       | 84       | 103      |
| 6        | 114                    | 108      | 110      | 68        | 88       | 114      | 80       | 118      | 96       |
| 7        | 110                    | 115      | 106      | 90        | 93       | 114      | 76       | 92       | 103      |
| 8        | 116                    | 95       | 109      | 100       | 100      | 116      | 78       | 111      | 100      |
| 9        | 105                    | 110      | 114      | 94        | 98       | 110      | 85       | 97       | 100      |
| 10       | 105                    | 102      | 115      | 102       | 94       | 98       | 87       | 104      | 116      |
| Average  | 108.8                  |          |          | 99.5      |          |          | 94.8     |          |          |
| sd.      | 7.8                    |          |          | 9.5       |          |          | 11.9     |          |          |

### F3 Water absorption of modified cotton films at different DS values

| Sample No. | High DS    |            |      | Medium DS  |            |      | Low DS     |            |       |
|------------|------------|------------|------|------------|------------|------|------------|------------|-------|
|            | dry weight | wet weight | % WA | dry weight | wet weight | % WA | dry weight | wet weight | % WA  |
| 1          | 157.0      | 163.8      | 4.33 | 214.2      | 227.8      | 6.35 | 214.0      | 259.6      | 21.31 |
| 2          | 170.2      | 178.3      | 4.76 | 245.5      | 264.1      | 7.58 | 153.2      | 184.8      | 20.63 |
| 3          | 168.1      | 174.3      | 3.69 | 226.9      | 235.4      | 3.75 | 136.7      | 155.8      | 13.97 |
| 4          | 180.5      | 188.3      | 4.32 | 133.8      | 139.4      | 4.19 | 169.8      | 184.7      | 8.78  |
| 5          | 158.7      | 165.5      | 4.28 | 232.5      | 239.9      | 3.18 | 128.8      | 157.2      | 22.05 |
|            | Average    |            | 4.28 | Average    |            | 5.01 | Average    |            | 17.35 |
|            | sd         |            | 0.38 | sd         |            | 1.87 | sd         |            | 5.78  |

%WA\*=%Water Absorption

### F4 Tensile properties of modified cotton films at different DS values

| Sample No. | High DS          |                 |                     |
|------------|------------------|-----------------|---------------------|
|            | Tensile Strength | Tensile Modulus | Elongation at break |
| 1          | 7.3494           | 449.98          | 4.5836              |
| 2          | 5.2277           | 804.58          | 2.8291              |
| 3          | 5.9376           | 638.26          | 3.4722              |
| 4          | 4.5085           | 716.54          | 2.7637              |
| 5          | 4.3454           | 569.25          | 2.3507              |
| Average    | 5.47             | 635.72          | 3.20                |
| sd.        | 1.22             | 135.99          | 0.87                |
| Sample No. | Medium DS        |                 |                     |
|            | Tensile Strength | Tensile Modulus | Elongation at break |
| 1          | 2.6131           | 593.1           | 2.0042              |
| 2          | 4.5455           | 383.64          | 2.7871              |
| 3          | 6.0103           | 554.36          | 3.1004              |
| 4          | 5.7173           | 532.96          | 2.728               |
| 5          | 5.2364           | 544.17          | 3.0413              |
| Average    | 4.82             | 521.65          | 2.73                |
| sd.        | 1.35             | 80.40           | 0.44                |
| Sample No. | Low DS           |                 |                     |
|            | Tensile Strength | Tensile Modulus | Elongation at break |
| 1          | 3.3343           | 470.93          | 2.0042              |
| 2          | 1.6716           | 495.53          | 1.7871              |
| 3          | 1.5624           | 406.01          | 2.1004              |
| 4          | 1.2145           | 517.65          | 2.728               |
| 5          | 0.9450           | 506.04          | 2.0413              |
| Average    | 1.75             | 479.23          | 2.13                |
| sd.        | 0.93             | 44.41           | 0.35                |

## G : Biodegradability of Pineapple Leaf Cellulose Film

G1 %weight loss of pineapple leaf cellulose films with high DS values in real composting condition

| Time (days) | Sample No. | Wi   | Wf   | % Weight loss | average | sd   |
|-------------|------------|------|------|---------------|---------|------|
| 10          | 1          | 65.4 | 59.9 | 8.41          | 8.38    | 3.64 |
|             | 2          | 50.2 | 45.2 | 9.96          |         |      |
|             | 3          | 35.3 | 30.5 | 13.60         |         |      |
|             | 4          | 78.9 | 75.1 | 4.82          |         |      |
|             | 5          | 56.6 | 53.7 | 5.12          |         |      |
| 20          | 6          | 85.1 | 74.0 | 13.04         | 14.95   | 5.13 |
|             | 7          | 59.7 | 51.9 | 13.07         |         |      |
|             | 8          | 72.6 | 63.3 | 12.81         |         |      |
|             | 9          | 62.1 | 54.8 | 11.76         |         |      |
|             | 10         | 56.9 | 43.2 | 24.08         |         |      |
| 30          | 11         | 65.9 | 53.7 | 18.51         | 23.14   | 4.07 |
|             | 12         | 37.3 | 27.6 | 26.01         |         |      |
|             | 13         | 55.1 | 40.0 | 27.40         |         |      |
|             | 14         | 29.2 | 22.0 | 24.66         |         |      |
|             | 15         | 68.5 | 55.4 | 19.12         |         |      |
| 40          | 16         | 71.7 | 56.1 | 21.76         | 22.56   | 2.22 |
|             | 17         | 58.9 | 46.5 | 21.05         |         |      |
|             | 18         | 89.9 | 71.7 | 20.24         |         |      |
|             | 19         | 87.6 | 66.3 | 24.32         |         |      |
|             | 20         | 50.7 | 37.8 | 25.44         |         |      |
| 50          | 21         | 69.4 | 49.4 | 28.82         | 27.78   | 2.07 |
|             | 22         | 66.0 | 46.5 | 29.55         |         |      |
|             | 23         | 55.6 | 41.1 | 26.08         |         |      |
|             | 24         | 83.7 | 59.1 | 29.39         |         |      |
|             | 25         | 54.3 | 40.7 | 25.05         |         |      |
| 60          | 26         | 59.4 | 42.2 | 28.96         | 32.53   | 4.52 |
|             | 27         | 58.7 | 39.5 | 32.71         |         |      |
|             | 28         | 66.4 | 45.4 | 31.63         |         |      |
|             | 29         | 57.1 | 34.2 | 40.11         |         |      |
|             | 30         | 64.9 | 45.9 | 29.28         |         |      |
| 70          | 31         | 73.5 | 49.2 | 33.06         | 30.34   | 1.92 |
|             | 32         | 51.5 | 35.7 | 30.68         |         |      |
|             | 33         | 69.9 | 49.2 | 29.61         |         |      |
|             | 34         | 74.6 | 51.8 | 30.56         |         |      |
|             | 35         | 60.5 | 43.7 | 27.77         |         |      |
| 80          | 36         | 70.6 | 49.5 | 29.89         | 32.17   | 3.40 |
|             | 37         | 58.8 | 41.2 | 29.93         |         |      |
|             | 38         | 54.2 | 38.0 | 29.89         |         |      |
|             | 39         | 73.8 | 49.0 | 33.60         |         |      |
|             | 40         | 46.1 | 28.8 | 37.53         |         |      |
| 90          | 41         | 31.0 | 17.9 | 42.26         | 35.61   | 5.49 |
|             | 42         | 69.7 | 49.6 | 28.84         |         |      |
|             | 43         | 27.9 | 19.2 | 31.18         |         |      |
|             | 44         | 61.1 | 38.3 | 37.32         |         |      |
|             | 45         | 32.0 | 19.7 | 38.44         |         |      |

G2 %weight loss of pineapple leaf cellulose films with medium DS values in real composting condition

