ผลของพลาสติไซเซอร์ต่อสมบัติทางกายภาพและสมบัติเชิงกลของฟิล์มเซลลูโลสดัดแปรจากเศษผ้าฝ้าย

นางสาว พนิตา หงษ์พฤกษ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาวิทยาศาสตร์พอลิเมอร์ประยุกต์และเทคโนโลยีสิ่งทอ ภาควิชาวัสดุศาสตร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2552

EFFECTS OF PLASTICIZERS ON PHYSICAL AND MECHANICAL PROPERTIES OF MODIFIED CELLULOSE FILMS FROM WASTE COTTON FABRICS

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Applied Polymer Science and Textile Technology
Department of Materials Science
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Chulalongkorn University
Academic Year 2009

ThesisTitle	EFFECTS OF PLASTICIZERS ON PHYSICAL AND MECHANICAL PROPERTIES OF MODIFIED CELLULOSE FILMS FROM WASTE COTTON FABRICS
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Field of Study	Applied Polymer Science and Textile Technology
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ACKNOWLEDGEMENTS

This research work was carried out at the Laboratory of the Department of Matereials Science, Faculty of Science, Chulalongkorn University, Thailand, from the year 2007 to 2009.

First, I would like to thank my advisor, Associate Professor Dr. Duangdao Aht-Ong, for her encouragement, valuable comments, reading and suggesting during this research, and for everything including her kindness. Working with her has been the best course of my study.

I want to acknowledge Assistant Professor Dr. Sirithan Jiemsililers, Associate Professor Paiparn Santisuk, Associate Professor Dr. Pranut Potiyaraj, and Associate Professor Dr. Kawee Srikulkit and for reviewing the thesis, motivating comments, and participating as thesis committee members.

I gratefully acknowledge the financial support and scholarship from Research Unit of Advanced Ceramic and Polymeric Materials, National Center of Excellence for Petroleum, Petrochemicals and Advanced Materials, Chulalongkorn University, Bangkok, Thailand and the research funding from the National Metal and Materials Technology center, National Science and Techpnology Development Agency, through the research grant No. MT- B- 51- POL- 09- 406- G.

Appreciation is also extended to the staffs at Mettler Toledo (Thailand) Co, Ltd., for their help with DSC experiment.

I also thank to all my friends at the Department of Materials Science who have been encouraging and helping me while I was studying at Chulalongkorn University.

Last but definitely not least, my deepest gratitude goes to my family who always standing by me regardless of what happened, supporting me, believing in me and encouraging me

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ABBREVIATIONS

DS	:	Degree of substitution
WI	:	Weight increase
XRD	:	X-Ray diffractometer
SEM	:	Scanning electron microscope
CH	:	Conventional heating
MH	:	Microwave heating
TEC	:	Triethyl citrate
DBP	:	Dibutyl phthalate
ESO	:	Epoxidized soybean oil

CHAPTER I

INTRODUCTION

Plastic is an important material widely used in daily life because it is light, easy to store and transport, comes in an endless variety of textures and shapes, and can hold almost anything. Those properties make it attractive to manufacturers and packagers. The current global consumption of plastic is more than 200 million tones in 2008; with an annual growth of approximately 5% [1, 2]. The accumulation of plastics in the environment is a matter of great concern leading to long-term environmental problem. Plastics are durable and degraded very slowly; the molecular bonds that make plastic so durable make it equally resistant to natural processes of degradation. They are not non-totally recyclable and/or biodegradable so they posses serious ecological problems. Environmental concerns associated with the handling of plastic waste have emphasized the importance of developing biodegradable polymers, which could degrade in nature after their use, to alleviate the plastic waste disposal problem. However, biodegradable polymers are not widely used because of the limitations in price. In addition, their properties may vary with the source of origin and the time of harvest. Besides, they are sensitive to heat and water. The biodegradable polymers may absorb considerable quantities of water, which can affect on their properties.

Cellulose is one of the interesting biodegradable materials. It is available in large quantities, cheap, and has great potential as an excellent industrial material. Moreover, cellulose can be recycled and is in itself a renewable resource. Nevertheless, cellulose consists of a lot of hydroxyl groups which can form intra-and intermolecular hydrogen bonds; as a result, it has high crystallinity and is difficult to be dissolved in common organic solvents. In addition, cellulose is not a thermoplastic material and is usually decomposed before melting [3]. The properties and processability of cellulose can be improved by both chemical and physical modification methods by using internal plasticizer (i.e., via esterification reaction of long chain fatty acid chloride) and external plasticizer, respectively. Typical chemical modifications of cellulose are the etherification and esterification reactions of the individual hydroxyl groups.

Usually, the chemical reaction of cellulose is performed under conventional heating, which can take quite a long time as 24 hr. Microwave irradiation is another interesting heating source. The development of microwave-assisted chemistry such as synthesis, catalysis, analytical chemistry, etc., has been intensively studied during the last decade [17, 18, and 38]. In particular, there is an increasing interest in the use of microwave irradiation to speed up chemical reaction. It has been showing that microwave irradiation can decrease the reaction time from several hours to one minute [17].

Our previous work regarding the esterification of cellulose with long chain acyl chloride in homogeneous media under conventional heating and microwave irradiation has found that the properties of cellulose ester could be enhanced by increasing the size of substituent and were also dependent upon the heating sources. The mechanical properties of the cellulose ester films prepared from the esterfied-cellulose under microwave irradiation were less ductile and more brittle than their counterparts. In order to overcome this problem, these plastic films should be plasticized.

Plasticizers are normally added to a polymeric matrix in order to overcome the film brittleness. The plasticizer is able to decrease the glass transition temperature and the melt viscosity of a polymer by increasing the free volume between polymer chains. It is usually incorporated into films for various reasons such as to reduce brittleness, impart flexibility, and also to improve processability [24]. A number of plasticizers such as triethyl citrate (TEC), dibutyl phthalate (DBP), and epoxidized soybean oil (ESO) have been investigated to be used with biodegradable polymers. Plasticization has important effects on the relationship between temperature and mechanical properties. The plasticizing efficiency of triethyl citrate (TEC), dibutyl phthalate (DBP), soybean oil (SO), and epoxidized soybean oil (ESO) as biodegradable plasticizers for poly 3-hydroxybutyrate-*co*-3-hydroxyvalerate (PHBV) were studied [28]. The result shown that TEC and DBP were more effective in depression of the glass transition temperature as well as in increasing the elongation at break and the impact strength of PHBV films than soybean oil (SO) and epoxidized soybean oil (ESO).

Therefore, the aim of this work was to investigate the effects of plasticizers on physical and mechanical properties of cellulose laurate films. Cellulose laurate was synthesized by using waste cotton fabrics and lauroyl chloride via esterification reaction under optimum conditions of microwave energy and conventional heating methods. Three types of plasticizer, triethyl citrate (TEC), dibutyl phthalate (DBP), and epoxidized soybean oil (ESO), were used as additives at a concentration of 3%, 5%, 7%, and 9%w/w of dry cellulose laurate. From literature, phthalate plasticizers are the most commonly used plasticizers in commercial cellulose acetate, whereas citrate and derivatized vegetable oil plasticizers were selected because they originate from a renewable resource and therefore are biodegradable. Furthermore, citrate was also used as a plasticizer for cellulose derivative, which has been extensively studied in medical and pharmaceutical coatings.

After modification, the plasticized cellulose laurate film was processed by solution casting. The properties of cellulose laurate powder were characterized in terms of chemical structure, morphology, and thermal properties. The effects of plasticizers on the physical, thermal, mechanical, and degradable properties of plasticized cellulose laurate film were evaluated. The influence of heating methods (i.e., conventional heating vs. microwave heating) on the properties of plasticized cellulose laurate films was also compared.

CHAPTER II

LITERATURE SURVEY

2.1 Biodegradable plastic and Definitions

The term “biodegradable plastics” normally refers to an attack by microorganisms on nonwater-soluble polymer-based materials (plastics). This implies that the biodegradation of plastics 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. 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.

Although the enzyme-catalyzed chain length reduction of polymers is in many cases the primary process of biodegradation, nonbiotic chemical and physical processes can also act on the polymer, either in parallel or as a first stage solely on the polymer. These nonbiotic effects include chemical hydrolysis, thermal polymer degradation, and oxidation or scission of the polymer chains by irradiation (photodegradation). For some materials, these effects are used directly to induce the biodegradation process [e.g., poly (lactic acid); pro-oxidant modified polyethylene], but they must also to be taken into account when biodegradation is caused predominantly by extracellular enzymes. Because of the coexistence of biotic and nonbiotic processes, the entire mechanism of polymer degradation could -in many cases- also be referred to as environmental degradation.

Environmental factors 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 plastics is tested.

Another complicating factor in plastics biodegradation is the complexity of the plastic materials with regard to their possible structures and compositions. In many cases plastics 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 present (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 predominantly to control the degradation behavior of many polymers. Additionally, the crystallinity and crystal morphology is dependent upon the processing conditions, and can change with time.

All of the above-described factors must be considered when measuring the biodegradation of plastics and interpreting the results and this makes the testing of plastics biodegradability a highly interdisciplinary process. The standardized evaluation of biodegradable plastics should always be based on definitions, and what biodegradation with regard to plastics actually means. Several different definitions have been published by national and international standardization bodies and organizations **(Table 2.1).**

Whilst in the ISO definition of biodegradable plastics only a chemical change of the material (e.g., oxidation) by microorganisms is requested, the CEN and DIN, in contrast, demand in their definitions the conversion of plastics into microbial metabolic products. Other definitions such as inherent biodegradability or ultimate biodegradability are adapted from the area of degradation of low molecular- weight chemicals, but these can also be applied to polymers. Generally, the definitions do not specify any environment or time frames; this must be carried out according to corresponding standards [4].

Table 2.1 Definitions used in correlation with biodegradable plastics

DIN FNK 103.2	Biodegradable plastics[1)] A plastic material is called biodegradable if all its organic compounds undergo a complete biodegradation process. Environmental conditions and rates of biodegradation are to be determined by standardized test methods. Biodegradation[3)] Biodegradation is a process, caused by biological activity, which leads under change of the chemical structure to naturally occurring metabolic products.
ASTM sub-committee D20-96	Biodegradable plastics[1)] A degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae.
Japanese Biodegradable Plastics Society	Biodegradable plastics[1)] Polymeric materials which are changed into lower molecular weight compounds where at least one step in the degradation process is though metabolism in the presence of naturally occurring organisms.

ISO 472	Biodegradable plastics[1] A plastic designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the plastic and the application in a period of time that determines its classification. The change in the chemical structure results from the action of naturally occurring microorganisms.
CEN	Biodegradable plastics[1] A degradable material in which the degradation results from the action of microorganisms and ultimately the material is converted to water, carbon dioxide and/or methane and a new cell biomass. Biodegradation[2] Biodegradation is a degradation caused by biological activity, especially by enzymatic action, leading to a significant change in the chemical structure of a material Inherent biodegradability[2] The potential of a material to be biodegraded, established under laboratory conditions. Ultimate biodegradability[2] The breakdown of an organic chemical compound by microorganisms in the presence of oxygen to biodegradability carbon dioxide, water and mineral salts of any other elements present (mineralization) and new biomass or in the absence of oxygen to carbon dioxide, methane, mineral salts and new biomass.

[1] Pagga (1998); [2] Calmon-Decriaud et al. (1998); [3] DIN V 94900 (1998)

2.1.1 Biodegradation of polymer [34]

Microorganisms such as bacteria and fungi are involved in the degradation of both natural and synthetic plastics. The biodegradation of plastics proceeds actively under different soil conditions according to their properties, because the microorganisms responsible for the degradation differ from each other and they have their own optimal growth conditions in the soil. Polymers especially plastics are potential substrates for heterotrophic microorganisms.

Biodegradation is governed by different factors that include polymer characteristics, type of microorganisms, and nature of pretreatment. The polymer characteristics such as its mobility, tacticity, crystallinity, molecular weight, the type of functional groups and substituents present in its structure, and plasticizers or additives added to the polymer all play an important role in its degradation.

During degradation the polymer is first converted to its monomers, then these monomers are mineralized. Most polymers are too large to pass through cellular membranes, so they must first be depolymerized to smaller monomers before they can be absorbed and biodegraded within microbial cells. The initial breakdown of a polymer can result from a variety of physical and biological forces. Physical forces, such as heating/cooling, freezing/thawing, or wetting/drying, can cause mechanical damage such as the cracking of polymeric materials. The growth of many fungi can also cause small-scale swelling and bursting, as the fungi penetrate the polymer solids. Synthetic polymers, such as poly (caprolactone), are also depolymerized by microbial enzymes, after which the monomers are absorbed into microbial cells and biodegraded. Abiotic hydrolysis is the most important reaction for initiating the environmental degradation of synthetic polymer like polycarboxylates, poly(ethylene terephthalate), polylactic acids and their copolymers, poly (α-glutamic acids), and polydimethylsiloxanes or silicones.

Generally, an increase in molecular weight results in a decline of polymer degradability by microorganisms. In contrast, monomers, dimers, and oligomers of a polymer's repeating units are much easily degraded and mineralized. High molecular weights result in a sharp decrease in solubility making them unfavorable for microbial attack because bacteria require the substrate to be assimilated through the cellular membrane and then further degraded by cellular enzymes. At least two categories of enzymes are actively involved in biological degradation of polymers extracellular and intracellular depolymerases. During degradation, exoenzymes from microorganisms break down complex polymers yielding smaller molecules of short chains, e.g., oligomers, dimers, and monomers, that are smaller enough to pass the semi-permeable outer bacterial membranes, and then to be utilized as carbon and energy sources. The process is called depolymerization. When the end products are CO_2, H_2O, or CH_4, the degradation is called mineralization. It is important to note that biodeterioration and degradation of polymer substrate can rarely reach 100% and the reason is that a small portion of the polymer will be incorporated into microbial biomass, humus and other natural products. Dominant groups of microorganisms and the degradative pathways associated with polymer degradation are often determined by the environmental conditions. When O_2 is available, aerobic microorganisms are mostly responsible for destruction of complex materials, with microbial biomass, CO_2, and H_2O as the final products as shown in **Figure 2.1.** In contrast, under anoxic conditions, anaerobic consortia of microorganisms are responsible for polymer deterioration. The primary products will be microbial biomass, CO_2, CH_4 and H_2O under methanogenic (anaerobic) conditions (e.g. landfills/ compost).

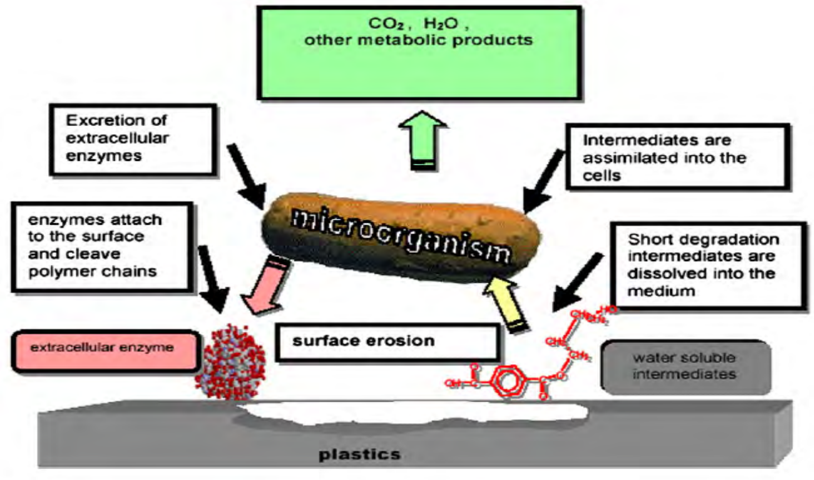


Figure 2.1 General mechanism of plastic biodegradation under aerobic conditions [34]

2.1.2 Biodegradable polymers from renewable resources

Biodegradable polymers from renewable resources have attracted much attention in recent years. Renewable sources of polymeric materials offer an alternative to maintaining sustainable development of economically and ecologically attractive technology. The innovations in the development of materials from biodegradable polymers, the preservation of fossil-based raw materials, complete biological degradability, the reduction in the volume of garbage and compostability in the natural cycle, protection of the climate through the reduction of carbon dioxide released, as well as the application possibilities of agriculture resources for the production of green materials are some of the reasons why such materials have attracted the academic and industrial interest [5].

Renewable sources-based biodegradable polymers may be divided into three main categories based on their origin and production [6]. The origin of different biologically based materials is outlined in **Figure 2.2.**

Category 1: Polymers directly extracted/removed from biomass. Examples are polysaccharides such as starch and cellulose and proteins like casein and gluten.

Category 2: Polymers produced by classical chemical synthesis using renewable biobased monomers. A good example is polylactic acid, a biopolyester polymerized from lactic acid monomers. The monomers themselves may be produced via fermentation of carbohydrate feedstock.

Category 3: Polymers produced by microorganisms or genetically modified bacteria. To date, this group of biobased polymers consists mainly of the polyhydroxyalkonoates , but developments with, for example, bacterial cellulose are in progress.

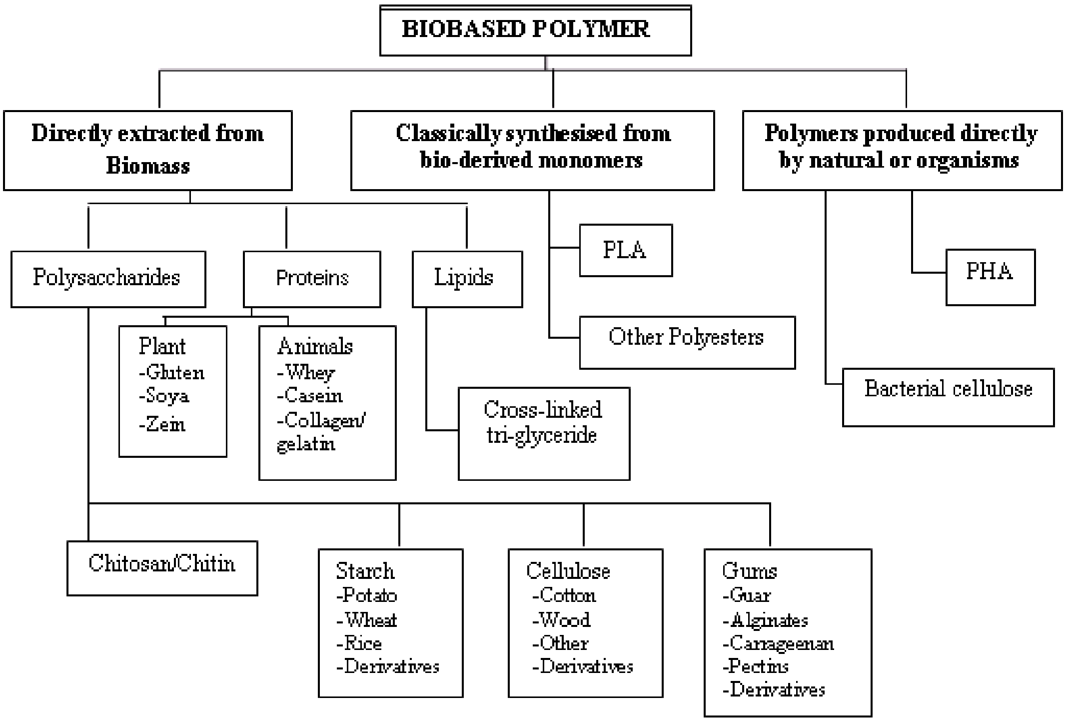


Figure 2.2 Origin of different categories of biologically based materials [6].