| Time (days) | Sample No. | Wi   | Wf   | % Weight loss | average | sd    |
|-------------|------------|------|------|---------------|---------|-------|
| 10          | 1          | 75.4 | 71.0 | 5.84          | 5.88    | 0.80  |
|             | 2          | 62.0 | 57.8 | 6.77          |         |       |
|             | 3          | 66.5 | 62.2 | 6.47          |         |       |
|             | 4          | 55.1 | 52.5 | 4.72          |         |       |
|             | 5          | 69.3 | 65.4 | 5.63          |         |       |
| 20          | 6          | 66.0 | 60.5 | 8.33          | 10.11   | 3.51  |
|             | 7          | 66.7 | 60.3 | 9.60          |         |       |
|             | 8          | 60.0 | 55.2 | 8.00          |         |       |
|             | 9          | 74.5 | 68.3 | 8.32          |         |       |
|             | 10         | 78.6 | 65.8 | 16.28         |         |       |
| 30          | 11         | 60.3 | 52.1 | 13.60         | 12.34   | 1.46  |
|             | 12         | 61.3 | 54.1 | 11.75         |         |       |
|             | 13         | 52.7 | 45.6 | 13.47         |         |       |
|             | 14         | 68.6 | 59.8 | 12.83         |         |       |
|             | 15         | 87.3 | 78.5 | 10.08         |         |       |
| 40          | 16         | 64.9 | 54.0 | 16.80         | 18.03   | 1.10  |
|             | 17         | 64.7 | 52.3 | 19.17         |         |       |
|             | 18         | 75.5 | 62.7 | 16.95         |         |       |
|             | 19         | 51.9 | 42.1 | 18.88         |         |       |
|             | 20         | 66.4 | 54.2 | 18.37         |         |       |
| 50          | 21         | 81.1 | 61.5 | 24.17         | 23.35   | 1.26  |
|             | 22         | 79.8 | 60.5 | 24.19         |         |       |
|             | 23         | 68.0 | 53.2 | 21.76         |         |       |
|             | 24         | 65.3 | 50.8 | 22.21         |         |       |
|             | 25         | 71.2 | 53.8 | 24.44         |         |       |
| 60          | 26         | 65.6 | 49   | 25.30         | 35.37   | 14.09 |
|             | 27         | 55.4 | 33.9 | 38.81         |         |       |
|             | 28         | 65.7 | 48.3 | 26.48         |         |       |
|             | 29         | 71.1 | 29.4 | 58.65         |         |       |
|             | 30         | 75.4 | 54.6 | 27.59         |         |       |
| 70          | 31         | 71.2 | 52.1 | 26.83         | 27.26   | 1.88  |
|             | 32         | 73.2 | 53.1 | 27.46         |         |       |
|             | 33         | 54.3 | 37.8 | 30.39         |         |       |
|             | 34         | 55.9 | 41.5 | 25.76         |         |       |
|             | 35         | 78.8 | 58.4 | 25.89         |         |       |
| 80          | 36         | 68.9 | 50.3 | 27.00         | 28.32   | 2.25  |
|             | 37         | 70.0 | 51.4 | 26.57         |         |       |
|             | 38         | 72.1 | 52.4 | 27.32         |         |       |
|             | 39         | 53.5 | 38.2 | 28.60         |         |       |
|             | 40         | 62.3 | 42.3 | 32.10         |         |       |
| 90          | 41         | 62.1 | 47.4 | 23.67         | 26.24   | 2.99  |
|             | 42         | 74.8 | 53   | 29.14         |         |       |
|             | 43         | 66.2 | 46.5 | 29.76         |         |       |
|             | 44         | 54.1 | 41.3 | 23.66         |         |       |
|             | 45         | 59.3 | 44.5 | 24.96         |         |       |

## G3 %weight loss of pineapple leaf cellulose films with low DS values in real composting condition

| Time (days) | Sample No. | Wi    | Wf   | % Weight loss | average | sd    |
|-------------|------------|-------|------|---------------|---------|-------|
| 10          | 1          | 100.8 | 71.1 | 29.46         | 24.94   | 4.91  |
|             | 2          | 83.2  | 62   | 25.48         |         |       |
|             | 3          | 82.9  | 58.2 | 29.79         |         |       |
|             | 4          | 81.5  | 64.2 | 21.23         |         |       |
|             | 5          | 74.7  | 60.7 | 18.74         |         |       |
| 20          | 6          | 73.8  | 41.0 | 44.44         | 29.99   | 8.32  |
|             | 7          | 66.4  | 49.4 | 25.60         |         |       |
|             | 8          | 48.7  | 34.9 | 28.34         |         |       |
|             | 9          | 53.7  | 38.6 | 28.12         |         |       |
|             | 10         | 52.0  | 39.8 | 23.46         |         |       |
| 30          | 11         | 57.4  | 37.6 | 34.49         | 31.55   | 6.11  |
|             | 12         | 58.0  | 43.4 | 25.17         |         |       |
|             | 13         | 58.7  | 43.6 | 25.72         |         |       |
|             | 14         | 56.4  | 37.9 | 32.80         |         |       |
|             | 15         | 60.9  | 36.8 | 39.57         |         |       |
| 40          | 16         | 59.1  | 7.9  | 86.63         | 51.63   | 20.33 |
|             | 17         | 90.3  | 55.1 | 38.98         |         |       |
|             | 18         | 68.5  | 32.6 | 52.41         |         |       |
|             | 19         | 58.6  | 34.8 | 40.61         |         |       |
|             | 20         | 73.4  | 44.4 | 39.51         |         |       |
| 50          | 21         | 26.0  | 15.2 | 41.54         | 38.89   | 6.22  |
|             | 22         | 35.4  | 19.4 | 45.20         |         |       |
|             | 23         | 73.6  | 50.6 | 31.25         |         |       |
|             | 24         | 96.8  | 55.0 | 43.18         |         |       |
|             | 25         | 86.2  | 57.5 | 33.29         |         |       |
| 60          | 26         | 69.1  | 41.3 | 40.23         | 41.50   | 3.31  |
|             | 27         | 72.5  | 40.4 | 44.28         |         |       |
|             | 28         | 54.3  | -    | #VALUE!       |         |       |
|             | 29         | 50.0  | 31.3 | 37.40         |         |       |
|             | 30         | 46.5  | 26.0 | 44.09         |         |       |
| 70          | 31         | 78.8  | 53.5 | 32.11         | 52.26   | 17.72 |
|             | 32         | 86.0  | 26.1 | 69.65         |         |       |
|             | 33         | 73.8  | -    | #VALUE!       |         |       |
|             | 34         | 46.0  | 16.4 | 64.35         |         |       |
|             | 35         | 67.1  | 38.3 | 42.92         |         |       |
| 80          | 36         | 80.8  | 35.2 | 56.44         | 53.60   | 17.19 |
|             | 37         | 40.4  | 24.4 | 39.60         |         |       |
|             | 38         | 66.8  | 41.0 | 38.62         |         |       |
|             | 39         | 74.1  | 43.3 | 41.57         |         |       |
|             | 40         | 56.0  | 13.0 | 76.79         |         |       |
| 90          | 41         | 70.4  | 41.5 | 41.05         | 40.52   | 5.18  |
|             | 42         | 78.3  | 41.3 | 47.25         |         |       |
|             | 43         | 61.6  | 41.9 | 31.98         |         |       |
|             | 44         | 80.4  | 49.1 | 38.93         |         |       |
|             | 45         | 102.5 | 66.8 | 34.83         |         |       |



G4 %weight loss of pineapple leaf cellulose films with high DS values in waste water treatment system condition

| Time (days) | Sample No. | Wi   | Wf   | % Weight loss | Average | SD   |
|-------------|------------|------|------|---------------|---------|------|
| 10          | 1          | 75.4 | 71.9 | 4.64          | 5.03    | 0.84 |
|             | 2          | 52.5 | 49.1 | 6.48          |         |      |
|             | 3          | 61.9 | 59.2 | 4.36          |         |      |
|             | 4          | 75.9 | 72.1 | 5.01          |         |      |
|             | 5          | 53.5 | 51.0 | 4.67          |         |      |
| 20          | 6          | 77.8 | 72   | 7.46          | 6.13    | 0.78 |
|             | 7          | 55.2 | 52.2 | 5.43          |         |      |
|             | 8          | 74.7 | 70.2 | 6.02          |         |      |
|             | 9          | 54.1 | 51.0 | 5.73          |         |      |
|             | 10         | 70.0 | 65.8 | 6.00          |         |      |
| 30          | 11         | 53.8 | 51.0 | 5.20          | 5.15    | 0.33 |
|             | 12         | 63.3 | 60.2 | 4.90          |         |      |
|             | 13         | 70.3 | 66.6 | 5.26          |         |      |
|             | 14         | 71.2 | 67.8 | 4.78          |         |      |
|             | 15         | 51.6 | 48.7 | 5.62          |         |      |
| 40          | 16         | 62.9 | 59.2 | 5.88          | 8.57    | 3.25 |
|             | 17         | 65.2 | 61.6 | 5.52          |         |      |
|             | 18         | 60.7 | 53.3 | 12.19         |         |      |
|             | 19         | 61.3 | 56.8 | 7.34          |         |      |
|             | 20         | 65.5 | 57.7 | 11.91         |         |      |
| 50          | 21         | 66.1 | 62.1 | 6.05          | 6.98    | 0.88 |
|             | 22         | 65.4 | 60.1 | 8.10          |         |      |
|             | 23         | 71.5 | 66.0 | 7.69          |         |      |
|             | 24         | 69.8 | 65.3 | 6.45          |         |      |
|             | 25         | 57.6 | 53.8 | 6.60          |         |      |
| 60          | 26         | 45.9 | 43.0 | 6.32          | 9.17    | 3.30 |
|             | 27         | 48.2 | 44.8 | 7.05          |         |      |
|             | 28         | 70.0 | 62.9 | 10.14         |         |      |
|             | 29         | 73.8 | 68.0 | 7.86          |         |      |
|             | 30         | 60.0 | 51.3 | 14.50         |         |      |
| 70          | 31         | 68.7 | 63.0 | 8.30          | 7.65    | 0.54 |
|             | 32         | 71.3 | 65.9 | 7.57          |         |      |
|             | 33         | 56.9 | 52.8 | 7.21          |         |      |
|             | 34         | 73.5 | 68.3 | 7.07          |         |      |
|             | 35         | 76.5 | 70.3 | 8.10          |         |      |
| 80          | 36         | 71.4 | 62.6 | 12.32         | 11.01   | 1.83 |
|             | 37         | 62.9 | 56.9 | 9.54          |         |      |
|             | 38         | 54.5 | 49.2 | 9.72          |         |      |
|             | 39         | 64.8 | 56.0 | 13.58         |         |      |
|             | 40         | 58.6 | 52.8 | 9.90          |         |      |
| 90          | 41         | 53.9 | 48.1 | 10.76         | 10.14   | 1.16 |
|             | 42         | 75.2 | 68.7 | 8.64          |         |      |
|             | 43         | 65.4 | 57.8 | 11.62         |         |      |
|             | 44         | 75.6 | 68.5 | 9.39          |         |      |
|             | 45         | 64.3 | 57.7 | 10.26         |         |      |

G5 %weight loss of pineapple leaf cellulose films with medium DS values in waste water treatment system condition

| Time (days) | Sample No. | Wi   | Wf   | % Weight loss | Average | SD    |
|-------------|------------|------|------|---------------|---------|-------|
| 10          | 1          | 62.9 | 60.1 | 4.45          | 8.76    | 3.53  |
|             | 2          | 86.6 | 80.1 | 7.51          |         |       |
|             | 3          | 57.9 | 50.6 | 12.61         |         |       |
|             | 4          | 65.5 | 57.5 | 12.21         |         |       |
|             | 5          | 86.6 | 80.5 | 7.04          |         |       |
| 20          | 6          | 60.3 | 55.7 | 7.63          | 9.48    | 2.70  |
|             | 7          | 43.5 | 38.5 | 11.49         |         |       |
|             | 8          | 66.6 | 57.8 | 13.21         |         |       |
|             | 9          | 68.9 | 63.9 | 7.26          |         |       |
|             | 10         | 75.8 | 69.9 | 7.78          |         |       |
| 30          | 11         | 53.3 | 44.9 | 15.76         | 11.52   | 3.41  |
|             | 12         | 54.5 | 46.5 | 14.68         |         |       |
|             | 13         | 75.3 | 68.4 | 9.16          |         |       |
|             | 14         | 66.3 | 60.6 | 8.60          |         |       |
|             | 15         | 71.4 | 64.7 | 9.38          |         |       |
| 40          | 16         | 72.9 | 66.8 | 8.37          | 10.63   | 3.45  |
|             | 17         | 60.2 | 54.7 | 9.14          |         |       |
|             | 18         | 56.1 | 46.7 | 16.76         |         |       |
|             | 19         | 55.1 | 49.8 | 9.62          |         |       |
|             | 20         | 87.2 | 79.1 | 9.29          |         |       |
| 50          | 21         | 69.7 | 63.1 | 9.47          | 11.42   | 3.58  |
|             | 22         | 65.1 | 58.6 | 9.98          |         |       |
|             | 23         | 48.2 | 43.1 | 10.58         |         |       |
|             | 24         | 54.6 | 44.9 | 17.77         |         |       |
|             | 25         | 54.7 | 49.6 | 9.32          |         |       |
| 60          | 26         | 54.0 | 43.1 | 20.19         | 15.28   | 4.45  |
|             | 27         | 66.1 | 59.2 | 10.44         |         |       |
|             | 28         | 49.2 | 43.9 | 10.77         |         |       |
|             | 29         | 59.4 | 48.5 | 18.35         |         |       |
|             | 30         | 54.1 | 45.1 | 16.64         |         |       |
| 70          | 31         | 58.2 | 40.9 | 29.73         | 17.21   | 10.02 |
|             | 32         | 65.2 | 52.0 | 20.25         |         |       |
|             | 33         | 79.3 | 70.5 | 11.10         |         |       |
|             | 34         | 64.0 | 50.4 | 21.25         |         |       |
|             | 35         | 51.0 | 49.1 | 3.73          |         |       |
| 80          | 36         | 59.8 | 48.1 | 19.57         | 18.99   | 4.81  |
|             | 37         | 58.6 | 43.7 | 25.43         |         |       |
|             | 38         | 59.6 | 52.4 | 12.08         |         |       |
|             | 39         | 64.0 | 51.1 | 20.16         |         |       |
|             | 40         | 53.0 | 43.6 | 17.74         |         |       |
| 90          | 41         | 68.2 | 60.6 | 11.14         | 22.46   | 7.65  |
|             | 42         | 51.8 | 39.1 | 24.52         |         |       |
|             | 43         | 43.7 | 32.9 | 24.71         |         |       |
|             | 44         | 48.6 | 38.9 | 19.96         |         |       |
|             | 45         | 46.3 | 31.5 | 31.97         |         |       |

G6 %weight loss of pineapple leaf cellulose films with low DS values in waste water treatment system condition

| Time (days) | Sample No. | Wi   | Wf   | % Weight loss | Average | SD    |
|-------------|------------|------|------|---------------|---------|-------|
| 10          | 1          | 59.3 | 55.9 | 5.73          | 6.60    | 2.62  |
|             | 2          | 97.4 | 88.2 | 9.45          |         |       |
|             | 3          | 63.9 | 61.5 | 3.76          |         |       |
|             | 4          | 90.4 | 82.0 | 9.29          |         |       |
|             | 5          | 54.3 | 51.7 | 4.79          |         |       |
| 20          | 6          | 50.7 | 46.2 | 8.88          | 14.76   | 4.51  |
|             | 7          | 79.2 | 64.0 | 19.19         |         |       |
|             | 8          | 72.2 | 58.8 | 18.56         |         |       |
|             | 9          | 93.3 | 82.7 | 11.36         |         |       |
|             | 10         | 49.9 | 42.0 | 15.83         |         |       |
| 30          | 11         | 82.8 | 63.4 | 23.43         | 21.40   | 2.14  |
|             | 12         | 75.6 | 59.3 | 21.56         |         |       |
|             | 13         | 50.0 | 40.2 | 19.60         |         |       |
|             | 14         | 87.1 | 66.6 | 23.54         |         |       |
|             | 15         | 55.1 | 44.7 | 18.87         |         |       |
| 40          | 16         | 93.8 | 69.6 | 25.80         | 20.54   | 6.74  |
|             | 17         | 62.3 | 45.8 | 26.48         |         |       |
|             | 18         | 50.9 | 41.1 | 19.25         |         |       |
|             | 19         | 88.7 | 69.7 | 21.42         |         |       |
|             | 20         | 50.2 | 45.3 | 9.76          |         |       |
| 50          | 21         | 37.3 | 30.4 | 39.44         | 17.85   | 12.16 |
|             | 22         | 70.4 | 62.0 | 11.93         |         |       |
|             | 23         | 75.0 | 63.8 | 14.93         |         |       |
|             | 24         | 51.7 | 45.6 | 11.80         |         |       |
|             | 25         | 60.2 | 53.5 | 11.13         |         |       |
| 60          | 26         | 71.2 | 52.8 | 25.84         | 21.62   | 6.80  |
|             | 27         | 68.8 | 60.4 | 12.21         |         |       |
|             | 28         | 74.7 | 62.3 | 16.60         |         |       |
|             | 29         | 69.7 | 50.6 | 27.40         |         |       |
|             | 30         | 71.0 | 52.5 | 26.06         |         |       |
| 70          | 31         | 65.8 | 47   | 28.57         | 24.35   | 3.92  |
|             | 32         | 77.5 | 57.5 | 25.81         |         |       |
|             | 33         | 70.7 | 52.3 | 26.03         |         |       |
|             | 34         | 70.7 | 57.8 | 18.25         |         |       |
|             | 35         | 72.7 | 55.9 | 23.11         |         |       |
| 80          | 36         | 60.4 | 42.3 | 29.97         | 28.61   | 6.89  |
|             | 37         | 69.8 | 57.7 | 17.34         |         |       |
|             | 38         | 60.8 | 39.2 | 35.53         |         |       |
|             | 39         | 57.2 | 38.8 | 32.17         |         |       |
|             | 40         | 68.5 | 49.3 | 28.03         |         |       |
| 90          | 41         | 60.4 | 51.6 | 14.57         | 48.89   | 46.66 |
|             | 42         | 70.7 | 60.2 | 14.85         |         |       |
|             | 43         | 59.9 | 50.9 | 15.03         |         |       |
|             | 44         | 74.6 | 0    | 100.00        |         |       |
|             | 45         | 63.9 | 0    | 100.00        |         |       |

## H : Biodegradability of Corn Husk Cellulose Film

H1 %weight loss of corn husk cellulose films with high DS values in real composting condition