2.2 Cellulose

Cellulose is the most abundant biopolymer on earth. It is a polydisperse linear homopolymer, consisting of regio- and enantioselectively ß-1, 4-glycosidic linked d-glucopyranose units (so-called anhydroglucose units [AGU]) as shown in **Figure 2.3**. This biopolymer is the principle constituent of higher plants (about 40-50%), some green algal and fungal (Valonia, a very pure from of cellulose) cell walls providing them with their structure strength.

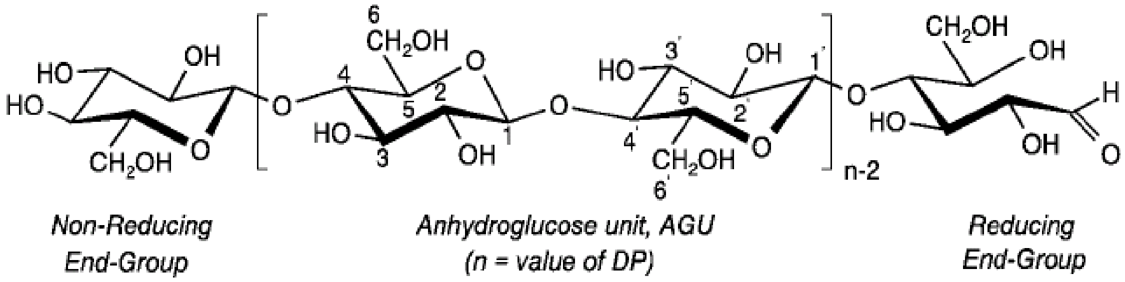


Figure 2.3 Molecular structure of cellulose. [7]

The primary occurrence of cellulose is the existing lignocelluloses material in forests, with wood as the most important source. Other cellulose-containing materials include agriculture residues, water plants, grasses, and other plant substances. As listed in **Table 2.2**, besides cellulose, they contain hemicelluloses, lignin, and a comparably small amount of extractives.

Table 2.2 Chemical composition of some typical cellulose-containing materials [7].

Source	Composition (%)			
	Cellulose	Hemicellulose	Lignin	Extract
Hardwood	43-47	25-35	16-24	2-8
Softwood	40-44	25-29	25-31	1-5
Bagasse	40	30	20	10
Coir	32-43	10-20	43-49	4
Corn cobs	45	35	15	5
Corn cobs	45	35	15	5
Corn stalks	35	25	35	
Cotton	95	2	1	0.4
Flax(retted)	71	21	2	6
Flax(unretted)	63	12	3	13
Hemp	70	22	6	2
Henequen	78	4-8	13	4
Istle	73	4-8	17	2
Jute	71	14	13	2
Kenaf	36	21	18	2
Ramie	76	17	1	6
Sisal	73	14	11	2
Sunn	80	10	6	3
Wheat straw	30	50	15	5

2.2.1 Structure of cellulose

As shown in **Figure 2.3** cellulose has been shown to be a long chain polymer with repeating units of D-glucose, a simple sugar. In the cellulose chain, the glucose units are in 6-membered rings, called pyranoses. They are joined by single oxygen atoms (acetal linkages) between the C-1 of one pyranose ring and the C-4 of the next ring. Since a molecule of water is lost when an alcohol and a hemiacetal react to form an acetal, the glucose units in the cellulose polymer are referred to as anhydroglucose units.

Solid cellulose shows 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 presents the same crystal lattice structure, called cellulose I. However, various modifications of native cellulose can alter the lattice structure to yield other types of crystals (cellulose II, III, and IV). Cellulose II can be formed cellulose I by treatment with aqueous sodium hydroxide (mercerization) or by dissolution of the cellulose and subsequent precipitation/regeneration, as is done in the formation of fiber or film.

The intermolecular forces in the crystalline domains are mainly hydrogen bonds between adjacent cellulose chains in the same lattice plane, which result 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 molecule 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 the width from 2.5 to 4 nm.

Because of the equatorial position of hydroxyls on the cellulose chain, they protrude laterally along the extended molecule. This positioning makes them readily available for hydrogen bonding. These hydrogen bonds cause the chains to group together in highly ordered (crystal-like) structures. Since the chains are usually longer than the crystalline regions, they are thought to pass though several different crystalline regions, with areas of disorder in between (the “fringed-micelle” model).

The inter-chain hydrogen bonds in the crystalline regions are strong, giving the good strength and insolubility in most solvents. They also prevent cellulose from melting. In the less ordered regions, the chains are further apart and more available for hydrogen bonding to other molecule, such as water. Most cellulose structure can absorb large quantities of water. Thus, cellulose swells but does not dissolve in water.

2.2.2 Esterification of cellulose [8]

As show in **Figure 2.3** the cellulose molecule contains three different kinds of anhydroglucose units, 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 rings joined at C-1 and C-4. But because of the long chain length, the chemistry of the alcohol groups of the internal units predominates, so long as the chains are not cleaved by the reaction conditions. Unlike simple alcohols, however, cellulose reactions are usually controlled more by steric factors than would be expected on the basis of the inherent reactivity of the different hydroxyl groups.

There are potentially three hydroxyls groups available on each anhydroglucose ring, so derivatives are usually characterized in terms of a “degree of substitution” (DS), which is an average for the whole chain and can range between 0 and 3. In most cases, partial reaction to DS < 3 gives products that are essentially block copolymers, where virtually all of the hydroxyls occurring in the less ordered regions may be derivatized, while those in the crystalline regions remain unreacted.

Higher degrees of substitution, or reaction conditions which disrupt the crystalline regions, can be used to reduce inter-chain hydrogen bonding and force the chains apart. This can result in a cellulose derivative that is soluble in common solvents, and thus capable of extrusion to form filaments, or other structures.

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 [41]:

(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 $–CH_2OH$ to –COOH

(6) Oxidation of secondary –OH groups to aldehyde and carboxyl

(7) Formation of addition compounds with acids, bases, and salts

Esterification is the general name for a chemical reaction in which two reactants (typically an alcohol and an acid) form an ester as the reaction product. Which are compounds of the chemical structure R-COOR', 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 (**Figure 2.4**). A mineral acid catalyst is usually needed to make the reaction occur at a useful rate [8].

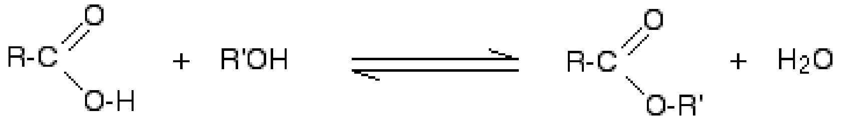


Figure 2.4 Esterification reaction

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 2.5**.

Figure 2.5 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-) form the acid, RCO-OH, with the alkoxide group (R'O-) from the alcohol, R'-OH, rather than other possible combinations.

Like simple alcohols, the hydroxyl groups of cellulose can be esterified by reaction with acids or other acylating agents. Acetylation with acetic acid or acetic anhydride produces a variety of different products with properties that depend on the DS.

2.3 Heating methods

2.3.1 Conventional Heating [10]

In all conventional means for heating reaction mixtures, heating proceeds from a surface, usually the inside surface of the reaction vessel. Whether one uses a heating mantle, oil bath, steam bath, or even an immersion heater, the mixture must be in physical contact with a surface that is at a higher temperature than the rest of the mixture.

In conventional heating, energy is transferred from a surface to the bulk mixture, and eventually to the reacting species. The energy can either make he reaction thermodynamically allowed or it can increase the reaction kinetics.

In conventional heating, spontaneous mixing of the reaction mixture may occur through convection, or mechanical means (stirring) can be employed to homogeneously distribute the reactions and temperature throughout the reaction vessel. Equilibrium temperature conditions can be established and maintained.

Although it is an obvious point, it should be noted here that in all conventional heating of open reaction vessels, the highest temperature that can be achieved is limited by the boiling point of the particular mixture. In order to reach a higher temperature in the open vessel, a higher-boiling solvent must be used.

2.3.2 Microwave Heating

In contrast, microwave irradiation produces efficient internal heating by direct coupling of microwave energy with the molecules of solvents, reagents, or catalysts presented in the reaction mixture. Since the preceding vessels are typically made out of microwave-transparent materials the radiation passes through the walls of the vessel directly into the whole reaction mixture volume and an inverted temperature gradient as compared to conventional thermal heating results. In addition, there are other features of the microwave heating aseptically for chemical reactions which will be described below.

2.3.2.1 Interaction of microwave irradiation

Microwave irradiation (microwave) consists in electromagnetic wave in the range of 300 MHz to 300 GHz that corresponds to wavelengths of 1 cm to 1 m. The microwave region of the electromagnetic spectrum lies between infrared and radio frequencies.

The term "microwave" denotes the techniques and concepts used as well as a range of frequencies. Microwaves travel in matter in the same manner as light waves: they are reflected by metals, absorbed by some dielectric materials, and transmitted without significant losses through other materials. For example, water, carbon, foods with a high water contents, some organic solvents are good microwave absorbers whereas ceramics, quartz glass, and most thermoplastic materials absorb microwaves slightly. All domestic microwave ovens, microwave reactors and other laboratory and industrial systems usually work at 2.45 GHz. To avoid interference with telecommunications and cellular phone frequencies the microwave photon corresponding to 2.45 GHz has energy close 0.0016 eV (~ 1 kJ/mol). From comparison with chemical bonds and Brownian motion energies (**Table 2.3**) it is clear that microwave photon is not sufficiently energetic to break even hydrogen bond and cannot induce chemical reaction as opposite to γ or X-ray photons, ultraviolet and visible radiation.

Table 2.3 Radiation and chemical bonds energies

Radiation type	Frequency (GHz)	Quantum energy (eV)	Bond type	Bond energy (eV)
γ-rays	3.0×10^{11}	1.24×10^{6}	C-C	3.61
X-rays	3.0×10^{11}	1.24×10^{5}	C=C	6.35
Ultraviolet	1.0×10^{6}	4.1	C-O	3.74
Visible light	6.0×10^{5}	2.5	C=O	7.71
Infrared light	3.0×10^{3}	1.2×10^{-2}	CH	4.28
Microwave irradiation	2.45	1.6×10^{-3}	OH	4.80
Radio frequencies	1×10^{-3}	4.0×10^{-9}	Hydrogen bond	0.04 – 0.44

2.3.2.2 The microwave heating mechanism

There are two specific mechanisms of interaction between materials and microwave: (1) dipolar polarization and (2) conduction mechanism. Both mechanisms require effective coupling between components of the target material and the rapidly oscillating electrical field of the microwaves. A third mechanism (3) interfacial polarization occurs, although this is often of limited importance.

(1) Dipolar Polarization

Dipolar polarization is a process by which heat is generated in polar molecules. On exposure to an oscillating electromagnetic field of appropriate frequency, polar molecules try to follow the field and align themselves in phase with the field. However, owing to inter-molecular forces, polar molecules experience inertia and are unable to follow the field. This results in the random motion of particles, and this random interaction generates heat. Dipolar polarization can generate heat by either one or both the following mechanisms:

- Interaction between polar solvent molecules such as water, methanol and ethanol
- Interaction between polar solute molecules such as ammonia and formic acid

The key requirement for dipolar polarization is that the frequency range of the oscillating field should be appropriate to enable adequate inter-particle interaction. If the frequency range is very high, inter-molecular forces will stop the motion of a polar molecule before it tries to follow the field, resulting in inadequate inter-particle interaction. On the other hand, if the frequency range is low, the polar molecule gets sufficient time to align itself in phase with the field. Hence, no random interaction takes place between the adjoining particles.

(2) Conduction mechanism

The conduction mechanism generates heat through resistance to an electric current. The oscillating electromagnetic field generates an oscillation of electrons or ions in a conductor, resulting in an electric current. This current faces internal resistance, which heats the conductor. The main limitation of this method is that it is not applicable for materials that have high conductivity, since such materials reflect most of the energy that falls on them.

(3) Interfacial polarization

The interfacial polarization method can be considered as a combination of the conduction and dipolar polarization mechanisms. It is important for heating systems that comprise a conducting material dispersed in a non-conducting material. For example, consider the dispersion of metal particles in sulphur. Sulphur does not respond to microwaves, and metals reflect most of the microwave energy they are exposed to, but combining the two makes them a good microwave-absorbing material. However, for this to take place, metals have to be used in powder form. This is because, unlike a metal surface, metal powder is a good absorber of microwave radiation. It absorbs radiation and is heated by a mechanism that is similar to dipolar polarization. The environment of the metal powder acts as a solvent for polar molecules and restricts the motion of ions by forces that are equivalent to inter-particle interactions in polar solvents. These restricting forces, under the effect of an oscillating field, induce a phase lag in the motion of ions. The phase lag generates a random motion of ions and results in the heating of the system.

2.3.2.3 Benefits of microwave chemistry

Microwave radiation has proved to be a highly effective heating source in chemical reactions. Microwaves can accelerate the reaction rate, provide better yields and uniform and selective heating, achieve greater reproducibility of reactions, and help in developing cleaner and greener synthetic routes.

- **Increased Rate of Reactions:** Compared to conventional heating, microwave heating enhances the rate of certain chemical reactions by 10 to 1,000 times. This is due to its ability to substantially increase the temperature of a reaction.

- **Liquid Phase Reactions:** The rate acceleration in liquid phase reaction, heated by microwave radiation, can be attributed to the superheating of solvents, for example, water, when heated by conventional methods, has a boiling point of 100 ºC. However, when a power input of 500 watts is employed for a minute in microwave equipment, the reaction can be performed at a temperature of 110 ºC. It has also been observed that the boiling point of water reaches 119 ºC at the reaction conditions mentioned above. This super heating of solvents enables the reaction to be performed at higher temperatures and results in an increase in the rate of the reaction.

- **Catalytic Reactions:** The rate acceleration in solid-state catalytic reactions, on exposure to microwave radiation, is attributed to high temperatures on the surface of the catalyst. The increase in the local surface temperature of the catalyst results in enhancement of the catalytic action, leading to an enhanced rate of reaction. It has been observed that when the catalyst is introduced in a solid granular form, the yield and rate of the heterogeneous oxidation, esterification and hydrolysis reactions increases with microwave heating, compared to conventional heating under the same conditions.

- **Efficient Source of Heating:** Heating by means of microwave radiation is a highly efficient process and results in significant energy saving. This is primarily because microwaves heat up just the sample and not the apparatus, and therefore energy consumption is less.

- **Higher Yields:** In certain chemical reactions, microwave radiation produces higher yields compared to conventional heating methods.

- **Uniform Heating:** Microwave radiation, unlike conventional heating methods, provides uniform heating throughout a reaction mixture **(Figure 2.6)**.

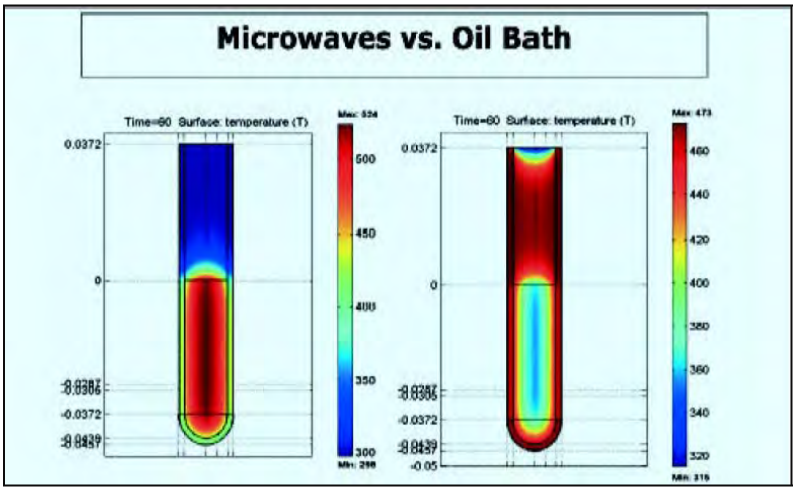


Figure 2.6 Uniforms Heating through Microwave Irradiation

In conventional heating, the walls of the oil bath get heated first, and then the solvent. As a result of this distributed heating in an oil bath, there is always a temperature difference between the walls and the solvent. In the case of microwave heating, only the solvent and the solute particles are excited, which results in uniform heating of the solvent. This feature allows the chemist to place reaction vessels at any location in the cavity of a microwave oven. It also proves vital in processing multiple reactions simultaneously, or in scaling up reactions that require identical heating conditions.

- **Selective heating**: Selective heating is based on the principle that different materials respond differently to microwaves. Some materials are transparent whereas others absorb microwaves. Therefore, microwaves can be used to heat a combination of such materials, for example, the production of metal sulphide with conventional heating requires weeks because of the volatility of sulphur vapours. Rapid heating of sulphur in a closed tube results in the generation of sulphur fumes, which can cause an explosion.

However, in microwave heating, since sulphur is transparent to microwaves, only the metal gets heated. Therefore, reaction can be carried out at a much faster rate, with rapid heating, without the threat of an explosion.

- **Environmentally-friendly Chemistry:** Reactions conducted through microwaves are cleaner and more environmentally friendly than conventional heating methods. Microwaves heat the compounds directly; therefore, usage of solvents in the chemical reaction can be reduced or eliminated. The use of microwaves has also reduced the amount of purification required for the end products of chemical reactions involving toxic reagents.

- **Greater Reproducibility of Chemical Reactions:** Reactions with microwave heating are more reproducible compared to conventional heating because of uniform heating and better control of process parameters. The temperature of chemical reactions can also be easily monitored. This is of particular relevance in the lead optimization phase of the drug development process in pharmaceutical companies.