| Time (days) | Sample No. | Wi   | Wf   | % Weight loss | average | sd    |
|-------------|------------|------|------|---------------|---------|-------|
| 10          | 1          | 51.9 | 38.1 | 26.59         | 14.35   | 7.22  |
|             | 2          | 57.5 | 53.0 | 7.83          |         |       |
|             | 3          | 45.4 | 40.4 | 11.01         |         |       |
|             | 4          | 48.5 | 41.6 | 14.23         |         |       |
|             | 5          | 60.4 | 53.1 | 12.09         |         |       |
| 20          | 6          | 33.0 | 27.8 | 15.76         | 18.68   | 5.55  |
|             | 7          | 45.5 | 33.5 | 26.37         |         |       |
|             | 8          | 36.3 | 29.9 | 17.63         |         |       |
|             | 9          | 44.3 | 39.0 | 11.96         |         |       |
|             | 10         | 54.4 | 42.6 | 21.69         |         |       |
| 30          | 11         | 45.8 | 31.2 | 31.88         | 28.74   | 4.31  |
|             | 12         | 42.3 | 30   | 29.08         |         |       |
|             | 13         | 49.4 | 32.7 | 33.81         |         |       |
|             | 14         | 51.7 | 39.6 | 23.40         |         |       |
|             | 15         | 57.6 | 42.9 | 25.52         |         |       |
| 40          | 16         | 53.6 | -    |               | 53.97   | 17.14 |
|             | 17         | 30.1 | 16.8 | 44.19         |         |       |
|             | 18         | 51.6 | 26.4 | 48.84         |         |       |
|             | 19         | 49.1 | 10.1 | 79.43         |         |       |
|             | 20         | 56.4 | 31.9 | 43.44         |         |       |
| 50          | 21         | 65.7 | 39.5 | 39.88         | 48.47   | 2.61  |
|             | 22         | 51.7 | 28.1 | 45.65         |         |       |
|             | 23         | 44.0 | 21.5 | 51.14         |         |       |
|             | 24         | 53.7 | 28.5 | 46.93         |         |       |
|             | 25         | 55.6 | 27.7 | 50.18         |         |       |
| 60          | 26         | 43.0 | 20.5 | 52.33         | 50.87   | 4.20  |
|             | 27         | 56.0 | 27.2 | 51.43         |         |       |
|             | 28         | 35.1 | 18.6 | 47.01         |         |       |
|             | 29         | 50.7 | 26.1 | 48.52         |         |       |
|             | 30         | 54.3 | 23.6 | 56.54         |         |       |
| 70          | 31         | 50.3 | 25.3 | 49.70         | 54.47   | 5.54  |
|             | 32         | 47.4 | 18.8 | 60.34         |         |       |
|             | 33         | 46.2 | 22.7 | 50.87         |         |       |
|             | 34         | 53.0 | 22.3 | 57.92         |         |       |
|             | 35         | 44.1 | 22.6 | 48.75         |         |       |
| 80          | 36         | 43.3 | -    | #VALUE!       | 62.70   | 7.76  |
|             | 37         | 46.1 | 14.9 | 67.68         |         |       |
|             | 38         | 47.5 | 18.9 | 60.21         |         |       |
|             | 39         | 42.3 | 12.1 | 71.39         |         |       |
|             | 40         | 45.5 | 19.8 | 56.48         |         |       |
| 90          | 41         | 50.2 | 13.9 | 72.31         | 61.16   | 4.79  |
|             | 42         | 39.3 | 4.3  | 89.06         |         |       |
|             | 43         | 56.7 | 20.1 | 64.55         |         |       |
|             | 44         | 52.1 | 22.0 | 57.77         |         |       |
|             | 45         | 46.6 | -    |               |         |       |

## H2 %weight loss of corn husk cellulose films with medium DS values in real composting condition

| Time (days) | Sample No. | Wi   | Wf   | % Weight loss | average | sd    |
|-------------|------------|------|------|---------------|---------|-------|
| 10          | 1          | 55.7 | 49.5 | 11.13         | 8.87    | 2.86  |
|             | 2          | 69.0 | 64.8 | 6.09          |         |       |
|             | 3          | 69.4 | 60.6 | 12.68         |         |       |
|             | 4          | 68.6 | 63.7 | 7.14          |         |       |
|             | 5          | 71.2 | 66.0 | 7.30          |         |       |
| 20          | 6          | 52.3 | 47.6 | 8.99          | 17.52   | 8.75  |
|             | 7          | 64.8 | 47.9 | 26.08         |         |       |
|             | 8          | 62.3 | 45.0 | 27.77         |         |       |
|             | 9          | 58.2 | 51.6 | 11.34         |         |       |
|             | 10         | 65.5 | 56.7 | 13.44         |         |       |
| 30          | 11         | 63.6 | 52.3 | 17.77         | 19.04   | 4.24  |
|             | 12         | 65.1 | 51.3 | 21.20         |         |       |
|             | 13         | 61.9 | 53.4 | 13.73         |         |       |
|             | 14         | 69.0 | -    | #VALUE!       |         |       |
|             | 15         | 65.2 | 49.9 | 23.47         |         |       |
| 40          | 16         | 69.4 | 51   | 26.51         | 33.07   | 17.79 |
|             | 17         | 55.5 | 19.7 | 64.50         |         |       |
|             | 18         | 69.2 | 54.4 | 21.39         |         |       |
|             | 19         | 54.7 | 38.9 | 28.88         |         |       |
|             | 20         | 48.2 | 36.6 | 24.07         |         |       |
| 50          | 21         | 45.0 | 12.8 | 71.56         | 70.93   | 23.16 |
|             | 22         | 59.7 |      | 100.00        |         |       |
|             | 23         | 59.1 | 14.1 | 76.14         |         |       |
|             | 24         | 64.3 | 18.2 | 71.70         |         |       |
|             | 25         | 68.9 | 44.6 | 35.27         |         |       |
| 60          | 26         | 54.5 | 25.8 | 52.66         | 58.21   | 21.01 |
|             | 27         | 58.0 | 11.8 | 79.66         |         |       |
|             | 28         | 52.3 | 11.0 | 78.97         |         |       |
|             | 29         | 75.1 | 38.2 | 49.13         |         |       |
|             | 30         | 60.1 | 41.7 | 30.62         |         |       |
| 70          | 31         | 63.2 | 9.6  | 84.81         | 81.82   | 4.23  |
|             | 32         | 62.8 | 13.3 | 78.82         |         |       |
|             | 33         | 60.2 | -    | #VALUE!       |         |       |
|             | 34         | 67.9 | -    | #VALUE!       |         |       |
|             | 35         | 59.1 | -    | #VALUE!       |         |       |
| 80          | 36         | 63.9 | 30.9 | 51.64         | 58.73   | 14.71 |
|             | 37         | 60.8 | 35.6 | 41.45         |         |       |
|             | 38         | 65.2 | 23.4 | 64.11         |         |       |
|             | 39         | 36.9 | 16.3 | 55.83         |         |       |
|             | 40         | 50.6 | 9.8  | 80.63         |         |       |
| 90          | 41         | 54.1 | 6.2  | 88.54         | 81.75   | 11.76 |
|             | 42         | 65.7 | 12.7 | 80.67         |         |       |
|             | 43         | 58.2 | 20   | 65.64         |         |       |
|             | 44         | 66.2 | 5.2  | 92.15         |         |       |
|             | 45         | 48.2 | -    |               |         |       |

## H3 %weight loss of corn husk cellulose films with low DS values in real composting condition

| Time (days) | Sample No. | Wi   | Wf   | % Weight loss | average | sd    |
|-------------|------------|------|------|---------------|---------|-------|
| 10          | 1          | 31.5 | 8.7  | 72.38         | 36.25   | 20.75 |
|             | 2          | 53.3 | 37.1 | 30.39         |         |       |
|             | 3          | 56.0 | 40.4 | 27.86         |         |       |
|             | 4          | 62.0 | 42.6 | 31.29         |         |       |
|             | 5          | 58.5 | 47.2 | 19.32         |         |       |
| 20          | 6          | 35.6 | 17.1 | 51.97         | 47.70   | 18.96 |
|             | 7          | 33.7 | 9.1  | 73.00         |         |       |
|             | 8          | 53.7 | 41.8 | 22.16         |         |       |
|             | 9          | 75.4 | 46.8 | 37.93         |         |       |
|             | 10         | 38.0 | 17.7 | 53.42         |         |       |
| 30          | 11         | 53.7 | 22.2 | 58.66         | 53.12   | 11.42 |
|             | 12         | 46.4 | 23.2 | 50.00         |         |       |
|             | 13         | 57.6 | 35.3 | 38.72         |         |       |
|             | 14         | 57.2 | -    | #VALUE!       |         |       |
|             | 15         | 59.3 | 20.7 | 65.09         |         |       |
| 40          | 16         | 58.0 | 28.4 | 51.03         | 55.63   | 20.08 |
|             | 17         | 50.5 | 34.2 | 32.28         |         |       |
|             | 18         | 43.3 | 8.3  | 80.83         |         |       |
|             | 19         | 63.3 | -    | #VALUE!       |         |       |
|             | 20         | 64.4 | 26.8 | 58.39         |         |       |
| 50          | 21         | 59.8 | 0    | 100.00        | 90.99   | 18.02 |
|             | 22         | 50.3 | 0    | 100.00        |         |       |
|             | 23         | 62.4 | 0    | 100.00        |         |       |
|             | 24         | 61.7 | 7.6  | 87.68         |         |       |
|             | 25         | 55.5 | 20.0 | 63.96         |         |       |
| 60          | 26         | 46.0 | 0    | 100           | 87.03   | 18.58 |
|             | 27         | 52.1 | 6.5  | 87.52         |         |       |
|             | 28         | 69.8 | 27.5 | 60.60         |         |       |
|             | 29         | 70.5 | 0    | 100           |         |       |
|             | 30         | 76.6 | 0    | 100           |         |       |
| 70          | 31         | 54.4 | 2.7  | 95.04         | 98.76   | 2.48  |
|             | 32         | 47.6 | 0    | 100           |         |       |
|             | 33         | 58.8 | 0    | 100           |         |       |
|             | 34         | 62.2 | 0    | 100           |         |       |
|             | 35         | 65.8 | 0    | 100           |         |       |
| 80          | 36         | 60.1 | 0    | 100           | 100.00  | 0.00  |
|             | 37         | 60.1 | 0    | 100           |         |       |
|             | 38         | 57.9 | 0    | 100           |         |       |
|             | 39         | 57.1 | 0    | 100           |         |       |
|             | 40         | 66.4 | 0    | 100           |         |       |
| 90          | 41         | 61.6 | 0    | 100           | 100.00  | 0.00  |
|             | 42         | 57.6 | 0    | 100           |         |       |
|             | 43         | 37.9 | 0    | 100           |         |       |
|             | 44         | 55.2 | 0    | 100           |         |       |
|             | 45         | 62.9 | 0    | 100           |         |       |

H4 %weight loss of corn husk cellulose films with high DS values in waste water treatment system condition

| Time (days) | Sample No. | Wi   | Wf   | % Weight loss | Average | SD    |
|-------------|------------|------|------|---------------|---------|-------|
| 10          | 1          | 43.9 | 42.1 | 4.10          | 4.46    | 0.32  |
|             | 2          | 46.8 | 44.6 | 4.70          |         |       |
|             | 3          | 50.4 | 48.3 | 4.17          |         |       |
|             | 4          | 47.6 | 45.3 | 4.83          |         |       |
|             | 5          | 39.9 | 38.1 | 4.51          |         |       |
| 20          | 6          | 54.5 | 50.0 | 8.26          | 7.78    | 0.45  |
|             | 7          | 47.4 | 44.0 | 7.17          |         |       |
|             | 8          | 63.3 | 58.5 | 7.58          |         |       |
|             | 9          | 57.4 | 52.7 | 8.19          |         |       |
|             | 10         | 53.4 | 49.3 | 7.68          |         |       |
| 30          | 11         | 42.2 | 37.2 | 11.85         | 12.98   | 1.70  |
|             | 12         | 34.4 | 29.7 | 13.66         |         |       |
|             | 13         | 54.4 | 46.1 | 15.26         |         |       |
|             | 14         | 38.5 | 33.4 | 13.25         |         |       |
|             | 15         | 48.8 | 43.5 | 10.86         |         |       |
| 40          | 16         | 67.4 | 56.4 | 16.32         | 17.46   | 4.66  |
|             | 17         | 46.0 | 39   | 15.22         |         |       |
|             | 18         | 66.1 | 49.5 | 25.11         |         |       |
|             | 19         | 52.6 | 43.2 | 17.87         |         |       |
|             | 20         | 50.8 | 44.3 | 12.80         |         |       |
| 50          | 21         | 38.9 | 33.8 | 13.11         | 18.86   | 5.17  |
|             | 22         | 42.1 | 33.9 | 19.48         |         |       |
|             | 23         | 45.6 | 37.7 | 17.32         |         |       |
|             | 24         | 47.4 | 35.3 | 25.53         |         |       |
|             | 25         | 53.4 | 0    | 100.00        |         |       |
| 60          | 26         | 38.8 | 29.4 | 24.23         | 20.76   | 2.65  |
|             | 27         | 48.5 | 37.7 | 22.27         |         |       |
|             | 28         | 54.9 | 43.4 | 20.95         |         |       |
|             | 29         | 53.8 | 44.3 | 17.66         |         |       |
|             | 30         | 43.8 | 35.6 | 18.72         |         |       |
| 70          | 31         | 53.3 | 30.9 | 42.03         | 30.08   | 7.51  |
|             | 32         | 48.9 | 37.8 | 22.70         |         |       |
|             | 33         | 43.2 | 32.4 | 25.00         |         |       |
|             | 34         | 41.7 | 29.5 | 29.26         |         |       |
|             | 35         | 36.9 | 25.3 | 31.44         |         |       |
| 80          | 36         | 40.1 | 30.4 | 24.19         | 32.82   | 11.71 |
|             | 37         | 48.4 | 34.8 | 28.10         |         |       |
|             | 38         | 52.2 | 36.3 | 30.46         |         |       |
|             | 39         | 42.9 | 20   | 53.38         |         |       |
|             | 40         | 43.6 | 31.4 | 27.98         |         |       |
| 90          | 41         | 40.1 | 27.9 | 30.42         | 32.20   | 7.63  |
|             | 42         | 48.4 | 33.8 | 30.17         |         |       |
|             | 43         | 49.4 | 36.4 | 26.32         |         |       |
|             | 44         | 37.8 | 27   | 28.57         |         |       |
|             | 45         | 43.7 | 23.8 | 45.54         |         |       |

H5 %weight loss of corn husk cellulose films with medium DS values in waste water treatment system condition

| Time (days) | Sample No. | Wi   | Wf   | % Weight loss | Average | SD    |
|-------------|------------|------|------|---------------|---------|-------|
| 10          | 1          | 77.8 | 72.9 | 6.30          | 6.45    | 2.11  |
|             | 2          | 61.2 | 56.9 | 7.03          |         |       |
|             | 3          | 58.6 | 56.3 | 3.92          |         |       |
|             | 4          | 57.3 | 54.2 | 5.41          |         |       |
|             | 5          | 63.5 | 57.4 | 9.61          |         |       |
| 20          | 6          | 65.6 | 52.8 | 19.51         | 13.55   | 5.59  |
|             | 7          | 60.3 | 49.5 | 17.91         |         |       |
|             | 8          | 53.1 | 50.3 | 5.27          |         |       |
|             | 9          | 65.1 | 57.0 | 12.44         |         |       |
|             | 10         | 68.9 | 60.2 | 12.63         |         |       |
| 30          | 11         | 63.3 | 36.7 | 42.02         | 37.58   | 24.51 |
|             | 12         | 64.8 | 38.3 | 40.90         |         |       |
|             | 13         | 55.7 | 47.4 | 14.90         |         |       |
|             | 14         | 64.5 | 54.5 | 15.50         |         |       |
|             | 15         | 61.8 | 15.7 | 74.60         |         |       |
| 40          | 16         | 61.3 | 24.6 | 59.87         | 51.17   | 22.12 |
|             | 17         | 61.4 | 31.5 | 48.70         |         |       |
|             | 18         | 67.1 | 52.4 | 21.91         |         |       |
|             | 19         | 64.7 | 16.7 | 74.19         |         |       |
|             | 20         | 65.0 | 65   | 0.00          |         |       |
| 50          | 21         | 62.2 | 16.9 | 72.83         | 40.66   | 24.27 |
|             | 22         | 61.7 | 45.1 | 26.90         |         |       |
|             | 23         | 68.9 | 55.7 | 19.16         |         |       |
|             | 24         | 66.2 | 26.2 | 60.42         |         |       |
|             | 25         | 58.0 | 44.1 | 23.97         |         |       |
| 60          | 26         | 58.3 | 40.2 | 31.05         | 44.83   | 27.34 |
|             | 27         | 66.3 | 36.6 | 44.80         |         |       |
|             | 28         | 60.6 | 9.9  | 83.66         |         |       |
|             | 29         | 69.4 | 31.6 | 54.47         |         |       |
|             | 30         | 66.7 | 59.9 | 10.19         |         |       |
| 70          | 31         | 62.5 | 41.1 | 34.24         | 42.37   | 10.39 |
|             | 32         | 67.3 | 31.1 | 53.79         |         |       |
|             | 33         | 47.1 | 22.6 | 52.02         |         |       |
|             | 34         | 47.2 | 27.7 | 41.31         |         |       |
|             | 35         | 50.5 | 35.1 | 30.50         |         |       |
| 80          | 36         | 66.8 | 54.8 | 17.96         | 44.05   | 15.24 |
|             | 37         | 47.9 | 21.8 | 54.49         |         |       |
|             | 38         | 65.5 | 33   | 49.62         |         |       |
|             | 39         | 68.5 | 31.2 | 54.45         |         |       |
|             | 40         | 71.1 | 40   | 43.74         |         |       |
| 90          | 41         | 42.8 | 27.5 | 35.75         | 87.15   | 28.73 |
|             | 42         | 70.1 | 0    | 100.00        |         |       |
|             | 43         | 50.5 | 0    | 100.00        |         |       |
|             | 44         | 60.7 | 0    | 100.00        |         |       |
|             | 45         | 53.1 | 0    | 100.00        |         |       |



H6 %weight loss of corn husk cellulose films with low DS values in waste water treatment system condition