2.3.2.4 Applications 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 various applications of microwave radiation in analytical chemistry include ashing, digestion, extraction, protein hydrolysis, moisture/solids analysis, and spectroscopic analysis.

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.

2.3.3 Literature review

There are many research publications reported on the esterification of cellulose under conventional and microwave heating method which are briefly summarized as follows:

In 1996, Sealey et. al [11] prepared cellulose ester under homogeneous solution (DMAc/LiCl) using a novel synthetic method based on the use of a mixed p-toluenesulfonic/carboxylic acid anhydride by conventional heating. The result showed cellulose esters obtained high degree of substitution (DS) between 2.8 and 2.9. The melting points and heats of fusion of side-chain crystals increased with increasing ester length, due to increasing crystal thickness. Side-chain melting points increased from -15°C for cellulose laurate (C_{12}) to 55°C for cellulose eicosanoate (C_{20}). Evidence of “main chain” crystallization was not observed for these samples, except in the case of peracetylated C_{12} and C_{14} esters, which had Tm values of 96°C and 107°C, respectively

In 1998, Vaca-Garcia et. al [12] studied homogeneous esterification of cellulose with saturated fatty acids (n-octanoic to n-octadecanoic) with acetic anhydride co-reactant in lithium chloride/ N, N-dimethylacetamide (LiCl/DMAc) medium under conventional heating. Cellulose mixed triesters (CMT) were obtained after 5 h at 130°C with an average of 2.2 acetyl groups and 0.8 fatty substituents per anhydroglucose unit. They found that the esterification of cellulose with unmodified fatty acids and acetic anhydride in DMAc/LiCl medium allowed the grafting of fatty acyl groups into cellulose, along with a dependent acetylation, due to the formation of a mixed anhydride. The obtained mixed esters were highly hydrophobic and more mechanically resistant than the corresponding fatty simple triesters.

In 1999, Gourson et. al [13] reported that cellulose-enriched residues from maize bran can be transformed into plastic films after esterification of the cellulose by various fatty acid chlorides under conventional heating. Alkali pretreatment and acidic activation of the sample are necessary before the esterification reaction in order to form esters. The result showed that the sample treated only with potassium hydroxide led to the best results; the yield was 75%. The utilization of a large excess of fatty acid chloride resulted in a 54% yield. The treatment with KOH is sufficient and that only the presence of the heteroxylans (58%) in the maize bran prevents esterification and/or formation of plastic. The lignin in the treated sample does not seem to prevent the reaction. The use of excess fatty acid did not improve the yield. The plastic showed a tensile strength of 2.3 MPa and an elongation of 149%. Esterification of the bran after basic pretreatment and acidic activation formed esters that can be used as biodegradable plastic.

Also in 1999, Fang et. al [14] esterified hemicelluloses in homogeneous solutions of DMF/LiCl by reacting the native hemicelluloses with various acyl chloride (C_3-C_{18}) in the presence of 4-dimethylaminopyridine as a catalyst and triethylamine a base within 30 min at 70-75°C. The product obtained were characterized by means of Fourier transform IR chromatography, thermal analysis, and solubility. The degree of substitution of esterified hemicelluloses was controlled between 0.38 and 1.75 as a function of experimental conditions. Under an optimum reaction condition (xylose unit/acyl chloride molar ratio 1:3, tetraethylammonia %160, 75°C, 30 minutes), about 95% hydroxyl groups in native hemicelluloses were esterified. The molecular weight measurements showed a minimal degradation and hydrolysis of the products. The thermal stability of the products was also increased by modification. Introduction of hydrophobic acyl groups in the molecular structure of hemicelluloses were considerably more hydrophobic than the nature hemicelluloses.

In 2000, Chauvelon et. al [15] investigated suitability of two agricultural by-products, wheat bran and maize bran, to be transformed into biomaterials by esterification with lauroyl chloride under conventional heating. Influence of biochemical characteristic of cellulose (cellulose content, viscosity-average degree of polymerization, crystallinity) was studied on eight samples enriched in cellulose after chemical removal of heteroxylans and lignin. After an acidic pre-treatment, esterification was carried out with lauroyl chloride and an optimized reaction time of 8 h was used. They found that wheat bran and maize bran needed different treatment for an efficient extraction of noncellulosic polymers. The main difference between wheat and maize bran was their lignin content, and more drastic treatment (concentration in alkali, pre-treatment with sodium chlorite or alkaline treatment with hydrogen peroxide) was necessary for wheat bran, which had high lignin content. An esterification time of 8 h was selected allowing the best yield of cellulose laurate and the lowest amount of by product. They reported that chemical compositions were similar for all cellulose esters obtained, but cellulose content of initial material had a marked influence on the amount of esterified product. A film was easily obtained by casting and the mechanical (tensile strength and elongation), and thermo mechanical properties seemed to be interesting. Tensile strength was about 2 MPa whereas elongation varied from 53 to 180%

In 2000, Tosh et. al [16] studied the homogeneous acetylation of cellulose in the LiCl/DMAc solvent system, with acetic anhydride in the presence of *p*-toluenesulfonyl chloride (*p*-TsCl) or pyridine as catalysts. The reaction temperature was varied from 28 to 70 °C and the time of reaction from 2 to 24 h. They found that the degrees of substitution (DS) of the esters prepared using both catalysts show that pyridine is a better catalyst than *p*-TsCl. Molecular weights of the esters, determined viscosimetrically, show that some degradation in the cellulose chain occurred at a reaction temperature of 70 °C. Hence, the optimum temperature for esterification appears to be 50°C – 60 °C at 10 h reaction time to obtain full degree of acetyl substitution

In 2001, Satge et. al [17] studied the esterification of cellulose with long chain acyl chloride in homogeneous media induced by microwave irradiation. They found that, the use of microwave resulted in a dramatic drop in reaction time: 1min irradiation was sufficient, the degrees of substitution (DS) ranging from 0.7 to 2.6.

In 2004, Joly et. al [18] synthesized of cellulosic plastic films obtained in homogeneous conditions by microwave-induced acylation of commercial or chestnut tree sawdust cellulose by fatty acids. They found that DMAP does not influence degrees of substitution (DS), massic, and molar yields. Plastic films synthesized in the absence of DMAP showed a decrease in mechanical behavior. Organic (tributylamine) or inorganic bases ($CaCO_3$, Na_2CO_3) were then added to replace DMAP basic activity, and no changes were observed. Concerning thermal and mechanical properties of plastics obtained with various bases, glass transition temperatures (Tg) and degradation temperature (Td) were found constant whatever the base, and the best mechanical properties were obtained for films synthesized in the presence of $CaCO_3$. The same remarks were made concerning the valorization of chestnut tree sawdust cellulose. Microbial biodegradation of plastic films with DS = 2.2 led to a loss of their mechanical behaviors.

In 2008, Peng et. al [19] synthesized hemicellulosic polymers under mild conditions (conventional heating) in homogeneous media (N,N-dimethylformamide–lithium chloride) by reacting the native wheat straw hemicellulosic polymers with lauroyl chloride using 4-dimethylaminopyridine and triethylamine (TEA) as a catalyst and a base, respectively. In comparison, other catalysts such as N-bromosuccinimide (NBS), N-methyl pyrrolidine (MPI), N-methyl pyrrolidinone (MPO), and pyridine were also investigated. The result showed that a wide DS range of lauroylated hemicelluloses between 0.46 and 1.54 with more hydrophobic properties have been prepared in homogeneous DMF–LiCl solution under mild reaction conditions, which represents a suitable, effective, and rapid method for lauroylation of wheat straw hemicelluloses. The modified polymers are more hydrophobic than the native polymers and may be suitable for the preparation of biodegradable plastic films to replace petrochemical commodity plastics for the food packaging industry. In this ideal modification system, reaction temperature and time were reduced to a rather mild condition (40 °C, 35 min), and the hydrochloric acid produced by fatty acid chloride during the reaction could be easily removed by adding 2 equiv of TEA. Under an optimum reaction condition (2 equiv of lauroyl chloride and TEA per hydroxyl group, 5% DMAP, 40 °C, 35 min), a high DS value of 1.54 was obtained. The results obtained by thermal analysis showed that no significant degradation of the lauroylated hemicelluloses occurred during the reaction, and the thermal stability of the product was increased by lauroylation under the mild conditions.

In 2009, Li et. al [20] used DMAP as a catalyst to prepare high DS of succinylated cellulosic derivatives under microwave irradiation . They found that, the succinoylation of cellulose was successfully carried out with succinic anhydride using ionic liquid 1-buty-3-methylimidazolium (BMIMCI) as solvent in the presence of DMAP. Parameters investigated included the mass ratio of DMAP/succinic anhydride in a range from 0% to 15%, reaction time (from 30 min to 120 min), reaction temperature (from 60°C to 110°C). The succinylated cellulosic derivatives had a degree of substitution (DS) ranging from 0.24 to 2.34. It was found that the DS of succinylated cellulosic derivatives using DMAP as a catalyst was higher than that without any catalyst under the same reaction conditions. The thermal stability of the succinylated cellulose decreased upon chemical modification.

Also in 2009, Joly et. al [21] prepared cellulose-based plastic films by acylating cellulose in homogeneous media under microwave irradiation with fatty acyl chlorides containing either saturated or unsaturated chains of various lengths (C_{12} to C_{18}). The result showed that, cellulose esters were synthesized successfully using a range of different saturated and unsaturated fatty chains, and various degrees of substitution were obtained ranging from 1.7 to 3. The mechanical properties of the samples were investigated and shown to have a direct relationship with the DS values. An increase of tensile strength and strain level until a maximum value was observed; on the contrary, the elastic modulus (E) decreased until a minimum value. The cellulose saturated and unsaturated ester plastic films displayed almost the same behavior, except concerning the strain value; cellulose oleate reached a maximum value before decreasing. With their mechanical and hydrophobic properties, cellulose ester plastic films are promising materials to replace petrochemical commodity plastics, such as polyethylene.

2.4 Plasticizer

Plasticizers are primarily liquids of low volatility, which are added to polymers to make them soft and flexible. Plasticizers are also used to improve melt processibility and toughness of rigid plastics such as cellulose esters and ethers, and in a variety of specialized applications. In some cases they perform dual functions such as thermal stabilization or flame retardance [22].

Plasticizers can be either internal or external, where external plasticizer molecules are not attached to polymer chains by primary bonds and can therefore be lost by evaporation, migration, or extraction. On the other hand, internal plasticizers are inherently part of the plastic and remain part of the product. For both types of plasticizers, there is often a marked temperature dependence of material properties, though this is more pronounced with internal plasticizers. Internal plasticizers also have problems with retaining dimensional stability at elevated temperatures. Plasticizers may also be divided into primary and secondary types. If a polymer is soluble in a plasticizer at a high concentration of the polymer, the plasticizer is said to be a primary plasticizer. Primary plasticizers should gel the polymer rapidly in the normal processing temperature range and should not exude from the plasticized material. Secondary plasticizers, on the other hand, have lower gelation capacity and limited compatibility with the polymer. In the case, two phases are present after plasticization process-one phase where the polymer is only slightly plasticized and one phase where it is completely plasticized. Polymer plasticized with secondary plasticizers do not, therefore, deform homogeneously when stressed as compared to primary plasticizers. The deformation appears only in the plasticizer –rich phase and the mechanical properties of the system are poor. Unlike primary plasticizers, secondary plasticizers cannot be used alone and are usually employed in combination with a primary plasticizer.

2.4.1 Theories of plasticizer action [24]

There are many theories to explain the plasticization effect on the polymers. The accepted theories are the three that expressed in 2.4.1.1-2.4.1.3

2.4.1.1 The lubricity theory

The theory considers the result of intermolecular friction, which is the major force resisting the deformation of a thermoplastic polymer. The plasticizer would act as a lubricant to facilitate movement of polymer chains over each other, or segments of the chain although other parts of the chain are of gel network. The plasticizer gives internal lubricity. **Figure 2.7** illustrates the Lubricity Theory.

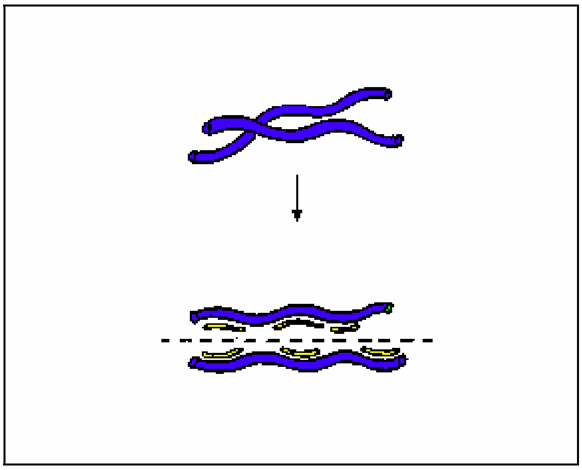


Figure 2.7 Plasticizer polymer response based on lubricity theory

2.4.1.2 The gel theory

The Gel Theory of plasticization starts with a model of the polymer molecules in a three dimensional structure. This structure is formed by more or less loose of attachments that occur at intervals along the polymer chain caused by weak intermolecular forces such as dipole-dipole interaction or hydrogen bonding. According to this theory, as shown in **Figure 2.8**, when the plasticizer solvates the polymer, it destroys and points of attachment by replacing polymer-polymer interactions. It has been suggested that the plasticizer might selectively solvates the polymer chain at these points.

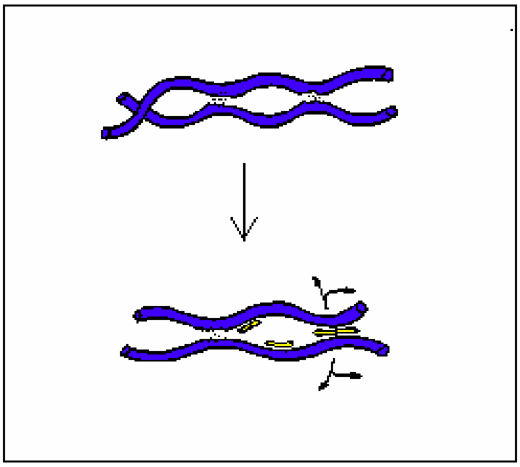


Figure 2.8 Gel theories of plasticizers

2.4.1.3 The free volume theory

The free volume theory assumes that there is a free surface (volume) between molecules which was increased by increasing temperature or molecular motion and chain end group plasticization. Addition of flexible side chains produces the same result. These effects are achieved by internal plasticization and the free volume is fixed with regard to the polymer molecule. Enough free volume permits a freedom of movement as if there were a hole for a nearby atom, molecule, or chain segment to move into. The normal result of adding more free volume to a polymer is that it is plasticized.

2.4.2 Plasticizers for biodegradable polymers [23]

Biodegradable polymers have gained much attention for environmental and biomedical applications. When disposed in biologically active environments, biodegradable polymers are completely converted to biological products (biogas, humic matter, biomass, etc.) within a certain period of time. These polymers, as well as their degradation products, must cause no deleterious effects on the environment.

Fully biodegradable synthetic polymers such as poly (lactic acid) or PLA, polycaprolactone (PCL), and polyhydroxybutyratevalerate (PHBV) have been commercially available since 1990. Plasticizers are used for biodegradable plastics as well. There are more stringent requirements on these plasticizers, though, since by definition they will be released to the environment during normal product use. Health and safety issues dominate the research in this field, with benign, often natural substances having nearly as great importance as the ability to lower the Tg of the polymer. Because of the prevalence and commercial applications of biodegradable polymers, recent research has focused on developing compatible plasticizers that also biodegrade.

The extensive use of polymers in short-term packaging and disposable applications, and in food and pharmaceutical industries, has stimulated research interest in biodegradable plasticizers as an alternative to the conventional nondegradable ones. This is one of the major research interests in the plasticizer industry now. With the expansion of biodegradable plastic industry, owing to the growing global concern about the environmental impact of persistent plastics, biodegradable plasticizer research continues to grow.

A number of plasticizers have been investigated to be used with biodegradable polymers as follows:

In 2000, Yang and Paulson [25] studied mechanical and water vapour barrier properties of edible gellan films as affected by plasticizer and environmental RH. They found that, addition of glycerol to gellan films increased extensibility moderately, but decrease tensile elongation only slightly. The amount of glycerol added to gellan film should be controlled due to its adverse effects on the mechanical strength and water vapor permeability (WVP) as well as stickiness and appearance of the film. The lowest effective glycerol concentration was ~60 %(film dry weight basic);below this concentration, the films trend to be brittle and difficult to handle, whereas films with more than ~75%glycerol tended to be sticky.

In 2002, Liu and Williams [26] studied the behavior of cellulose acetate phthalate (CAP) free films at heat-only and heat-humidity curing conditions and the differences between diethyl phthalate (DEP) and triethyl citrate (TEC) plasticized films. The result showed that TEC was less volatile and produced films with increased % elongation, and decreased tensile strength and elastic modulus compared to the films plasticized with DEP. However, the DEP plasticized films were less permeable than TEC-plasticized films following heat-humidity curing

In 2003, Carvalho et. al [45] evaluated the chain degradation that occurs in the processing of thermoplastic starch-glycerol composites reinforced with wood pulp fibre. The extent of degradation was determined by high performance size exclusion chromatography (HPSEC) from samples prepared with different amounts of fibre and glycerol. They found that the addition of glycerol and fibres to starch influences the extent of degradation during the processing of these thermoplastic starch composites. The effects are more important on the high molecular weight fraction of starch, that is, the molecular weight reduction during extrusion occurs mainly on the amylopectin fraction. The effects of glycerol and fibres were of similar magnitudes, but with opposite effects, since an increase in glycerol content reduced chain degradation, whereas an increase in the fibre content amplified it. The process involved in the degradation of starch chains in thermoplastic starch (TPS) composites seems to be shear-induced and thus affect only the high molecular weight components of the natural polymer.

In 2004 Choi and Park [28] studied the effect of triethyl citrate (TEC), dibutyl phthalate (DBP), soybean oil (SO), and epoxidized soybean oil (ESO) as biodegradable plasticizers of poly 3-hydroxybutyrate-*co*-3-hydroxyvalerate (PHBV). The result show that TEC and DBP were more effective in depression of the glass transition temperature as well as increasing the elongation at break and the impact strength of PHBV films than soybean oil (SO) and epoxidized soybean oil (ESO).

In 2004, Park et. al [29] have chosen triethyl citrate (TEC) as the plasticizer for nanocomposites of cellulose acetate and clay. They found that cellulose plastic-based nanocomposites with 20 wt% TEC plasticizer and 5%wt organoclay showed better intercalation and an exfoliated structure than the counterpart having 30/40 wt% plasticizer. The tensile strength, modulus, and thermal stability of cellulosic plastic reinforced with organoclay showed a decreasing trend with an increase of plasticizer content from 20-40wt%.

In 2007, Talja et. al [30] investigated the effects of plasticizer (glycerol, xylitol, and sorbital) and relative humidity on physical and mechanical properties of potato starch-based edible films. The result showed that water content of films increased with increasing relative humidity and plasticizer content.Water vapor permeability of films increased with increasing plasticizer content and storage relative humidity. Young’s modulus decreased with increasing polyol content with a concurrent increase in elasticity of films.

In 2007, Osés et. al [31] studied the effect of storage time on the mechanical properties of whey protein isolate (WPI) films plasticized with two low molecular weight polyols: glycerol (Gly) and sorbitol (Sor). The result showed that Gly was found to be a more efficient plasticizer than Sor. Films plasticized with Gly were found to be more flexible and weaker and to have higher moisture content than films with the some amount of Sor. There was a saturation value for plasticizer content (40% for Gly and 50% for Sor), above which the film become weaker, but not more flexible. Storage time did not effect either the appearance or the mechanical properties of films plasticized with Gly, However, films plasticized with Sor become harder and less flexible with time likely due to Sor crystallization.

In 2009 Behjat et. al [32] investigated the biodegradability of kenaf cellulose-PE biocomposites. Soil burial test is used to determine the biodegradability on the polymer blends. The effects of plasticizer, PEG, in biodegradation of these polymers were also studied. It was found that the cellulose/LDPE and cellulose/HDPE blends were biodegradable in a considerable rate. The bio-composites with high content of cellulose had higher degradation rate. In addition, biodegradability of the bio-composites made up using PEG was superior to those of the bio-composites fabricated without PEG, due to the improved wetting of the plasticizer in the matrix polymer.

In 2009, Schlemmer et. al [33] evaluated the behavior of glycerol and buriti oil as plasticizers in PS/TPS blend degradations. Changes on the composition of such material exposed to natural microflora present in soil during indoor experiments were evaluated by solid state ^{13}C NMR spectroscopy (CPMAS 13C NMR). Weight loss as a function of degradation time was determined by thermogravimetry (TG). The addition of starch to polystyrene plastics has been promoted as a technique to achieve biodegradability. From TG curves for PS/TPS blends with glycerol or buriti oil it was verified that all the samples presented less stages of thermal degradation after the period of soil buried test than the original ones. Furthermore, TG curves of PS/TPS blends with buriti oil presented even less degradation stages than blends with glycerol. The CPMAS ^{13}C NMR analyzes indicated that the blends of PS and TPS with glycerol or buriti oil were consumed in different levels after 6 months of buried test in soil. Blends with buriti oil showed more degradability compared to glycerol ones. Biodegradation mainly affects the starch, whose thermal stability increases, and has no significant effect on the PS. The obtained results show that buriti oil, a natural raw material can be used as an environmentally-friendly alternative to other materials, and has superior properties compared to glycerol, the most used plasticizer for starch.

CHAPTER III

EXPERIMENTAL

3.1 Materials and Chemicals

3.1.1 Waste cotton fabric obtained from local textile factory was used as a raw material.

3.1.2 Hydrochloric acid (HCl, 36.5–38.0%) purchased from J.T.Baker, United state of America was used as a hydrolysis.

3.1.3 N, N-dimethylacetamide (DMAc, assay (GC) 99.5%) purchased from Lab-Scan Asia Co., Ltd., Thailand was used as a solvent.

3.1.4 Lithium chloride (LiCl, assay 99.0%) purchased from Unilab (Ajax Finechem) was used as a solvent.

3.1.5 N, N-dimethyl-4-aminopyridine (DMAP, assay (NT) ≥98.0%) purchased from Fluka Analytical (Sigma Aldrich China) was used as a catalyst.

3.1.6 Lauroyl chloride (assay (GC) ≥97.5%) purchased from Fluka Analytical (Sigma Aldrich Germany) was used as an esterifying agent.

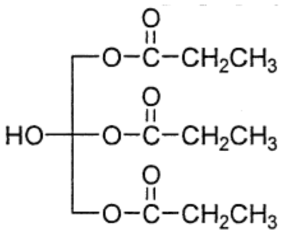
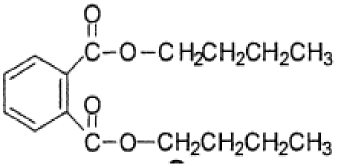
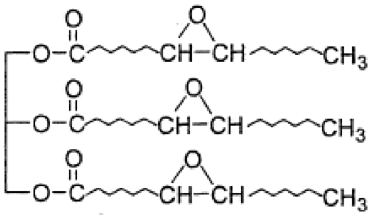
3.1.7 Chloroform (assay (GC) 99.8%) purchased from Lab-Scan Asia Co., Ltd., Thailand was used as a solvent in solvent-based free film.

3.1.8 Triethyl citrate (TEC, assay ≥98%) purchased from Fluka Analytical (Sigma Aldrich Germany) was used as a plasticizer.

3.1.9 Dibutcfyl phthalate (DBP, assay 99%) manufactured by Merck Ltd.,Germany was used as a plasticizer.

3.1.10 Epoxidized soy bean oil (ESO) provided by Multipleplus Co.,Ltd Thailand was used as a plasticizer.

Table 3.1 Properties of the plasticizers used in the study [28].

Chemical name	Designation	Chemical structure	Mw (g/mol)	Tm (°C)
Triethyl citrate	TEC		276.1	-
Dibutyl phthalate	DBP		278.2	-35.0
Epoxidized soy bean oil	ESO		872.2	-15.7

3.2 Equipments and Instruments

Details of each instrument are classified according to the experimental procedure as follows.

3.2.1 Cellulose modification

-Hot plate, MR Hei-Standard, Heidolph, Germany
-Electronic Temperature Controller, EKI-CON, Heidolph, Germany
-Magnetic Stirrer, Bel-Art, USA
-Microwave oven, MS2447BB, LG

3.2.2 Physical property testing

- Micrometer, Model G, Peacock, Japan
-Scanning electron microscope (SEM), JSM-6400, JEOL
-X-ray diffractometer, PW 3710, Philips

3.2.3 Chemical structure

-Fourier transforms spectroscopy (FT-IR), Nicolet 6700, Thermoscientific.
-Proton nuclear magnetic resonance spectroscopy, DPX-300, Bruker

3.2.4 Thermal property characterization

-Thermogravimetric analyzer, TGA/SDTA851^e, Mettler Toledo
-Differential scanning calorimeter, DSC1, Mettler Toledo

3.2.5 Mechanical property testing

-Tensile Testing Machine, LR 100K, LLOYD

3.3 Experimental Procedure

Preparation of cellulose laurate films was described in three steps as follows:

Step 1: Hydrolysis of cellulose

Waste cotton fabric was hydrolyzed with 2.5N hydrochloric acid at 80 °C for 2 hrs and washed with distilled water until pH 6-7. The obtain cellulose powder was dried in an oven at 60 °C overnight prior to use in the next step.

Step 2: Esterification of cellulose powder

The cellulose powder (2g) was dissolved in 50 ml of Licl/DMAc system (8%w/v) by stirring at 60 °C for 1 hr. After that, the cellulose solution was cooled to room temperature. Then, 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 under microwave heating and conventional heating. For conventional heating method, the mixture was esterified using a hot plate as a heating source. The reaction times and temperatures were varied from 4 to 20 h and 30 to 80 °C, respectively. For microwave heating method, the mixture was heated and esterified in a domestic microwave oven. The reaction times ranging from 60 to 180 sec and microwave power output varying from 80 to 320 watts were employed. At the end of the reaction, the cellulose solution was precipitated and washed with ethanol. Finally, the precipitate was recovered by filtration. The conditions for cellulose esterification by conventional heating and microwave heating are summarized in **Table 3.2.**

Table 3.2 Reaction conditions for esterification of cellulose.

Heading Method	Esterification Condition	
Conventional heating	Temperature (°C)	30, 60, 80
	Time (hour)	4, 8, 12, 16, 20
Microwave heating	Power (Watts)	80, 160, 240, 320
	Time (second)	60, 90, 120, 150, 180

Step 3: Film formation

The cellulose laurate powder was dissolved in chloroform at room temperature. A plasticizer was added into the esterified-cellulose solution and stirred with a magnetic stirrer for 5 min. After that, the solution was cast on to petri dishes and dried at ambient condition. Three types of plasticizer used were triethyl citrate (TEC), dibutyl phthalate (DBP), and epoxidized soy bean oil (ESO). Each plasticizer was added in the ratios of 0, 3, 5, 7, and 9 %(w/w) of dry cellulose laurate.

The entire experimental procedure for preparation and characterization of esterified-cotton under conventional heating and microwave heating methods is shown below in **Figure 3.1**.

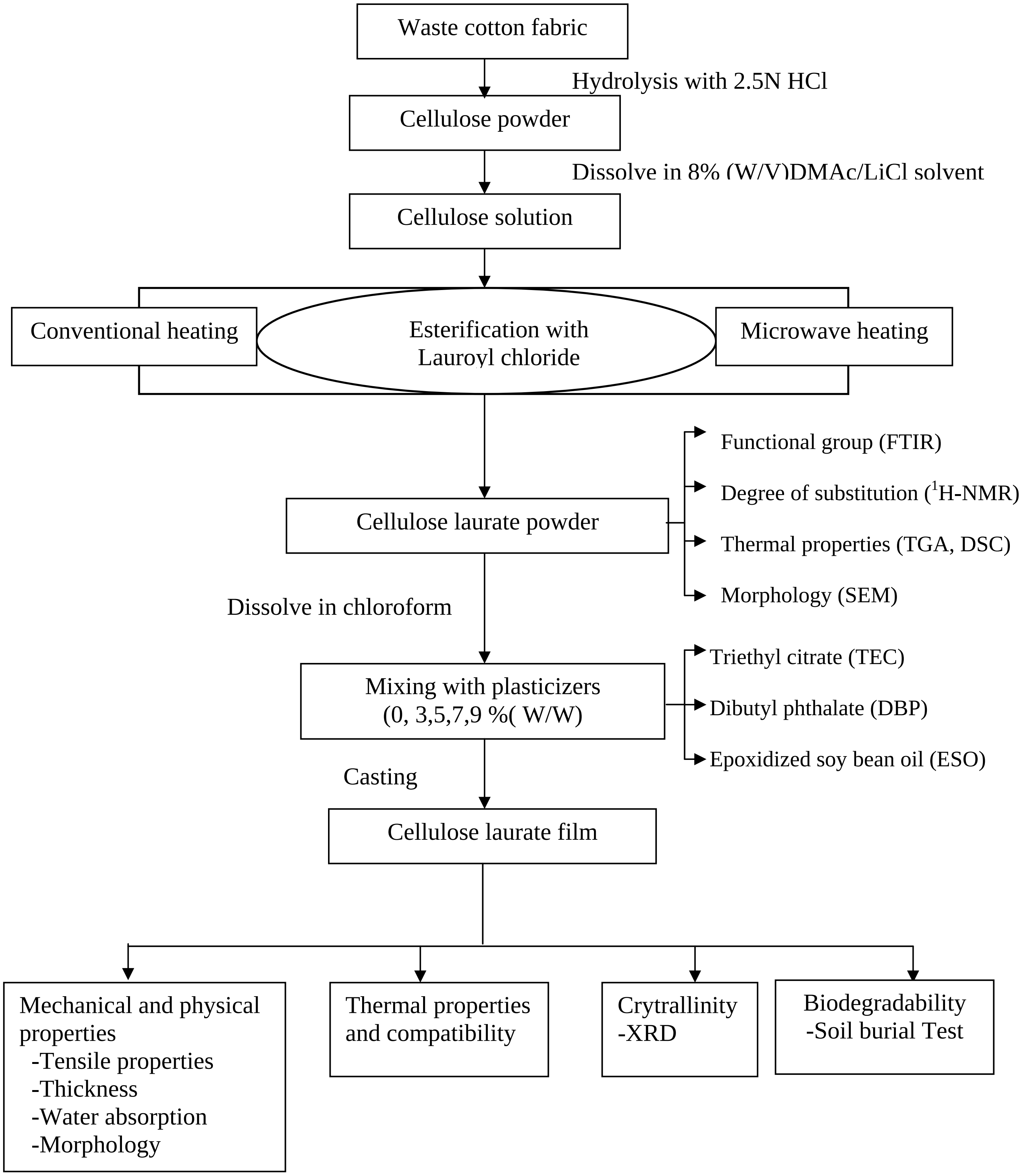


Figure 3.1 Flow diagram of experimental procedure

3.4 Characterization and Testing of Cellulose Powder

3.4.1 Functional group by FTIR technique

FT-IR spectra were obtained on a Nicolet 6700 spectrometer using a KBr disc containing 1% finely ground sample. Resolution for all infrared spectra was 4 cm^{-1} with 32 consecutive scans. The samples were scanned at a frequency range of 4000-400cm^{-1}.

3.4.2 Determination of the degree of substitution by ^{1}H-NMR technique

The degree of substitution (DS) of the modified cellulose was determined by ^{1}H-NMR spectroscopy in $CDCL_3$ using a Bruker DPX-300 spectrometer. The DS value was evaluated by ^{1}H-NMR, with an integration measurement, using the following formula[43].

$$DS = \frac{10 \times I_{CH3}}{3 \times I_c + I_{CH3}}$$

In which:

I_{CH3} = methyl protons integration

I_c = carbohydrate protons integration

3.4.3 Thermal properties

3.4.3.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed using a Mettler Toledo TGA/SDTA851^e at a heating rate of 10 °C/min from 50 °C to 800 °C under nitrogen atmosphere. 6 mg of each sample was used. Prior to do the experiment, the samples were dried in an oven at 60 ^{o}C overnight. The thermal degradation temperature (T_d) was reported as the onset of weight loss of heated sample.

3.4.3.2 Differential scanning calorimetry (DSC)

Differential scanning calorimetry was carried out using a Mettler Toledo DSC1 to characterize thermal properties regarding the transition temperature of sample**.** The sample of about 7 mg was placed in a hermitically sealed aluminum pan and heated from -50 to 200°C at a scanning rate of 10°C/min under a constant flow of nitrogen.

3.4.4 Morphological studies

The morphology of unesterified and esterified-cotton was characterized by scanning electron microscope (JEOL:JSM-6400). The scanning electron microscopy was operated at 15 KV. The surface of each sample was sputter-coated with a thin layer of gold before being scanned to avoid surface charing under electron beam.

3.5 Characterization and Testing of Cellulose Film

3.5.1 Physical properties

3.5.1.1 Film thickness measurement

The thickness of the free film was measured by a micrometer at five different places on the film. An average of film thickness was used to determine mechanical properties for each film replicate.

3.5.1.2 Morphological studies

The morphology of esterified-cotton film was investigated by scanning electron microscope (JEOL:JSM-6400). The scanning electron microscopy was operated at 15 KV. The surface of the film samples was sputter-coated with a thin layer of gold before being scanned to avoid surface charing under electron beam.

3.5.1.3 Water absorption

Water absorption of films was measured by twenty-four hours immersion method according to the ASTM D 570 standard test. First, the 25.4x76.2 mm with the dimensions of specimens was dried in an oven at 60 °C for 24 hours. After cooling in a decicator for 10 min, they were weighed (WI). Then, the specimens were entirely immersed in a container of distilled water maintained at ambient temperature up to the equilibrium (24 h). After 24 hours, the specimens were removed from the water one at a time, all surface water was wiped off with a dry cloth, and immediately weighed (W_2). The water absorption was calculated as the weight difference and reported as percentage of weight increase from the initial dry weight of the specimen.

The result of each sample represents the average of five tests. The water absorption of films was calculated as follows:

$$\%\text{Water Absorption} = \frac{W_2 - W_1}{W_1} \times 100$$

Where W_2 is the weight of the film at the equilibrium and W_1 is the initial dry weight of the specimen

3.5.2 Mechanical properties

3.5.2.1 Tensile properties

Tensile properties were measured on a tensile testing machine (LLOYD LR 100K). The test was carried out according to ASTM D 882 standard method, with a crosshead speed of 10 mm/min and a gauge length of 100 mm. A 50 N static load cell was used. The films were cut into 10 x150 mm rectangular specimens. 5 specimens for each sample were tested and averaged. The parameters determined were: tensile stress(MPa), strain at break(%), and Young's Modulus(MPa).

3.5.3 Thermal Properties

3.5.3.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed using a Mettler Toledo TGA/SDTA851^e at a heating rate of 10 °C/min from 50 °C to 800 °C under nitrogen atmosphere. 6 mg of each sample was used.

3.5.3.2 Differential scanning calorimetry (DSC)

. Differential scanning calorimetry was carried out using a Mettler Toledo DSC1 to determine the transition temperature of the sample**.** 7 mg of each sample was placed in a hermitically sealed aluminum pan and heated from -50 to 160 °C at a scanning rate of 10 °C/min under a constant flow of nitrogen.

3.5.4 Crystallinity

3.5.4.1 X-ray diffraction (XRD)

Crystallinity determines the flexibility of the molecular chains of polymers. Polymers with higher crystallinity have better mechanical strength. X-ray diffraction was performed using a PW 3710 Philips diffractometer with CuKα radiation (λ = 0.1542 nm) in a sealed tube operated at 40 kV and 30 mA. The diffraction curves were obtained from 2 to 30°, in steps of 0.01°. The scan speed was 5.0 sec/step.

3.5.5 Biodegradation Test

Soil burial degradation experiments were carried out at ambient temperature which is depeneding on natural environment. In this method, the samples were incubated in soil having several microorganisms including both fungi and bacteria. The cellulosic film samples were cut into the size of 20 mm x 20 mm and weighed (Wi) before being buried 50 mm beneath the surface of soil, which was regularly moistened with distilled water. The degradation of the sample was determined every 10 days, for a period of 80 days, carefully washed with distilled water, dried at 60 °C in an oven for 24 hours, and then kept in a desiccator. The weight loss of films was measured by weighing of the samples before and after biodegradation. The percentage weight loss of the film samples were calculated using the following equation:

$$\%\ \text{Weight loss} = \frac{W_i - W_f}{W_i} \times 100$$

Where W_i is weight of sample before degradation test (g)

W_f is weight of sample after degradation test (g)

Besides weight loss measurement, physical appearance of degradation film samples was also observed from SEM analysis.