| Time (days) | Sample No. | Wi   | Wf   | % Weight loss | Average | SD    |
|-------------|------------|------|------|---------------|---------|-------|
| 10          | 1          | 45.2 | 16.9 | 62.61         | 27.03   | 22.20 |
|             | 2          | 83.4 | 68.3 | 18.11         |         |       |
|             | 3          | 59.9 | 54.1 | 9.68          |         |       |
|             | 4          | 44.7 | 40.0 | 10.51         |         |       |
|             | 5          | 58.1 | 38.2 | 34.25         |         |       |
| 20          | 6          | 84.6 | 39.8 | 52.96         | 21.07   | 18.51 |
|             | 7          | 40.0 | 34.1 | 14.75         |         |       |
|             | 8          | 58.3 | 53.6 | 8.06          |         |       |
|             | 9          | 41.9 | 33.3 | 20.53         |         |       |
|             | 10         | 71.9 | 65.4 | 9.04          |         |       |
| 30          | 11         | 40.5 | 30.2 | 25.43         | 29.80   | 8.07  |
|             | 12         | 45.5 | 33.1 | 27.25         |         |       |
|             | 13         | 70.3 | 45.8 | 34.85         |         |       |
|             | 14         | 68.9 | 40.7 | 40.93         |         |       |
|             | 15         | 56.0 | 44.5 | 20.54         |         |       |
| 40          | 16         | 42.4 | 24.2 | 42.92         | 51.26   | 23.30 |
|             | 17         | 52.8 | 40.4 | 23.48         |         |       |
|             | 18         | 59.6 | 10.1 | 83.05         |         |       |
|             | 19         | 55.4 | 18.9 | 65.88         |         |       |
|             | 20         | 54.2 | 32   | 40.96         |         |       |
| 50          | 21         | 70.0 | 55.3 | 21.00         | 64.94   | 31.25 |
|             | 22         | 61.5 | 40.8 | 33.66         |         |       |
|             | 23         | 65.4 | 0    | 100.00        |         |       |
|             | 24         | 54.4 | 17.3 | 68.20         |         |       |
|             | 25         | 58.7 | 19.5 | 66.78         |         |       |
| 60          | 26         | 56.4 | 0    | 100.00        | 100.00  | 0.00  |
|             | 27         | 55.5 | 0    | 100.00        |         |       |
|             | 28         | 61.4 | 0    | 100.00        |         |       |
|             | 29         | 61.6 | 0    | 100.00        |         |       |
|             | 30         | 63.4 | 0    | 100.00        |         |       |
| 70          | 31         | 58.2 | 0    | 100.00        | 100.00  | 0.00  |
|             | 32         | 61.2 | 0    | 100.00        |         |       |
|             | 33         | 52.7 | 0    | 100.00        |         |       |
|             | 34         | 69.8 | 0    | 100.00        |         |       |
|             | 35         | 58.3 | 0    | 100.00        |         |       |
| 80          | 36         | 50.3 | 0    | 100.00        | 100.00  | 0.00  |
|             | 37         | 48.6 | 0    | 100.00        |         |       |
|             | 38         | 59.9 | 0    | 100.00        |         |       |
|             | 39         | 51.1 | 0    | 100.00        |         |       |
|             | 40         | 63.4 | 0    | 100.00        |         |       |
| 90          | 41         | 46.9 | 0    | 100.00        | 100.00  | 0.00  |
|             | 42         | 53.3 | 0    | 100.00        |         |       |
|             | 43         | 63.7 | 0    | 100.00        |         |       |
|             | 44         | 60.1 | 0    | 100.00        |         |       |
|             | 45         | 56.7 | 0    | 100.00        |         |       |

## I : Biodegradability of Cotton Cellulose Film

I1 %weight loss of cotton cellulose films with high DS values in real composting condition

| Time (days) | Sample No. | Wi    | Wf    | % Weight loss | average | sd   |
|-------------|------------|-------|-------|---------------|---------|------|
| 10          | 1          | 98.4  | 97.7  | 0.71          | 0.79    | 0.22 |
|             | 2          | 110.7 | 110.2 | 0.45          |         |      |
|             | 3          | 95.6  | 94.7  | 0.94          |         |      |
|             | 4          | 71.9  | 71.3  | 0.83          |         |      |
|             | 5          | 100.0 | 99.0  | 1.00          |         |      |
| 20          | 6          | 142.0 | 140.9 | 0.77          | 0.99    | 0.34 |
|             | 7          | 96.6  | 95.8  | 0.83          |         |      |
|             | 8          | 53.0  | 52.2  | 1.51          |         |      |
|             | 9          | 102.7 | 102.0 | 0.68          |         |      |
|             | 10         | 43.8  | 43.3  | 1.14          |         |      |
| 30          | 11         | 98.7  | 97.9  | 0.81          | 0.85    | 0.30 |
|             | 12         | 121.7 | 120.8 | 0.74          |         |      |
|             | 13         | 66.7  | 65.9  | 1.20          |         |      |
|             | 14         | 96.1  | 95.7  | 0.42          |         |      |
|             | 15         | 93.9  | 92.9  | 1.06          |         |      |
| 40          | 16         | 70.2  | 69.5  | 1.00          | 0.84    | 0.73 |
|             | 17         | 68.6  | 68.2  | 0.58          |         |      |
|             | 18         | 87.9  | 87.6  | 0.34          |         |      |
|             | 19         | 84.3  | 84.1  | 0.24          |         |      |
|             | 20         | 64.1  | 62.8  | 2.03          |         |      |
| 50          | 21         | 105.8 | 104.5 | 1.23          | 1.03    | 0.17 |
|             | 22         | 76.1  | 75.5  | 0.79          |         |      |
|             | 23         | 82.6  | 81.7  | 1.09          |         |      |
|             | 24         | 83.2  | 82.3  | 1.08          |         |      |
|             | 25         | 94.8  | 93.9  | 0.95          |         |      |
| 60          | 26         | 84.7  | 82.9  | 2.13          | 2.77    | 0.86 |
|             | 27         | 75.5  | 72.5  | 3.97          |         |      |
|             | 28         | 103.1 | 99.6  | 3.39          |         |      |
|             | 29         | 103.4 | 101.3 | 2.03          |         |      |
|             | 30         | 119.7 | 116.9 | 2.34          |         |      |
| 70          | 31         | 82.8  | 78.6  | 5.07          | 2.30    | 1.88 |
|             | 32         | 95.8  | 94.6  | 1.25          |         |      |
|             | 33         | 67.8  | 65.5  | 3.39          |         |      |
|             | 34         | 100.2 | 99.1  | 1.10          |         |      |
|             | 35         | 89.1  | 88.5  | 0.67          |         |      |
| 80          | 36         | 89.7  | 87.6  | 2.34          | 2.26    | 0.38 |
|             | 37         | 77.2  | 75.3  | 2.46          |         |      |
|             | 38         | 87.8  | 85.9  | 2.16          |         |      |
|             | 39         | 126.6 | 124.5 | 1.66          |         |      |
|             | 40         | 109.4 | 106.5 | 2.65          |         |      |
| 90          | 41         | 119.8 | 116.1 | 3.09          | 2.18    | 0.99 |
|             | 42         | 89.0  | 87.2  | 2.02          |         |      |
|             | 43         | 98.3  | 97.4  | 0.92          |         |      |
|             | 44         | 85.9  | 83.1  | 3.26          |         |      |
|             | 45         | 135.1 | 132.9 | 1.63          |         |      |

## 12 %weight loss of cotton cellulose films with medium DS values in real composting condition

| Time (days) | Sample No. | Wi    | Wf    | % Weight loss | average | sd    |
|-------------|------------|-------|-------|---------------|---------|-------|
| 10          | 1          | 108.6 | 107.0 | 1.47          | 1.42    | 0.21  |
|             | 2          | 109.2 | 107.3 | 1.74          |         |       |
|             | 3          | 156.8 | 154.7 | 1.34          |         |       |
|             | 4          | 120.5 | 119.1 | 1.16          |         |       |
|             | 5          | 72.6  | 71.6  | 1.38          |         |       |
| 20          | 6          | 90.2  | 89.6  | 0.67          | 1.75    | 1.05  |
|             | 7          | 65.2  | 64.4  | 1.23          |         |       |
|             | 8          | 88.9  | 87.6  | 1.46          |         |       |
|             | 9          | 61.3  | 59.2  | 3.43          |         |       |
|             | 10         | 51.2  | 50.2  | 1.95          |         |       |
| 30          | 11         | 77.2  | 75.5  | 2.20          | 1.42    | 0.52  |
|             | 12         | 75.3  | 74.3  | 1.33          |         |       |
|             | 13         | 55.5  | 54.6  | 1.62          |         |       |
|             | 14         | 92.3  | 91.5  | 0.87          |         |       |
|             | 15         | 147.6 | 146.0 | 1.08          |         |       |
| 40          | 16         | 142.4 | 142   | 0.28          | 0.83    | 1.09  |
|             | 17         | 86.3  | 86.1  | 0.23          |         |       |
|             | 18         | 83.9  | 83.6  | 0.36          |         |       |
|             | 19         | 111.7 | 108.6 | 2.78          |         |       |
|             | 20         | 77.7  | 77.3  | 0.51          |         |       |
| 50          | 21         | 69.3  | 67.9  | 2.02          | 3.69    | 4.07  |
|             | 22         | 159.4 | 156.2 | 2.01          |         |       |
|             | 23         | 61.8  | 60.6  | 1.94          |         |       |
|             | 24         | 66.6  | 59.3  | 10.96         |         |       |
|             | 25         | 138.0 | 135.9 | 1.52          |         |       |
| 60          | 26         | 63.2  | 62    | 1.90          | 8.99    | 10.77 |
|             | 27         | 101.4 | 98.1  | 3.25          |         |       |
|             | 28         | 69.8  | 61.6  | 11.75         |         |       |
|             | 29         | 40.4  | 29.6  | 26.73         |         |       |
|             | 30         | 90.8  | 89.6  | 1.32          |         |       |
| 70          | 31         | 85.3  | 83.1  | 2.58          | 6.52    | 7.13  |
|             | 32         | 83.9  | 67.9  | 19.07         |         |       |
|             | 33         | 80.6  | 78.9  | 2.11          |         |       |
|             | 34         | 60.4  | 57.1  | 5.46          |         |       |
|             | 35         | 56.6  | 54.7  | 3.36          |         |       |
| 80          | 36         | 63.4  | 48.6  | 23.34         | 11.43   | 9.37  |
|             | 37         | 85.8  | 83.9  | 2.21          |         |       |
|             | 38         | 63.3  | 55    | 13.11         |         |       |
|             | 39         | 96.3  | 94.6  | 1.77          |         |       |
|             | 40         | 82.6  | 68.8  | 16.71         |         |       |
| 90          | 41         | 68.2  | 69.3  | -1.61         | 12.27   | 24.05 |
|             | 42         | 66.7  | 30.0  | 55.02         |         |       |
|             | 43         | 80.5  | 80.0  | 0.62          |         |       |
|             | 44         | 86.3  | 85.0  | 1.51          |         |       |
|             | 45         | 58.7  | 55.3  | 5.79          |         |       |