CHAPTER IV

RESULTS AND DISCUSSION

This chapter was divided into 2 parts. The first part, hydroxyl groups of the cellulose containing in the waste cotton fabrics were esterified by lauroyl chloride (**Figure 4.1**) under conventional and microwave heating methods.

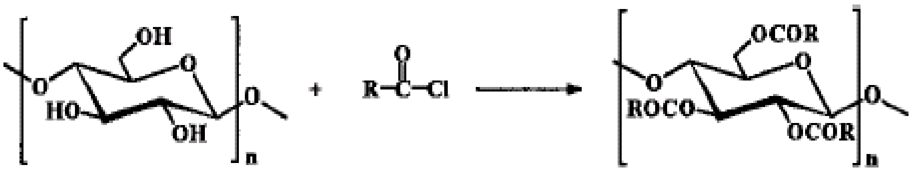


Figure 4.1 Esterification of cellulose by fatty acid chlorides

Then, the cellulose laurate powder from both heating methods was converted into plastic film by casting method. Three types of plasticizer, triethyl citrate (TEC), dibutyl phthalate (DBP), and epoxidized soy bean oil (ESO), were used as an additive at a concentration of 3, 5, 7, and 9 (%w/w) of dry cellulose laurate.

4.1 Characterization and testing of cellulose powder

4.1.1 The optimum conditions for esterification reaction of cellulose laurate under conventional heating and microwave heating methods.

The optimum conditions of esterified cellulose were investigated by %weight increase (WI) and degree of substitution (DS). The effects of the reaction conditions on %weight increase and DS of cellulose laurate by conventional heating and microwave heating methods are presented in Figure 4.2 and 4.3, respectively

The weight increase of esterified cellulose was measured by weighing the cellulose powder before and after esterification. The percentage weight increase of cellulose laurate was calculated using the following equation:

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

Where W_f = final weight of sample after esterification (g)
W_i = initial weight of sample before esterification (g)

The degree of substitution (DS) of esterified cellulose was evaluated by ^{1}H-NMR investigation of aliphatic chain protons and cellulosic sugar protons intensity, calculated from the following equation [35]:

$$DS = \frac{10 \times I_{CH3}}{3 \times I_c + I_{CH3}}$$

In which:

I_{CH3} = methyl protons integration
I_c = carbohydrate protons integration

The H-NMR spectra of cellulose laurate (**Figure 4.2**) showed peaks between 0.9 and 2.3 ppm, corresponding to the alkyl groups of lauric chain, and peaks of the anhydroglucose unit of cellulose between 3.5 and 5.5 ppm **(Table 4.1)**.

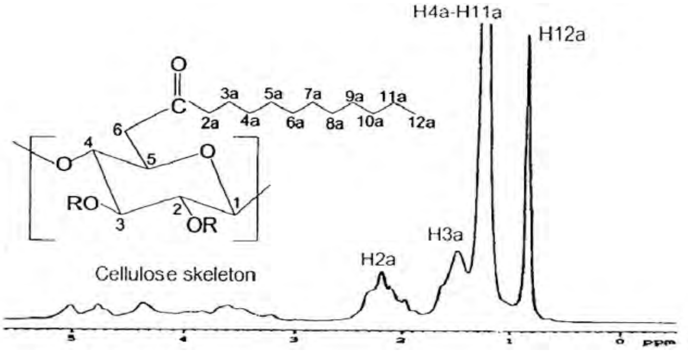
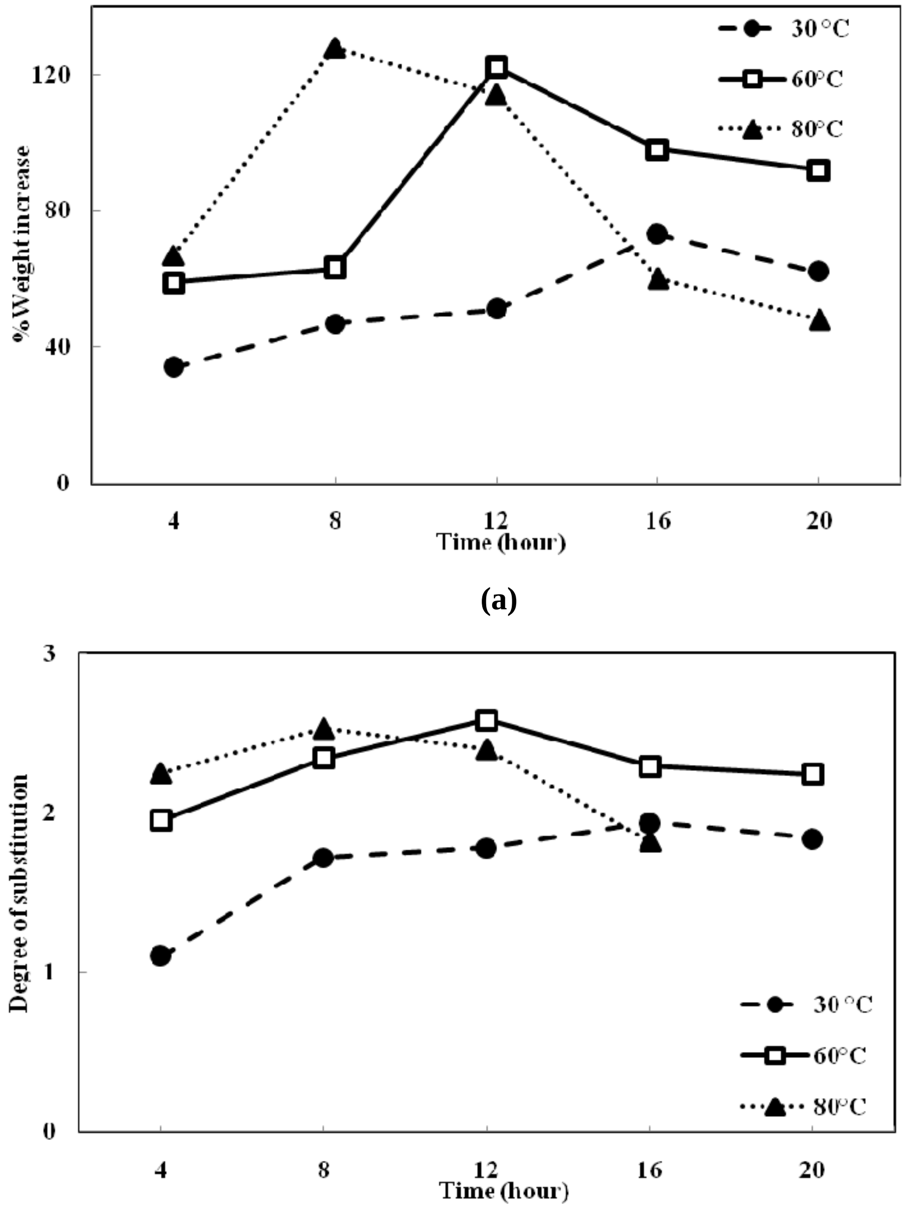


Figure 4.2 ^{1}H-NMR signal of cellulose laurate

Table 4.1 ^{1}H-NMR signal of cellulose laurate [38]

Anhydroglucose Unit		Lauric Chain	
Position	δ(ppm)	Position	δ(ppm)
1	4.3		
2	4.8	2	2.3
3	5.0	3	1.6
4	3.6	4-11	1.3
5	3.5	12	0.9
6	4.0		

The effects of the reaction conditions (i.e., temperature and time) on %weight increase and DS of cellulose laurate by conventional heating method were illustrated in **Figure 4.3.** Examples of how to calculate the DS values were presented in an Appendix (A1).



(a)

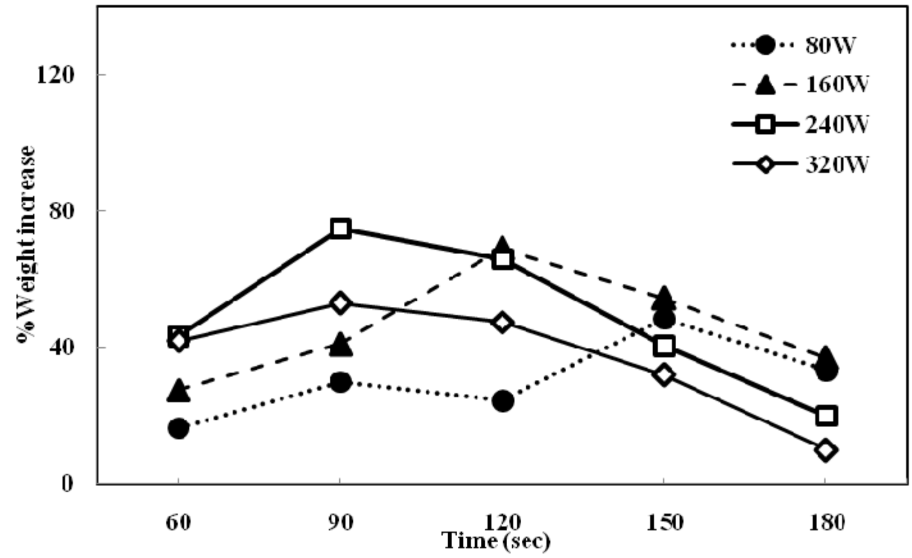
(b)

Figure 4.3 Relationship between (a) %weight increase and (b) degree of substitution (DS) of cellulose laurate and time (hour) at various reaction temperatures.

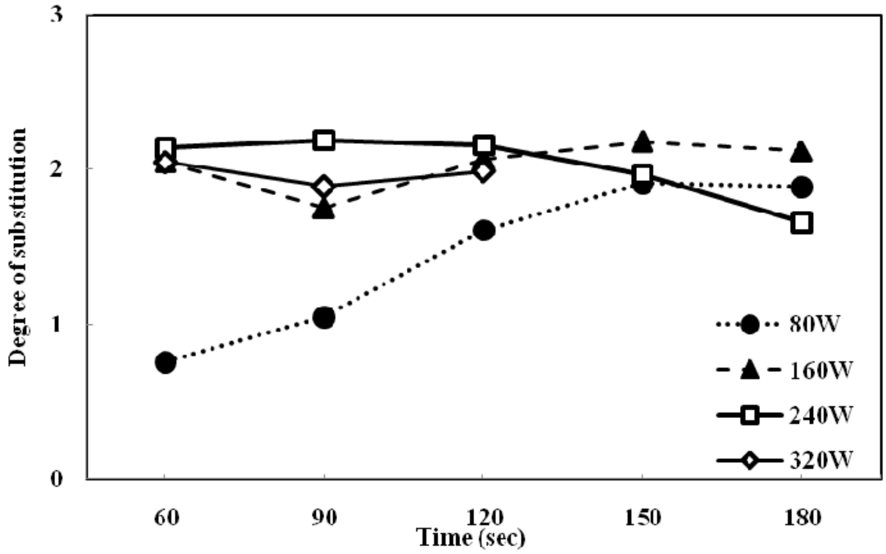
As shown in **Figure 4.3(a)** %weight increase of cellulose laurate increased with increasing reaction time and temperature. The maximum % weight increase value at the reaction temperature of 30 °C, 60 °C, and 80 °C was 73%, 122%, and 128% which were achieved at 16, 12, and 8 hours of reaction time, respectively. Clearly, the results showed that the higher the reaction temperature, the lower the reaction time required to yield the maximum %weight increase value. Similar trend was also found for the degree of substitution as shown in **Figure 4.3(b)**. The DS value of cellulose laurate increased with increasing reaction time and temperature. The maximum DS value at each reaction temperature (1.94, 2.58, and 2.53 for 30°C, 60°C, and 80°C, respectively) occurred coincidentally at the same reaction time of %weight increase. The reason for this enhancement of esterification reaction with increasing temperature and time was probably due to the favorable effect of temperature on mobility of the reactant molecules, diffusion of acid chloride into the cellulosic molecules, and swellability of the cellulose.

However, after reaching the highest value, %weight increase and DS values turned to decrease with increasing of reaction time and temperature. For example, the %weight increase values at the reaction time of 12 hr were 51%, 122%, and 114%; whereas the DS values were 1.78, 2.58, and 2.40 at the reaction temperature of 30°C, 60°C, and 80°C, respectively. The decrement in %weight increase and the degree of substitution at the higher temperature and longer reaction time could be denoted that the excess reaction time and temperature can cause the degradation of cellulose laurate as evidenced by the color change of the cellulose laurate powder. Before approaching the maximum reaction temperature or time, the cellulose laurate powder was seen as white fine powder; however, after that due to the excess energy, the degradation occurred resulted in the brown color of cellulose laurate.

For microwave heating method, the effects of various reaction power (watt) and time (second) on %weight increase and DS value of cellulose laurate were presented in **Figure 4.4**



(a)



(b)

Figure 4.4 Relationship between (a) %weight increase and (b) degree of substitution (DS) of cellulose laurate and time(sec) at various microwave power.

Similar to the conventional heating, **Figure 4.4(a)** shows that %weight increase of cellulose laurate enhanced as a function of microwave power and reaction time until it reached the maximum value and then dropped. The maximum values of % weight increase for microwave power of 80, 160, 240 and 320 watt occurred at 150, 120, 90, and 90 seconds were 49%, 69%, 75%, and 53%, respectively, and after that %weight increase of cellulose laurate decreased with the increasing of reaction time. At microwave power of 320 watt, %weight increase was less than that at the microwave power of 240 watt because of the partial degradation of cellulose laurate. Increasing microwave power and time resulted in an increase in the temperature; as a result, the degradation of cellulose laurate occurred, as evidenced by the development of a light brown color.

The effect of microwave power and reaction time on the degree of substitution for cellulose laurate was illustrated in **Figure 4.4(b)**. The degree of substitution of cellulose laurate increased with increment of power and reaction time. For example, at the constant microwave power of 240 watt the degree of substitution, at the reaction time of 60, 90, 120,150, and 180 seconds were 2.14, 2.19, 2.16, 1.97, and 1.66, respectively. At this microwave power the maximum DS value (2.19) was obtained at 90 seconds, after that the DS value continuously declined. Similarly, at 90 seconds, the degree of substitution was increased from 1.05, 1.75, and 2.19 when microwave power was raised from the 80 watt to 160 and 240 watt, respectively. Upon increasing the microwave power to 320 watt, the degree of substitution was found to be decreased.

The decrement of %weight increase and degree of substitution of cellulose laurate after it reached the optimum value was resulted from the excess microwave power. The overheating of microwave power led to an increase in the temperature of esterification reaction, causing the degradation of cellulose laurate as confirmed by a brown color of cellulose laurate powder and a drop in% weight increase and degree of substitution.

From the above results, the suitable condition for esterification reaction of cellulose laurate was chosen from the maximum value of %WI and degree of substitution without the degradation of cellulose. The maximum %WI and DS values of cellulose laurate are summarized in **Table 4.2**. As shown, the appropriated condition which yielded the maximum DS value (2.58) and suitable % weight increase (122) for conventional heating was at 60°C for 12hr; whereas the optimum condition (i.e, highest DS and %WI values) for microwave heating was 240 watt at 90 seconds.

Table 4.2 Maximum value of degree of substitution (DS) and %weight increase (WI) of modified cellulose under conventional and microwave heating

Heating method	Reaction condition	DS	%WI
Conventional heating	80 °C, 8 hours	2.53	128
	60 °C, 12 hours	2.58	122
Microwave heating	240 watt, 90seconds	2.19	75

Although the esterification reaction under conventional heating takes longer time, the results revealed that the obtained cellulose laurate had higher DS and %WI values, which were contributed to the properties of the cellulose laurate films as will be discussed later

]

4.1.2 Chemical structure of cellulose

Functional groups of cellulose before and after esterification were monitored by FTIR spectra. The effect of heating method on chemical structure of esterified cellulose **is** presented in **Figure 4.5**. The infrared analysis before and after esterification proved that chemical changes had occurred in the cellulose structure. These spectra showed the existance of the ester carbonyl group stretching at 1746 cm^{-1}(C=O). The occurrence of two peaks of strong intensities at 2924 and 2853 cm^{-1} in the spectra is attributed to the methyl and methylene C-H stretching associated with the lauroyl substituent. The decrease in the intensity of strong band at 3345 cm^{-1}of the hydroxyl group indicated the substitution of long chain fatty acid chloride on the celullose structure. The heating methods had no effect on the chemical structure of modified cellulose. Similar results can be observed for cellulose laurate prepared from conventional heating and microwave heating methods.

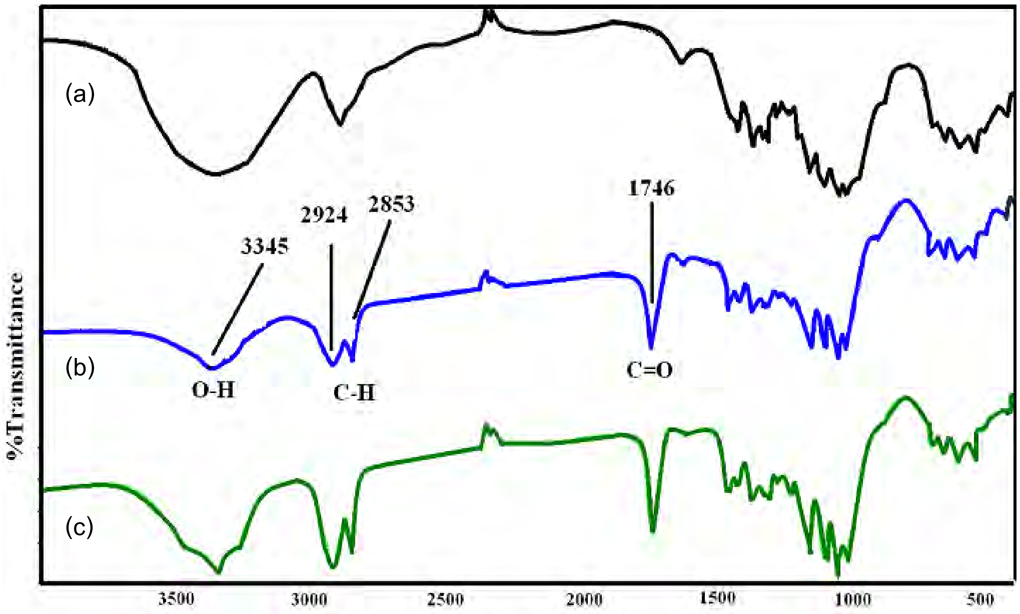


Figure 4.5 FT-IR spectra of cellulose (a) before and after esterification under (b) conventional and (c) microwave heating methods

4.1.3 Thermal properties

4.1.3.1 Thermogravimetric analysis (TGA)

The degradation temperature (Td) of cellulose before and after esterification was determined by thermogravimetric analysis as presented in **Figure 4.6**.

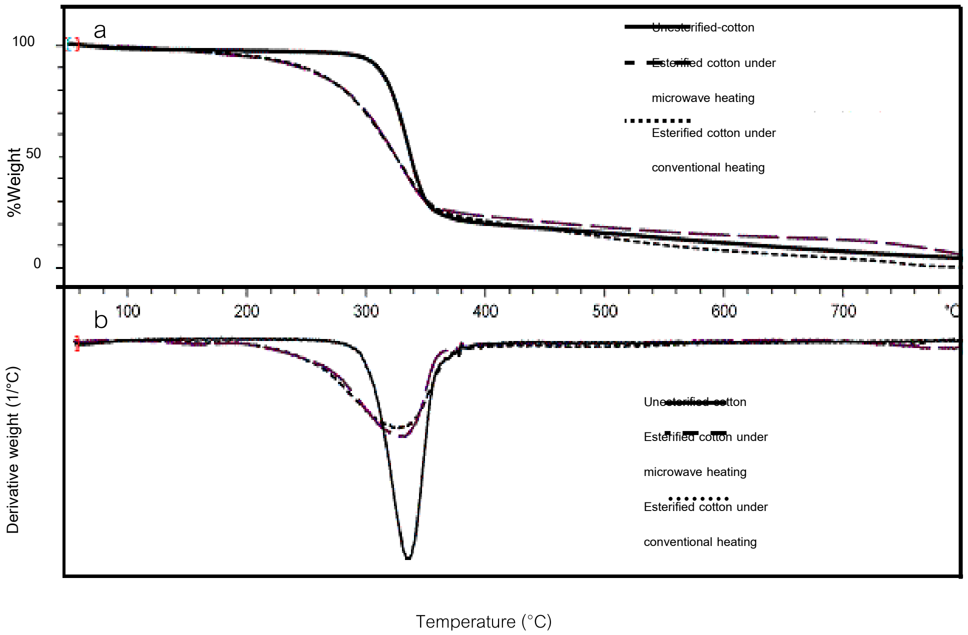


Figure 4.6 TGA (a) and DTG (b) thermograms of cotton cellulose powder before and after esterified under conventional and microwave heating methods.

Before esterification, the cellulose showed two steps of weight loss. The first step occurred around 60-90°C with about 1.65% of weight loss corresponding to the moisture decomposition in cellulose. While the second step exhibited thermal decomposition temperature at 312°C was resulted from the cellulose degradation. For the modified cellulose, the thermograms showed single step of weight loss. The onset of degradation temperature of the modified cellulose under conventional and microwave heating methods occurred around 241°C and 266°C, respectively. Obviously, the modified cellulose started to decompose at a temperature substantially lower than the unmodified cellulose. This behavior was probably attributed to the decrease in crystallinity associated with an acyl substitution of long chain aliphatic on hydroxyl groups of cellulose [40].

The differences in Td onset of both films was believed due to the effect of the degree of substitution. Higher the DS, higher is the decrystallization of cellulose. Since the esterified cotton under conventional heating had higher DS value (DS = 2.58), it exhibited lower crystallinity; as a result, it started to decompose at lower temperature. In other words, the esterified cellulose with lower DS value (under microwave heating) essentially preserved the characteristic of the unesterified cellulose. The lower in crystallinity of esterified cellulose under conventional heating with higher DS value, suggested by the TGA thermogram, was confirmed by the XRD pattern as will be discussed later.

The esterified cellulose under both heating methods presented one step of weight loss. The disappearing of step change of absorbed moisture was because substitution with alkyl groups reduced the number of free hydroxyl groups of cellulose to form hydrogen bondings with moisture. Substituent disturbs the inter- and intra molecular hydrogen bonds in cellulose, which leads to liberation of the hydrophilic character of the numerous hydroxyl groups and restriction of the chains to closely associate.

However, The degradation profiles of cellulose esters obtained in this work is difference from what would be expected and earlier reported by Frier et al in 2006 [40], who observed two main separate degradation steps at 240 – 290 °C and 315 -360 °C. The first degradation step was attributed to the esterified to the nonmodified cellulose. Nevertheless, our result was in agreement with the report from Jundura et al; [44] they also observed one main degradation step at 200 – 300 °C. The differences in this behavior was suggested by Freire et al that they were not related with the heating rate used.

4.1.3.2 Differential scanning calorimetry (DSC)

Thermal transition temperature was characterized by a differential scanning calorimetry (DSC). Glass transition temperature (Tg) values of cellulose and modified cellulose were reported the midpoint of the heat capacity change in the glass transition region during the second heating scan.

The second heating scans for the DSC thermograms of unesterified cellulose and esterified cellulose under conventional and microwave heating methods are presented in **Figure 4.7.** Thermogram of unesterified cellulose reveal distinct transition that occurring at a temperature of 100.47 °C, while the second order-transition temperature of esterified cellulose under conventional and microwave heating method are 46.82 °C and 78.23 °C, respectively.

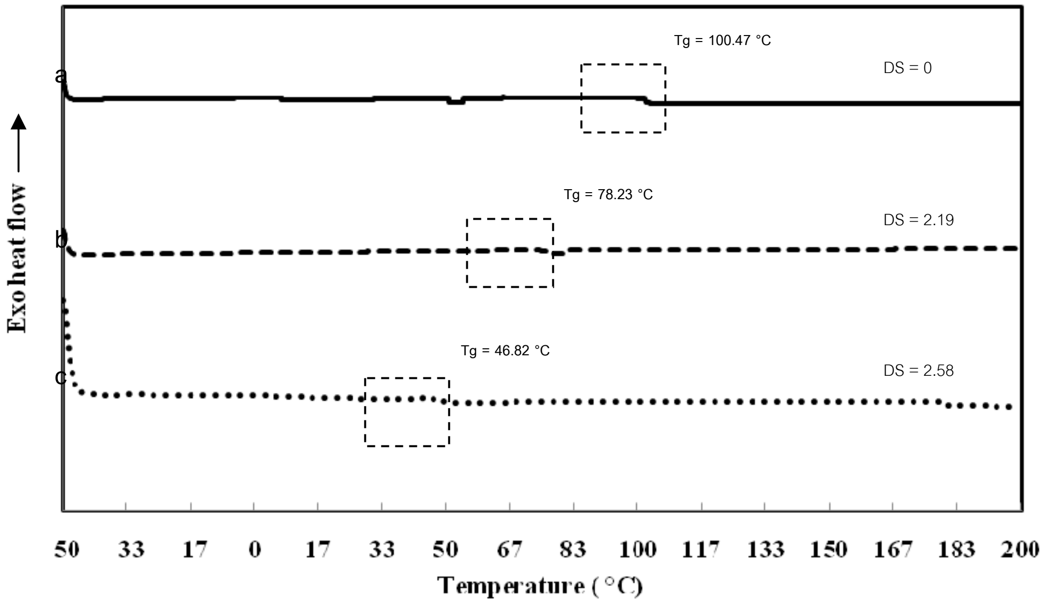


Figure 4.7 DSC heating scan of (a) cellulose; (b) esterified cellulose under microwave heating; (C) esterified cellulose under conventional heating.

The second-order transition of unesterified cellulose shown higher Tg value than esterified cellulose, because the structure of unesterified cellulose consists of a lot of hydroxyl groups which can form intra-and intermolecular hydrogen bond; as a result, it has high crystallinity; therefore cellulose must be heated to a high temperature before the polymer has acquired enough free volume to allow fast movement of the segments, and Tg will accordingly be high.

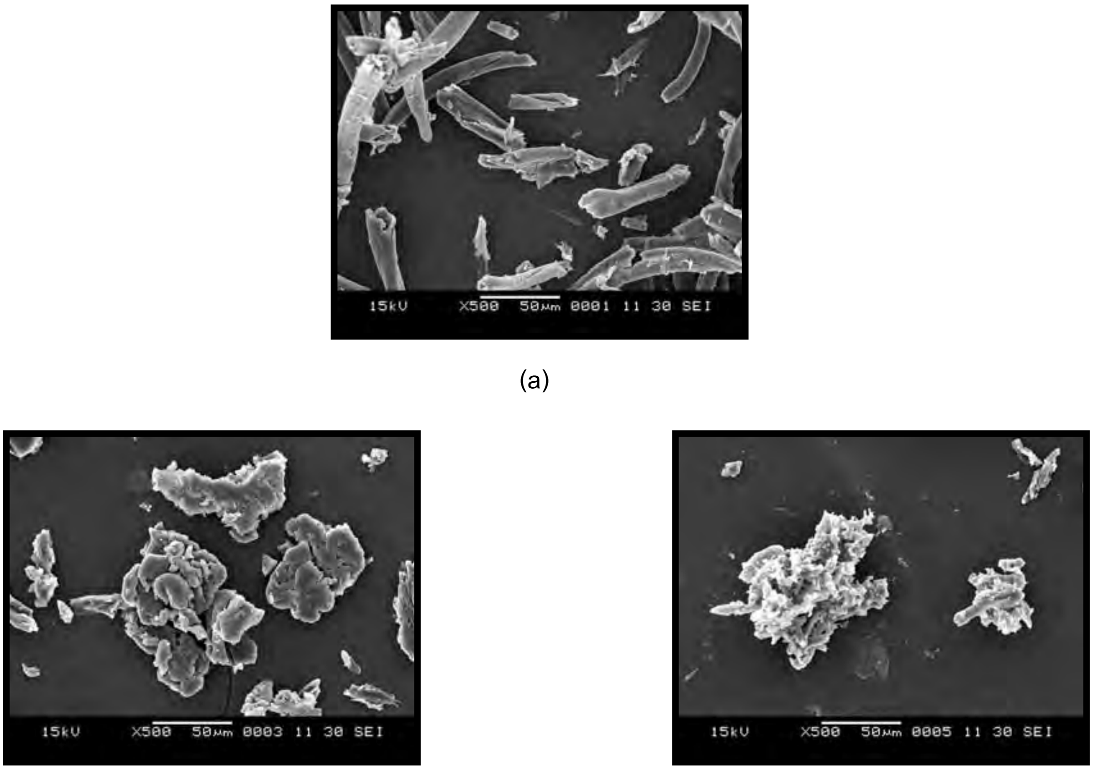
The second-order transition found in thermal transition of esterified cellulose was designated as Tg of cellulose laurate that occurred from long-chain substitution of lauroyl chloride at hydroxyl groups of cellulose, causing an increase in amorphous region and a decrease in the crystalline structure of cellulose. After esterification, the Tg decrease due to increased spacing between cellulose chains and dilution of secondary bonding, increasing the mobility of cellulose chains so called a plasticization effect

The esterified cellulose under conventional heating method presented Tg value which was lower than the Tg of esterified cellulose under microwave heating method. Similar to the degradation temperature previously described, the transition temperature behavior can be explained in terms of the degree of substitution. The acyl substituent on hydroxyl groups of cellulose destroys or decreases the crystallization of hydrogen bond in esterified cellulose. Thus, higher DS value means higher the decrystallization of cellulose since the esterified cellulose under conventional heating method (DS = 2.58) had higher degree of substitution than microwave heating method (DS=2.19), it exhibited more amorphous structure. The intermolecular bonds along the cellulose chain were far apart, resulting in increasing of free volume and chain mobility; as a result, its Tg was lowered.

However, the DSC scans were limited to a maximum temperature of 200°C to avoid sample decomposition since the thermal decomposition temperature ranged from 241-266°C. Beside, from the literature, it was found that and our previous work Pattananuwat [27] and Sealey et al [11] Tm of esterified cellulose can be detected from the third heating scan. Nevertheless, its endotherm peak (Tm) was barely visible at -15°C, which was attributed to melting of side-chain crystals designated as Tm,l or low-temperature endotherm. This side-chain crystallization generally occurred in linear aliphatic esters of cellulose when the ester substituent is 12 or more carbon atoms in length.

4.1.4 Morphological studies

Scanning electron microscope was used to characterize any changes regarding the surface morphology of cellulose. After hydrolyzed, as seen by naked eyes, the cellulose was in a white powder form. However, under microscope (**Figure 4.8**), it can be seen that unesterified cellulose appeared as a short fiber shape with its diameter approximately 12 µm and had smooth surface. After esterification, its size becomes bigger, having some agglomeration and rough surface. The difference in morphology between before and after esterified cellulose was resulted from the acyl substitution of lauroyl chloride leading an aggregation of acyl group on the cellulose surface. No significant effect between heating methods on the surface of cellulose laurate was observed.



(a)

(b) (c)

Figure 4.8 SEM micrographs of (a) unesterified-cellulose (b) cellulose esterified under conventional heating (at 60°C, 12 hour), (c) cellulose esterified under microwave heating (at 240 watt at 90 seconds)

4.2 Characterization and Testing of Cellulose Film

The cellulose laurate powder from both heating methods (i.e., conventional and microwave) was converted into plastic film by casting method, used triethyl citrate (TEC), dibutyl phthalate (DBP), and epoxidized soy bean oil (ESO) as the plasticizer. The films from cellulose laurate powder prepared under conventional heating and microwave heating are called in this thesis as CH and MH, respectively.

4.2.1 Physical properties

4.2.1.1 Appearance of cellulose laurate films

As a qualitative observation, the appearance of all plasticized cellulose laurate films is shown in **Figure 4.9** and **4.10**. Unplasticized CH film was homogeneous, transparent, and brittle. While the unplasticized MH film was opaque, rigid, and brittle and had some white spots spreaded on the film surface. The CH films contained less insoluble particles compared to MH films. The transparent and homogeneous of CH films structure resulted from the better solubility of CH powder in chloroform solvent.

The solubility of esterified cellulose is depending on the degree of substitution. The substitution of acyl substitutions leads to the destruction of highly organized hydrogen-bonding of cellulose structure, resulted in an increasing of its solubility in chloroform. Since the MH powder (DS=2.19) had lower degree of substitution value than the CH powder (DS=2.58); as a result, its solubility in chloroform was poorer leading to the film with such appearance similar results were reported by Fang et al [36] that the hydrophobic acyl groups in the molecular structure of hemicelluloses would be expected to alter the solubility properties. Interestingly, the esterified hemicelluloses are considerably more hydrophobic than the nature hemicelluloses. Presence of acyl groups in the cellulose molecules may open the structure of celluloses. This together with the physical changes in the hemicelluloses structure and molecular degradation occurring during esterification would act in favor of solubility.

Another possible explanation of the difference in the transparency of CH and MH films is probably due to higher crystallinity of the MH films resulting in white and opaque film as evidenced by WAXD patterns which will be discussed shortly. Generally, amorphous polymers tend to be transparent whereas crystalline polymers are translucent or opaque. This is because the crystalline regions will have a different refractive index from the amorphous regions and hence will refract light.

After plasticization, all plasticized CH and MH films were a homogeneous and had smooth surface. Particularly, they were softer compared to the unplasticized films. The homogeneous films structure resulted from both compatibility of the plasticizer with the polymer and the suitability of chloroform as a solvent for both polymers.

At low plasticizer content (3%), both CH and MH films were still brittle; however; upon increasing plasticizer concentration, the plasticized films become softer. Nevertheless, at high DBP content (9%), the MH films become softer and turned to be white and opaque, referring to blooming. This may be occurs when the plasticizer concentration exceeds its compatibility limit in the polymer causing phase segregation and physical exclusion of the plasticizer.

The reason that plasticized films were softer with increasing plasticizer concentration is that a plasticizer can penetrate into the amorphous areas of the rigid polymer and disrupt intermolecular attractions. When a sufficient amount of plasticizer has entered this matrix, a general relaxation occure, and partial mobility is imparted to the polymer chains, thereby weakening the polymer intermolecular attractions and increasing the polymer’s free volume. Effective plasticization leads to a decrease in the glass transition temperature of the polymer. Both plasticized CH and MH films could be easily separated from the casting plates when increasing of plasticizer concentration.

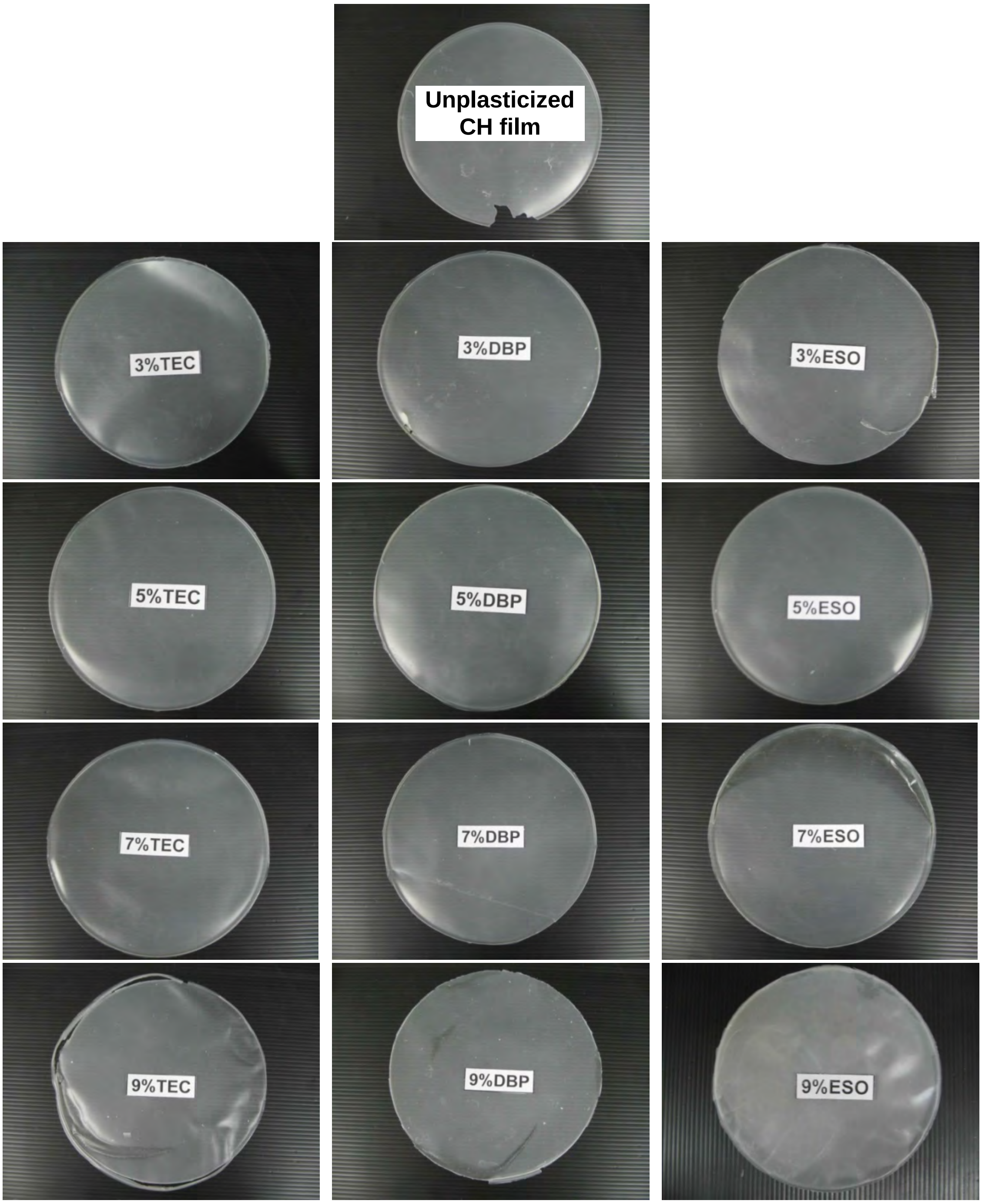


Figure 4.9 Appearance of unplasticized and plasticized CH films at 3%, 5%, 7%, and 9%w/w.