## 13 %weight loss of cotton cellulose films with low DS values in real composting condition

| Time (days) | No. | Wi    | Wf   | % Weight loss | average | sd    |
|-------------|-----|-------|------|---------------|---------|-------|
| 10          | 1   | 82.4  | 74.6 | 9.47          | 9.54    | 2.31  |
|             | 2   | 72.5  | 65.1 | 10.21         |         |       |
|             | 3   | 67.7  | 58.9 | 13.00         |         |       |
|             | 4   | 75.3  | 70.1 | 6.91          |         |       |
|             | 5   | 75.3  | 69.2 | 8.10          |         |       |
| 20          | 6   | 81.1  | 74.3 | 8.38          | 7.70    | 0.55  |
|             | 7   | 49.8  | 45.9 | 7.83          |         |       |
|             | 8   | 85.5  | 78.8 | 7.84          |         |       |
|             | 9   | 48.8  | 45.1 | 7.58          |         |       |
|             | 10  | 62.5  | 58.2 | 6.88          |         |       |
| 30          | 11  | 50.2  | 46.0 | 8.37          | 8.28    | 0.78  |
|             | 12  | 83.4  | 77.0 | 7.67          |         |       |
|             | 13  | 87.0  | 78.7 | 9.54          |         |       |
|             | 14  | 79.1  | 73.1 | 7.59          |         |       |
|             | 15  | 100.7 | 92.4 | 8.24          |         |       |
| 40          | 16  | 50.8  | 46.2 | 9.06          | 12.83   | 5.62  |
|             | 17  | 91.8  | 85.4 | 6.97          |         |       |
|             | 18  | 95.0  | 77.0 | 18.95         |         |       |
|             | 19  | 67.9  | 60.8 | 10.46         |         |       |
|             | 20  | 57.2  | 46.5 | 18.71         |         |       |
| 50          | 21  | 95.0  | 84.2 | 11.37         | 12.78   | 5.20  |
|             | 22  | 31.1  | 24.7 | 20.58         |         |       |
|             | 23  | 60.8  | 55.3 | 9.05          |         |       |
|             | 24  | 74.4  | 63.1 | 15.19         |         |       |
|             | 25  | 84.2  | 77.7 | 7.72          |         |       |
| 60          | 26  | 89.5  | 81.5 | 8.94          | 16.18   | 14.17 |
|             | 27  | 81.4  | 47.8 | 41.28         |         |       |
|             | 28  | 73.9  | 64   | 13.40         |         |       |
|             | 29  | 70.1  | 64.2 | 8.42          |         |       |
|             | 30  | 81.1  | 73.9 | 8.88          |         |       |
| 70          | 31  | 56.3  | 46.6 | 17.23         | 20.32   | 13.28 |
|             | 32  | 53.3  | 45.9 | 13.88         |         |       |
|             | 33  | 82.3  | 74.2 | 9.84          |         |       |
|             | 34  | 78.0  | 64.6 | 17.18         |         |       |
|             | 35  | 70.2  | 39.7 | 43.45         |         |       |
| 80          | 36  | 92.6  | 74.8 | 19.22         | 15.19   | 3.75  |
|             | 37  | 72.8  | 63.3 | 13.05         |         |       |
|             | 38  | 111.8 | 100  | 10.55         |         |       |
|             | 39  | 96.8  | 78.6 | 18.80         |         |       |
|             | 40  | 58.7  | 50.3 | 14.31         |         |       |
| 90          | 41  | 84.9  | 55.4 | 34.75         | 24.55   | 19.75 |
|             | 42  | 62.0  | 29   | 53.23         |         |       |
|             | 43  | 90.7  | 73.9 | 18.52         |         |       |
|             | 44  | 94.6  | 81.8 | 13.53         |         |       |
|             | 45  | 80.8  | 78.6 | 2.72          |         |       |

14 %weight loss of cotton cellulose films with high DS values in waste water treatment system condition

| Time (days) | No. | Wi    | Wf    | % Weight loss | Average | SD    |
|-------------|-----|-------|-------|---------------|---------|-------|
| 10          | 1   | 82.4  | 77.8  | 5.58          | 3.28    | 3.38  |
|             | 2   | 106.1 | 97.5  | 8.11          |         |       |
|             | 3   | 133.7 | 132.4 | 0.97          |         |       |
|             | 4   | 137.8 | 136.9 | 0.65          |         |       |
|             | 5   | 111.1 | 109.9 | 1.08          |         |       |
| 20          | 6   | 97.6  | 90.6  | 7.17          | 2.77    | 2.98  |
|             | 7   | -     | -     | -             |         |       |
|             | 8   | 134.7 | 133.5 | 0.89          |         |       |
|             | 9   | 132.7 | 131.4 | 0.98          |         |       |
|             | 10  | 97.3  | 95.3  | 2.06          |         |       |
| 30          | 11  | 97.9  | 95.4  | 2.55          | 1.91    | 0.53  |
|             | 12  | 120.0 | 118.3 | 1.42          |         |       |
|             | 13  | 102.1 | 100.6 | 1.47          |         |       |
|             | 14  | 117.2 | 114.4 | 2.39          |         |       |
|             | 15  | 110.2 | 108.3 | 1.72          |         |       |
| 40          | 16  | 101.2 | 101.2 | 0.00          | 4.61    | 2.22  |
|             | 17  | 108.8 | 107.1 | 1.56          |         |       |
|             | 18  | 95.8  | 89.2  | 6.89          |         |       |
|             | 19  | 94.4  | 89.8  | 4.87          |         |       |
|             | 20  | 99.5  | 94.4  | 5.13          |         |       |
| 50          | 21  | 83.5  | 81.7  | 2.16          | 6.38    | 7.44  |
|             | 22  | 97.0  | 92.8  | 4.33          |         |       |
|             | 23  | 138.6 | 135.7 | 2.09          |         |       |
|             | 24  | 146.7 | 144.2 | 1.70          |         |       |
|             | 25  | 89.6  | 74.0  | 17.41         |         |       |
| 60          | 26  | 106.2 | 103.0 | 3.01          | 5.16    | 4.92  |
|             | 27  | 110.9 | 108.2 | 2.43          |         |       |
|             | 28  | 85.7  | 80.8  | 5.72          |         |       |
|             | 29  | 87.7  | 75.9  | 13.45         |         |       |
|             | 30  | 100.8 | 99.6  | 1.19          |         |       |
| 70          | 31  | 81.3  | 59.5  | 26.81         | 12.42   | 10.30 |
|             | 32  | 106.7 | 104.1 | 2.44          |         |       |
|             | 33  | 95.4  | 93.0  | 2.52          |         |       |
|             | 34  | 119.2 | 99.3  | 16.69         |         |       |
|             | 35  | 76.3  | 65.9  | 13.63         |         |       |
| 80          | 36  | 126.6 | 113.2 | 10.58         | 13.16   | 6.41  |
|             | 37  | 102.5 | 85.0  | 17.07         |         |       |
|             | 38  | 97.1  | 88.0  | 9.37          |         |       |
|             | 39  | 75.8  | 58.9  | 22.30         |         |       |
|             | 40  | 120.5 | 112.7 | 6.47          |         |       |
| 90          | 41  | 116.5 | 84.6  | 27.38         | 13.71   | 10.29 |
|             | 42  | 117.3 | 92.4  | 21.23         |         |       |
|             | 43  | 128.6 | 114.3 | 11.12         |         |       |
|             | 44  | 108.3 | 104.1 | 3.88          |         |       |
|             | 45  | 136.9 | 130.1 | 4.97          |         |       |

15 %weight loss of cotton cellulose films with medium DS values in waste water treatment system condition