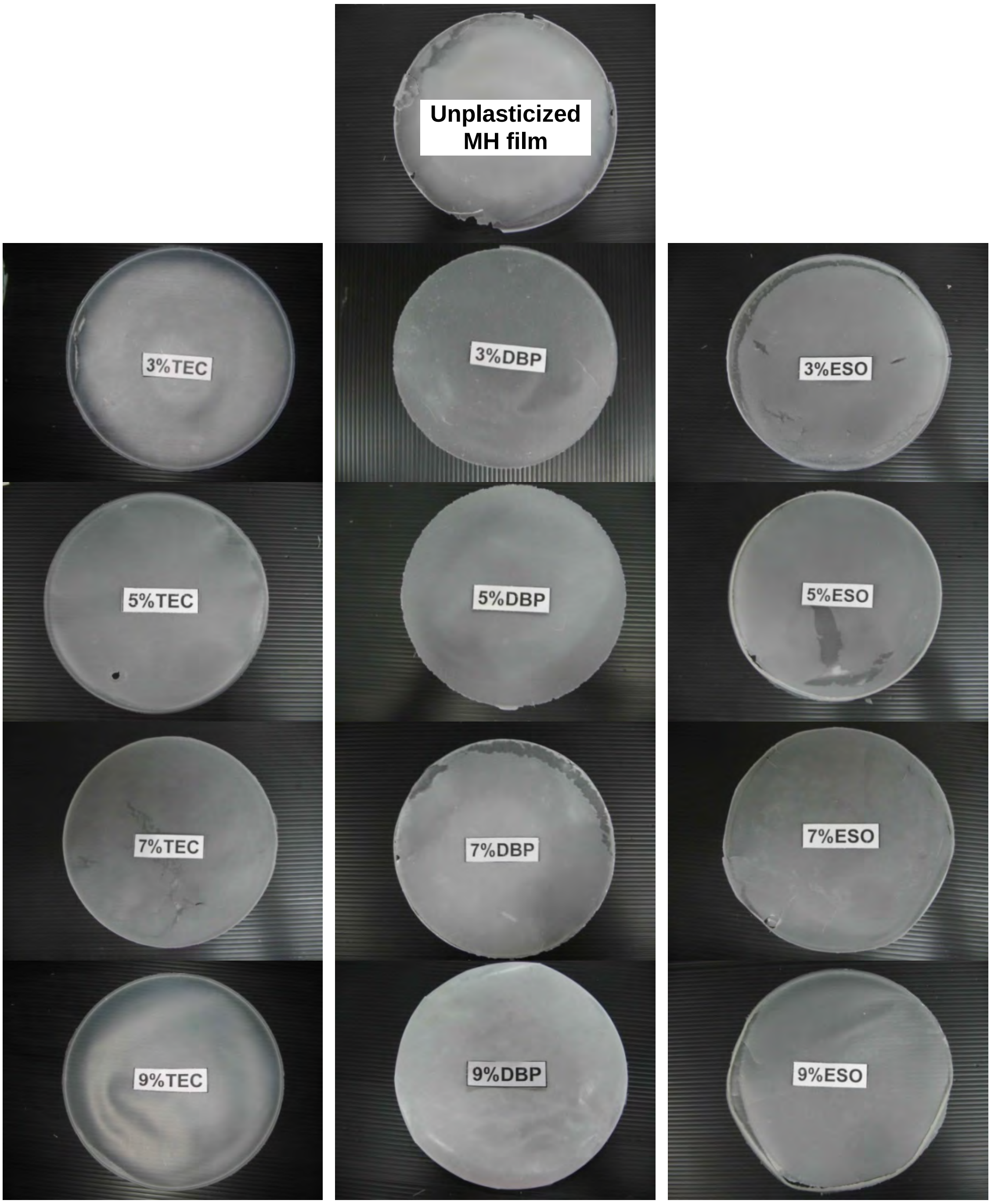


Figure 4.10 Appearance of unplasticized and plasticized MH films at 3%, 5%, 7%, and 9%w/w.

4.2.1.2 Morphological studies

The cellulose films plasticized with 5%w/w TEC, DBP, and ESO were selected for the observation of the fractured surface, and their morphologies were compared using scanning electron microscopy (SEM). The result is shown in **Figure 4.11** and **4.12.**

The morphology of the fractured surface of CH and MH films was different. The fractured surface of CH films showed the relatively smooth and homogenous surface. On the other hand, the MH films had a surface roughness, uneven and small porous. This difference is probably due to the degree of substitution in which the microwave assisted esterified-cellulose laurate had lower DS value than its counterpart leading to the lower solubility in chloroform; as a result the MH films exhibited rougher fractured surface.

This surface character was altered by the addition of plasticizer. The result of CH and MH films revealed that both CH and MH films plasticized with TEC, DBP, and ESO shows improve compatibility, uninterrupted and homogenous.

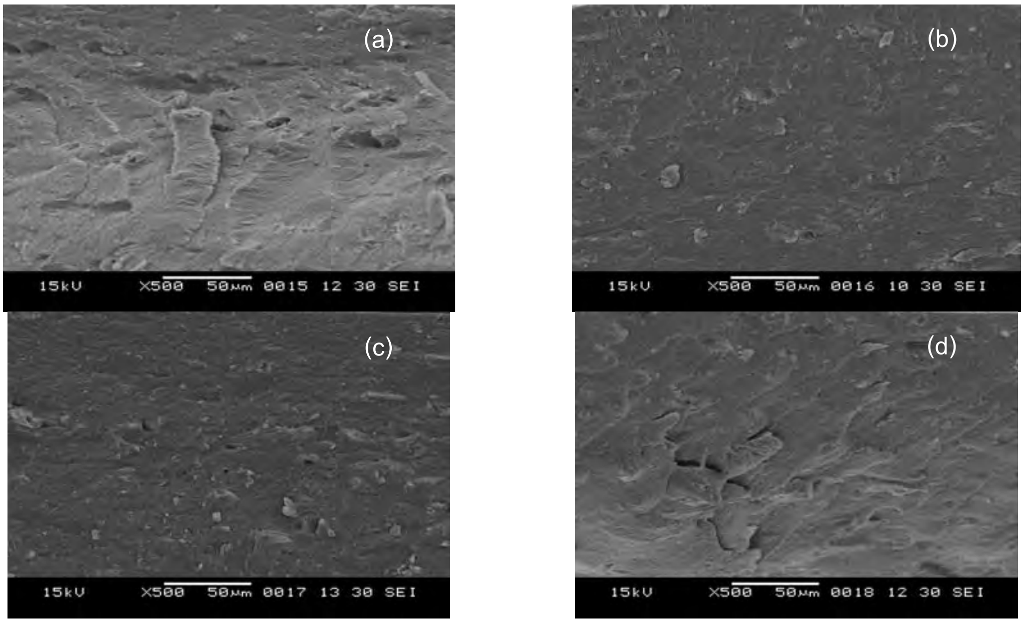


Figure 4.11 Cross-section scanning electron micrographs of (a) CH films and CH films plasticized with (b) TEC, (c) DBP and (d) ESO of 5%w/w.

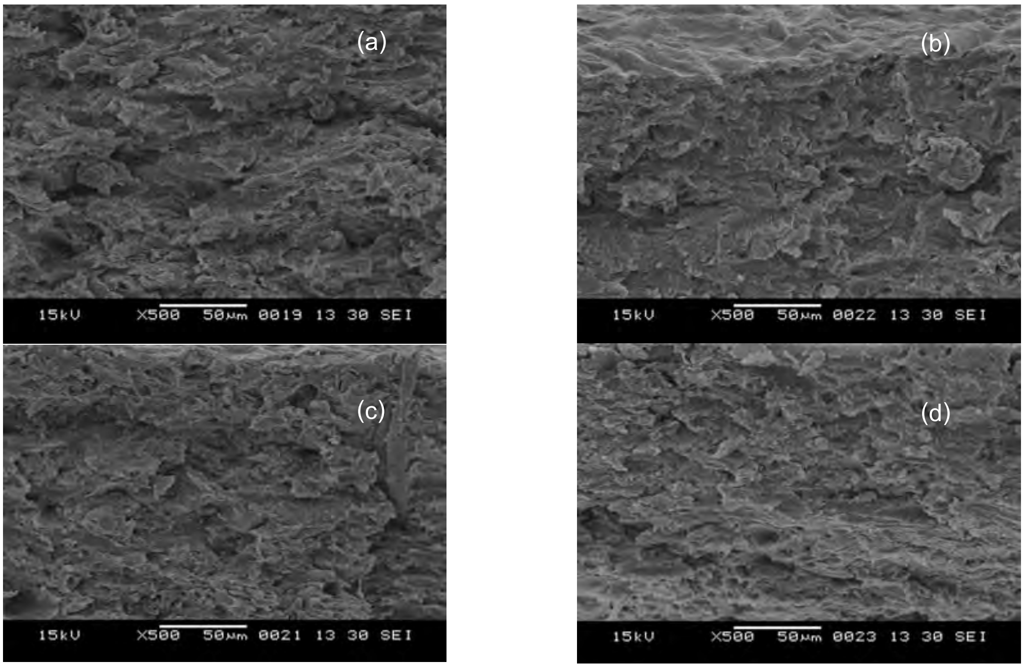
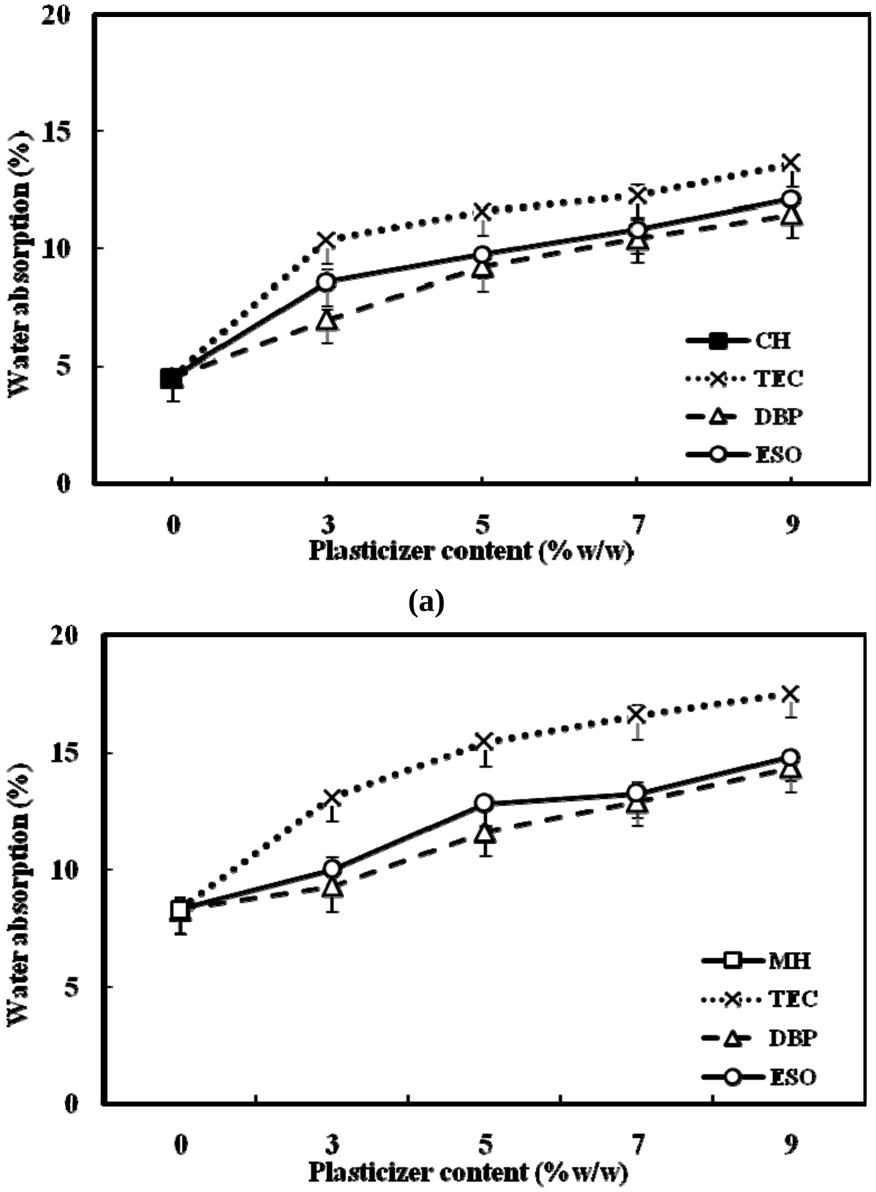


Figure 4.12 Cross-section scanning electron micrographs of (a) CH films and CH films plasticized with (b) TEC, (c) DBP and (d) ESO of 5%w/w.

4.2.1.3 Water absorption

The results revealed that both type and content of plasticizer had great effect on the %water absorption values of CH and MH films (**Figure 4.13** (a) and (b)).



(a)

(b)

Figure 4.13 Effect of type and content of plasticizer on %water absorption of (a) CH and (b) MH films.

The plasticized and unplasticized CH films gave lower %water absorption than the plasticized and unplasticized MH films. As shown, the %water absorption of unplasticized CH film was 4.53% whereas that of unplasticized MH film was 8.29%. The difference in %water absorption of CH and MH films was expectedly attributed to the degree of substitution value. The hydroxyl groups of cellulose were partially replaced by long chain fatty acid of acyl substitutions to produce cellulose laurate. The esterification with fatty acid chloride enhanced the hydrophobic character of the cellulose. The higher degree of substitution of cellulose laurate; the greater hydrophobicity or the lower the ability to absorb water. Since the degree of substitution value of CH (DS = 2.58) was higher than that of MH (DS=2.19); as a result, the CH films can absorb lower amount of water. In other words, higher degree of substitution value means that the hydroxyl groups of cellulose were greatly replaced by long chain aliphatic of lauric chain; therefore, the ability to form hydrogen bondings with water was decreased.

Regarding the effect of plasticizer, the water absorption values of both CH and MH films increased with increasing of plasticizer content. The increase in water absorption values of plasticized films could be caused by a plasticizing effect that the plasticizers work by embedding themselves between the chains of polymers and, spacing them apart (increasing the “free volume”). As a result, the intermolecular forces along polymer chains thus are decreased, increasing the diffusion of the water molecules into the polymeric matrix.

Comparing among three types of plasticizer, both CH and MH films plasticized with TEC gave higher water absorption values when comparing to the other plasticizers. At highest plasticizer content (9%), the CH and MH films plasticized with TEC can absorb water as high as 13.66% and 17.55%, respectively. This is because TEC is hydrophilic and has a free hydroxyl group that can form hydrogen bondings with water, while DBP and ESO are insoluble in water [48]. Films containing more hydrophilic plasticizer (TEC) absorbed considerably higher water absorption values than the hydrophobic plasticizer (DBP and ESO). The addition of TEC in cellulose laurate films provides more active sites by exposing its hydrophilic hydroxyl group in which the water molecule could be adsorbed. Water exerted a plasticizing effect acting as a mobility enhancer; its low molecular weight leads to a large increase in molecular mobility of amorphous and partially crystalline polymers resulting in an increased free volume, thus decreasing glass transition of films as will be discussed later.