| Time (days) | No. | Wi    | Wf    | % Weight loss | Average | SD    |
|-------------|-----|-------|-------|---------------|---------|-------|
| 10          | 1   | 82.1  | 75.3  | 8.28          | 7.59    | 6.91  |
|             | 2   | 59.4  | 48.1  | 19.02         |         |       |
|             | 3   | 81.9  | 77.4  | 5.49          |         |       |
|             | 4   | 90.7  | 89.8  | 0.99          |         |       |
|             | 5   | 115.7 | 110.9 | 4.15          |         |       |
| 20          | 6   | 78.5  | 61.1  | 22.17         | 7.06    | 9.23  |
|             | 7   | 88.7  | 87.8  | 1.01          |         |       |
|             | 8   | 92.1  | 91.1  | 1.09          |         |       |
|             | 9   | 99.8  | 98.5  | 1.30          |         |       |
|             | 10  | 84.4  | 76.2  | 9.72          |         |       |
| 30          | 11  | 92.0  | 90.5  | 1.63          | 9.68    | 12.24 |
|             | 12  | 53.6  | 37.2  | 30.60         |         |       |
|             | 13  | 110.4 | 107.1 | 2.99          |         |       |
|             | 14  | 103.3 | 100.7 | 2.52          |         |       |
|             | 15  | 88.9  | 79.4  | 10.69         |         |       |
| 40          | 16  | 84.7  | 84.7  | 0.00          | 14.39   | 15.81 |
|             | 17  | 84.0  | 78.8  | 6.19          |         |       |
|             | 18  | 84.2  | 79.5  | 5.58          |         |       |
|             | 19  | 90.1  | 55.8  | 38.07         |         |       |
|             | 20  | 118.2 | 109.1 | 7.70          |         |       |
| 50          | 21  | 78.0  | 66.1  | 15.26         | 13.25   | 2.21  |
|             | 22  | 84.2  | 71.5  | 15.08         |         |       |
|             | 23  | 101.0 | 89.1  | 11.78         |         |       |
|             | 24  | 137.7 | 122.7 | 10.89         |         |       |
|             | 25  | -     | -     | -             |         |       |
| 60          | 26  | 104.2 | 92.4  | 11.32         | 14.70   | 4.35  |
|             | 27  | 65.6  | 51.9  | 20.88         |         |       |
|             | 28  | 98.6  | 83.8  | 15.01         |         |       |
|             | 29  | 59.6  | 53.7  | 9.90          |         |       |
|             | 30  | 76.9  | 64.3  | 16.38         |         |       |
| 70          | 31  | 72.5  | 52.3  | 27.86         | 22.11   | 11.09 |
|             | 32  | 61.1  | 42.6  | 30.28         |         |       |
|             | 33  | 86.2  | 58.5  | 32.13         |         |       |
|             | 34  | 84.4  | 77.1  | 8.65          |         |       |
|             | 35  | 77.5  | 68.5  | 11.61         |         |       |
| 80          | 36  | 93.9  | 75.8  | 19.28         | 19.02   | 7.14  |
|             | 37  | 104.2 | 89.2  | 14.40         |         |       |
|             | 38  | 61.0  | 43.3  | 29.02         |         |       |
|             | 39  | -     | -     | -             |         |       |
|             | 40  | 92.5  | 80.1  | 13.41         |         |       |
| 90          | 41  | 160.0 | 155.9 | 2.56          | 19.66   | 12.28 |
|             | 42  | 91.7  | 76.3  | 16.79         |         |       |
|             | 43  | 67.8  | 44    | 35.10         |         |       |
|             | 44  | 85.5  | 62.3  | 27.13         |         |       |
|             | 45  | 89.8  | 74.8  | 16.70         |         |       |

16 %weight loss of cotton cellulose films with low DS values in waste water treatment system condition

| Time (days) | No. | Wi    | Wf   | % Weight loss | Average | SD    |
|-------------|-----|-------|------|---------------|---------|-------|
| 10          | 1   | 65.3  | 26.9 | 58.81         | 25.90   | 23.27 |
|             | 2   | 83.2  | 74.2 | 10.82         |         |       |
|             | 3   | 59.4  | 55.1 | 7.24          |         |       |
|             | 4   | 66.3  | 59.4 | 10.41         |         |       |
|             | 5   | 95.4  | 55.1 | 42.24         |         |       |
| 20          | 6   | 56.8  | 31.1 | 45.25         | 26.02   | 11.96 |
|             | 7   | 96.0  | 81.6 | 15.00         |         |       |
|             | 8   | 55.5  | 43.3 | 21.98         |         |       |
|             | 9   | 72.8  | 51.5 | 29.26         |         |       |
|             | 10  | 74.1  | 60.3 | 18.62         |         |       |
| 30          | 11  | 95.8  | 86.0 | 10.23         | 26.95   | 26.78 |
|             | 12  | 85.2  | 72.5 | 14.91         |         |       |
|             | 13  | 61.3  | 44.0 | 28.22         |         |       |
|             | 14  | 68.1  | 18.5 | 72.83         |         |       |
|             | 15  | 57.1  | 52.2 | 8.58          |         |       |
| 40          | 16  | 58.2  | 13.6 | 76.63         | 56.84   | 23.40 |
|             | 17  | 63.7  | 34.2 | 46.31         |         |       |
|             | 18  | 64.7  | 46.6 | 27.98         |         |       |
|             | 19  | 75.2  | 11.4 | 84.84         |         |       |
|             | 20  | 69.8  | 36   | 48.42         |         |       |
| 50          | 21  | 71.5  | 14.7 | 79.44         | 46.58   | 27.09 |
|             | 22  | 66.8  | 19.4 | 70.96         |         |       |
|             | 23  | 90.2  | 62.8 | 30.38         |         |       |
|             | 24  | 97.0  | 80.3 | 17.22         |         |       |
|             | 25  | 100.5 | 65.4 | 34.93         |         |       |
| 60          | 26  | 63.1  | 0    | 100.00        | 84.23   | 14.65 |
|             | 27  | 88.5  | 27.2 | 69.27         |         |       |
|             | 28  | 70.1  | 0    | 100.00        |         |       |
|             | 29  | 63.6  | 15.2 | 76.10         |         |       |
|             | 30  | 69.4  | 16.8 | 75.79         |         |       |
| 70          | 31  | 97.0  | 53.3 | 45.05         | 70.34   | 33.26 |
|             | 32  | 74.8  | 56.1 | 25.00         |         |       |
|             | 33  | 49.8  | 3.5  | 92.97         |         |       |
|             | 34  | 47.2  | 0    | 100.00        |         |       |
|             | 35  | 54.8  | 6.2  | 88.69         |         |       |
| 80          | 36  | 37.2  | 3.6  | 90.32         | 69.00   | 22.20 |
|             | 37  | 72.3  | 4.4  | 93.91         |         |       |
|             | 38  | 100.0 | 35.5 | 64.50         |         |       |
|             | 39  | 94.5  | 47.6 | 49.63         |         |       |
|             | 40  | 92.0  | 49.1 | 46.63         |         |       |
| 90          | 41  | 74.2  | 0    | 100.00        | 100.00  | 0.00  |
|             | 42  | 110.3 | 0    | 100.00        |         |       |
|             | 43  | 62.1  | 0    | 100.00        |         |       |
|             | 44  | 63.4  | 0    | 100.00        |         |       |
|             | 45  | 55.6  | 0    | 100.00        |         |       |

## J : Biodegradability in Enzymatic Degradation

%weight loss of pineapple Leaf, corn husk, and cotton cellulose films in enzymatic degradation with different DS values

| Time | Sample      | Wi    | Wf    | % WL  |
|------|-------------|-------|-------|-------|
| 5    | COTTON H-DS | 146.4 | 143.2 | 2.19  |
|      | COTTON M-DS | 78.9  | 75.7  | 4.06  |
|      | COTTON L-DS | 82.7  | 77.8  | 5.93  |
|      | PINE H-DS   | 82.1  | 81.3  | 0.97  |
|      | PINE M-DS   | 75.8  | 74.1  | 2.24  |
|      | PINE L-DS   | 58.6  | 56.2  | 4.10  |
|      | CORN H-DS   | 42.5  | 40.9  | 3.76  |
|      | CORN M-DS   | 61.8  | 59.7  | 3.40  |
|      | CORN L-DS   | 72.2  | 69.1  | 4.29  |
| 10   | COTTON H-DS | 81.1  | 79.2  | 2.34  |
|      | COTTON M-DS | 78.1  | 74.2  | 4.99  |
|      | COTTON L-DS | 70.1  | 66.2  | 5.56  |
|      | PINE H-DS   | 74.9  | 73.9  | 1.34  |
|      | PINE M-DS   | 73.4  | 71.9  | 2.04  |
|      | PINE L-DS   | 70.6  | 68.6  | 2.83  |
|      | CORN H-DS   | 62.6  | 61    | 2.56  |
|      | CORN M-DS   | 66.8  | 64.6  | 3.29  |
|      | CORN L-DS   | 60.2  | 57.5  | 4.49  |
| 15   | COTTON H-DS | 110.1 | 107.1 | 2.72  |
|      | COTTON M-DS | 67.5  | 65    | 3.70  |
|      | COTTON L-DS | 84.7  | 80.6  | 4.84  |
|      | PINE H-DS   | 63.9  | 61.8  | 3.29  |
|      | PINE M-DS   | 60.8  | 58.4  | 3.95  |
|      | PINE L-DS   | 47.6  | 44.8  | 5.88  |
|      | CORN H-DS   | 58.7  | 57.5  | 2.04  |
|      | CORN M-DS   | 62.4  | 61.1  | 2.08  |
|      | CORN L-DS   | 51.1  | 48.4  | 5.28  |
| 20   | COTTON H-DS | 119.6 | 116.6 | 2.51  |
|      | COTTON M-DS | 115.3 | 109.7 | 4.86  |
|      | COTTON L-DS | 72.2  | 67.4  | 6.65  |
|      | PINE H-DS   | 52.3  | 51    | 2.49  |
|      | PINE M-DS   | 69.4  | 67.3  | 3.03  |
|      | PINE L-DS   | 68.2  | 62.9  | 7.77  |
|      | CORN H-DS   | 67.9  | 65.5  | 3.53  |
|      | CORN M-DS   | 60.3  | 53.5  | 11.28 |
|      | CORN L-DS   | 61.6  | 53.0  | 13.96 |



## Biography

Miss Jittiporn Saeng-on was born in Suratthani, Thailand on October 18, 1984. She received her Bachelor's Degree of Science in Polymer Science from Faculty of Science, Prince of Songkla University in 2007. After that, she started as a graduate student in Department of Materials Science, with Master Degree in the field of Applied Polymer Science and Textile Technology at Chulalongkorn University in June 2007, and graduated in October 2009.