4.2.1.4 Crystallinity

Crystallinity determines the flexibility of the molecular chains of polymers. X-ray diffractograms were used to observe the crystallinity of cellulose laurate film. X-ray diffraction patterns of CH and MH films are shown in **Figure 4.14.**

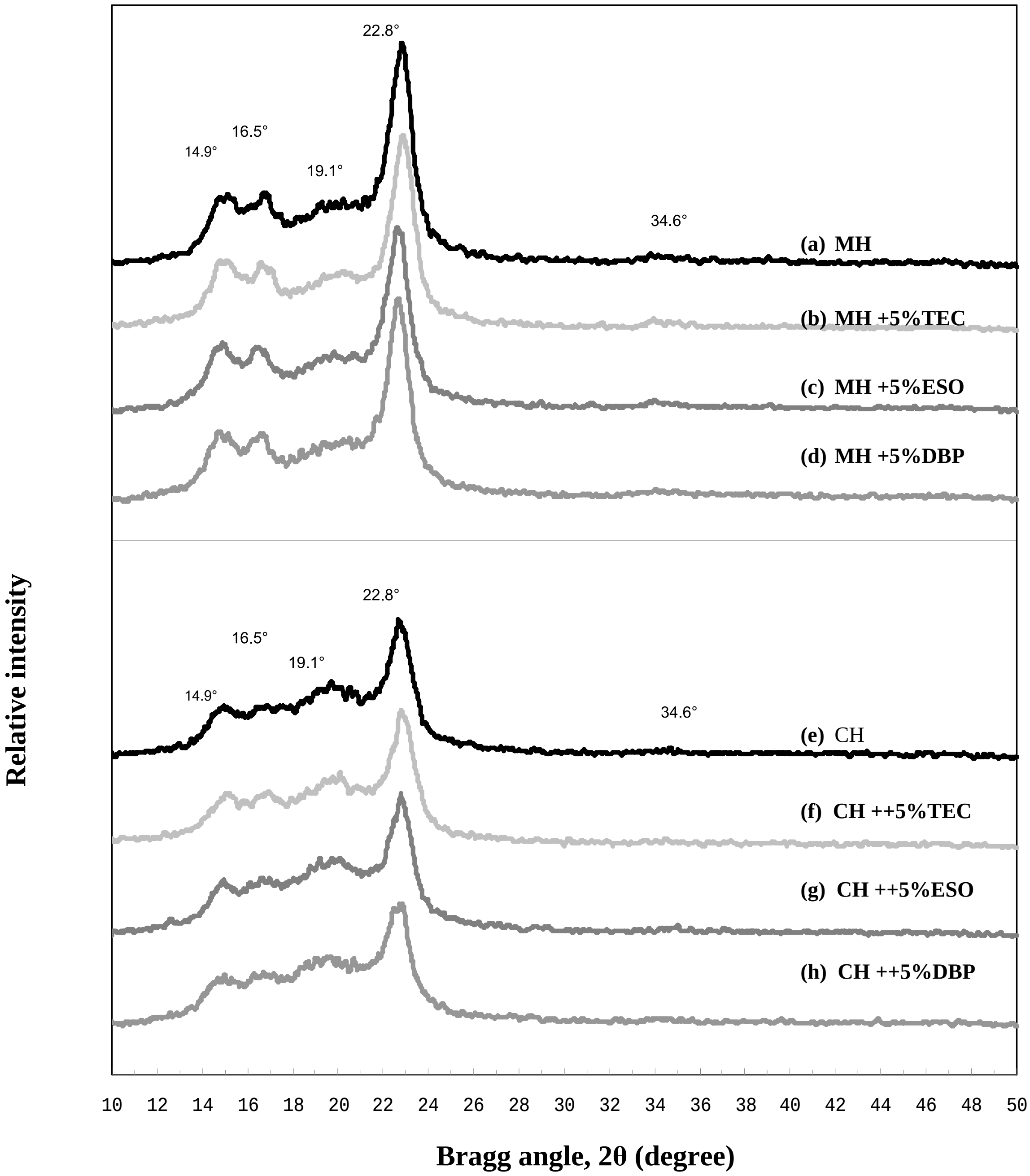


Figure 4.14 X-ray diffraction patterns of cellulose laurate films

The diffractograms of unplasticized cellulose laurate films (CH and MH) present in **Figure 4.14** (a) and (e) show the crystalline peaks (2θ) at 14.9°, 16.5°, and 22.8° degrees and the amorphous region of cellulose at around 18° which is attributed to the less-ordered region of cellulose chains. However, as reported by Freire et al. [40], perhaps a new ordered region associated with the cellulose esters, with peaks appearing at diffraction angles between 18° and 20°, should also be taken into account.

Comparing between the MH and CH films, it was found that the MH film had higher crystallinity than the CH film, as indicated by sharper reflection with higher intensity at 22.8°, 16.5°, and 14.9°. On the other had, The CH film showed broader amorphous region at 19.1° (or perhaps a new well-ordered ester) confirming that the CH film had higher amorphous than MH films. The differences in the crystalline structure of esterified-cellulose depended on the degree of substitution obtained. In other words, the degree of substitution value had effect on the crystalline structure of cellulose laurate films. The increase or greater in the DS value of cellulose laurate ester enhanced the decrystallization of cellulose or increased amorphous region in cellulose ester by decreasing the hydrogen bondings between cellulose ester molecules. Since the CH film had higher DS value(DS=2.58) than the MH film(DS=2.19), its XRD pattern showed lower intensity of the crystalline peaks and higher of diffraction intensity in the amorphous region.This result supported the appearance of CH and MH films that the transparency of CH films was due to the lower crystallinity.

The crystallinity of plasticized cellulose laurate films were revealed from the diffractograms illustrated in **Figure 4.14** (b, c, d, f, g, and h). The plasticizing effect of both CH and MH was seemingly similar. Comparing to the unplasticized cellulose laurate films, the X-ray pattern of plasticized cellulose laurate films showed slightly decrease in the crystallinity of films as in dictated by a lower peak at 22.8°. However, the changes in the X-ray diffraction patterns of plasticized cellulose laurate films are very small, probably because of the lower content plasticizer in cellulose laurate, as a result, the sensitivity of X-ray diffraction is quite low.

4.2.2 Tensile properties

The mechanical properties of films were measured in terms of tensile strength, Young’s modulus, and % elongation at break according to ASTM D882. The results are shown in **Table 4.3.**

Table 4.3 Tensile properties of cellulose laurate films

Sample	Plasticizer (%)	Tensile properties (MPa)	Young's Modulus (MPa)	%Elongation at break
CH	0	7.73 ± 0.94	397.80 ± 60.09	6.80 ± 1.03
TEC	3	5.79 ± 0.08	277.19 ± 26.00	10.88 ± 0.91
	5	6.10 ± 0.34	285.21 ± 51.74	14.57 ± 1.08
	7	4.82 ± 0.52	246.03 ± 73.87	11.08 ± 1.67
	9	3.39 ± 0.44	249.20 ± 48.00	4.74 ± 0.67
DBP	3	5.38 ± 0.30	261.38 ± 19.77	7.35 ± 0.34
	5	4.75 ± 0.23	257.80 ± 61.62	7.57 ± 1.96
	7	4.37 ± 0.21	227.03 ± 22.01	9.26 ± 0.73
	9	3.09 ± 0.16	213.42 ± 30.45	4.28 ± 0.41
ESO	3	5.32 ± 0.18	263.87 ± 41.40	8.87 ± 1.14
	5	5.96 ± 0.30	258.73 ± 66.52	12.07 ± 2.11
	7	5.28 ± 0.20	213.01 ± 7.96	11.86 ± 1.67
	9	3.75 ± 0.55	234.42 ± 38.35	4.88 ± 1.14
MH	0	5.10 ± 0.17	746.97 ± 163.77	1.87 ± 0.12
TEC	3	4.99 ± 0.69	475.18 ± 98.33	3.17 ± 0.07
	5	4.92 ± 0.17	436.86 ± 27.48	3.76 ± 0.32
	7	3.95 ± 0.23	387.40 ± 44.29	3.05 ± 0.06
	9	3.61 ± 0.20	347.52 ± 44.78	2.82 ± 0.15
DBP	3	4.56 ± 0.34	542.95 ± 80.14	2.28 ± 0.07
	5	4.89 ± 0.47	456.77 ± 69.49	3.34 ± 0.14
	7	3.98 ± 0.45	424.16 ± 19.91	2.49 ± 0.17
	9	3.49 ± 0.23	369.33 ± 65.12	2.51 ± 0.10
ESO	3	4.47 ± 0.20	402.81 ± 35.52	3.25 ± 0.13
	5	4.58 ± 0.16	418.65 ± 66.61	3.69 ± 0.15
	7	3.90 ± 0.15	332.70 ± 37.40	3.10 ± 0.19
	9	3.63 ± 0.25	360.49 ± 29.23	2.79 ± 0.12

The CH films showed better mechanical properties than the MH films. Obviously,the CH films exhibited significant higher tensile stength and %elongation at break including lower Young's Modulus compared with the MH films. The tensile stength and %elongation at break values of the CH films were about 7.7 MPa and 6.8%; whereas, these of the MH films were 5.10 MPa and 1.87%, respectively.

These results might be explained by the degree of substitution of the CH (DS = 2.58) film which was higher than the MH film(DS = 2.19). The increasing of tensile strength as increasing of long-chain substitutent may be attributed to the partial crystallization and overlepping of C_{12} side chains in lauroyl chloride as esterifying agent, and the increasing of %elongation at break with degree of substitution 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 resulted in increasing of %elongation at break and decreasing Young’s modulus**.**

The effect of plasticizer content on the mechanical properties of the CH and MH films was investigrated. The results were shown in **Table 4.3** and **Figure 4.15**. Obviously, the effect of plasticizer on the CH films was more pronounced the MH films. Generally, an increase in plasticizer content resulted in weaker and more flexible films. This was reflected in a decrease in tensile strength and Young's Modulus and improves elongation at break value of films. The addition of plasticizer leads to decrease in intermolecular forces along polymer chain, increasing the mobility of the polymer chains, causing the mechanical strength of the films to be decreased and the extensibility enhanced. In our study, the expected effect of plasticizer on mechanical properties; i.e., increase elongation at break and decrease tensile strength and Young’s modulus, was observed for all plasticization systems of the MH and CH films.

Comparing among three types of plasticizer, it was found that the cellulose laurate films contain TEC had more %Elongation at break values than the films plasticized with ESO and DBP. The results from the elongation at break of plasticized CH and MH films indicated that the flexibility of the films increased in the order of TEC>ESO>DBP. For example, the maximum % elongation at break of CH films plasticized with TEC, ESO, and DBP was 14.57%, 12.07%, and 9.26% at a plasticizer content of and 5, 5, and 7(% w/w). For the MH films, the maximum %elongation at break of the films plasticized with TEC, ESO, and DBP was 3.76%, 3.69%, and 3.34% at plasticizer content of 5(%w/w).

To explain these results, the difference in molecular weight may be taken into account. Generally, plasticizer efficiency depends on its molecular weight; i.e., plasticizer efficiency increase with increasing molecular weight. In our study, the plasticizer efficiency follows the order TEC>ESO>DBP; whereas the molecular weight decreased following the order ESO (872.2 g/mol)> DBP (278.2 g/mol)> TEC (276.1 g/mol). Films contained TEC showed higher elongation at break than the films made with ESO and DBP suggesting that molecular features other than molecular weight as “molecular volume” may also influence the plasticizer efficiency. Since the TEC has a small molecular volume and it can diffuse into and interact with cellulose laurate chains and the chain segmental mobility was increased. Whereas, for ESO, although it has higher molecular weights than DBP and TEC, its lower efficiency than TEC is associated with increasing the molecular volume. ESO with higher molecular weight has a great number of segments, each chain; is too long and will tangle with the chains of polymer, thus impedes the interaction between the molecules of polymer themselves.

However, it was found that, an addition of 5 %(w/w) TEC could enhance elongation at break of the films; however, when the amount was more than 5 %(w/w), the mechanical properties of cellulose laurate films were decreased. This is probably due to the cellulose laurate film saturated with the plasticizer content.

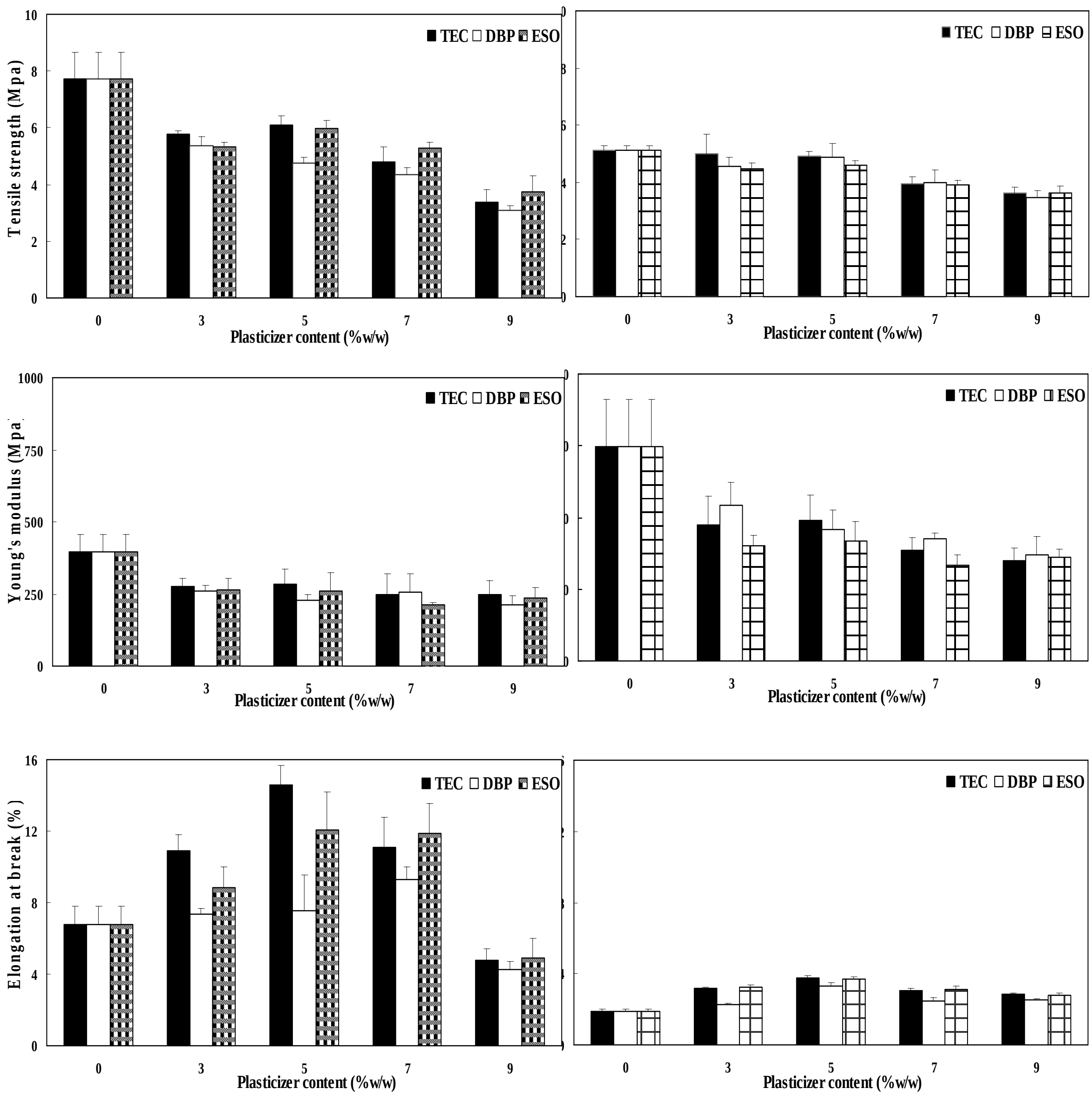


Figure 4.15 Effects of type and content of plasticizer on tensile properties of cellulose laurate films: CH (left) and MH (right) films

4.2.3 Thermal Properties

4.2.3.1 Thermogravimetric analysis (TGA)

The decomposition temperature (Td) of films was studied by TGA. The values of the onset of the decomposition temperature are vary important, since they could indicate the processing and manufacturing temperature without continuing or initiating a process of decomposition. The effect of type and content of plasticizer on decomposition temperature of the plasticized CH and MH films is summarized in **Table 4.4** and **Table 4.5**

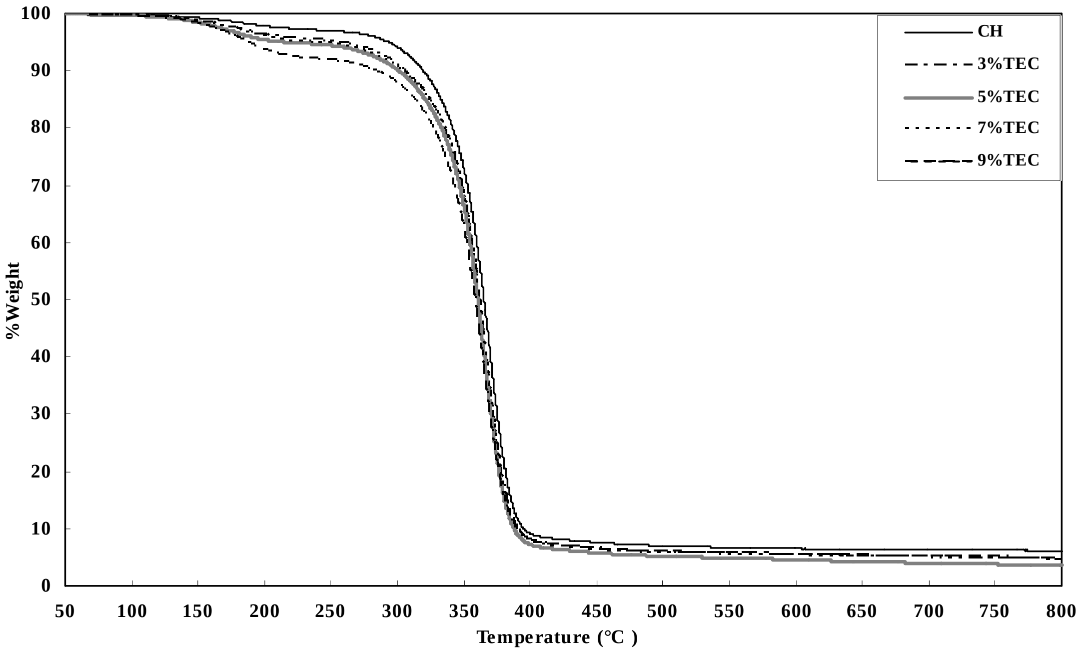
From **Figure 4.16** and **4.17** the CH and MH films present one main decomposition peak at 354.21 °C and 309.43 °C, respectively. While the plasticized CH and MH films present two main decomposition steps at 140 °C – 220 °C and 230°- 400 °C which were attributed from the evaporation of plasticizers and thermal decomposition of the cellulose laurate films. However, for both plasticized and unplasticized MH films, additional weight loss around 100 °C can be noticed due to moisture evaporation from the films. The first degradation peak around 140 °C-220 °C could derive from the different volatility of plasticizer content in cellulose laurate films; Whereas the onset temperatures of the second weight loss steps are of the cellulose structure and strongly related to the interactions between plasticizers and the cellulose.

The effects of plasticizer contents on the thermal stability of CH and MH films were also presented in **Figure 4.16** and **4.17.** The films selected were CH and MH films plasticized with TEC content of 3%, 5%, 7%, and 9%w/w. As listed in **Table 4.4** and from figure CH and MH, the plasticizer content affected the amount of first stage of weight loss. Upon increasing the TEC content, weight loss of the films at200 °C was increased. These results confirm that the first step of weight loss must be due to the decomposition of TEC. This thermal behavior was similarly found in both plasticized CH and MH films. Considering the second step of weight loss, it was found that the thermal stability of both CH and MH films decreased as increasing plasticizer content, although with different magnitude. Upon increasing the TEC content, weight loss of the films at 300 °C continuously increased and the onset of the thermal degradation temperature were clearly decreased. Comparing with an unesterified CH and MH films, the addition of 9%w/w TEC lowered the onset of decomposition temperature about 254.56 °C and 233.80 °C, respectively. The shift of the second step of weight loss towards lower temperature implied the interaction between cellulose and plasticizer.

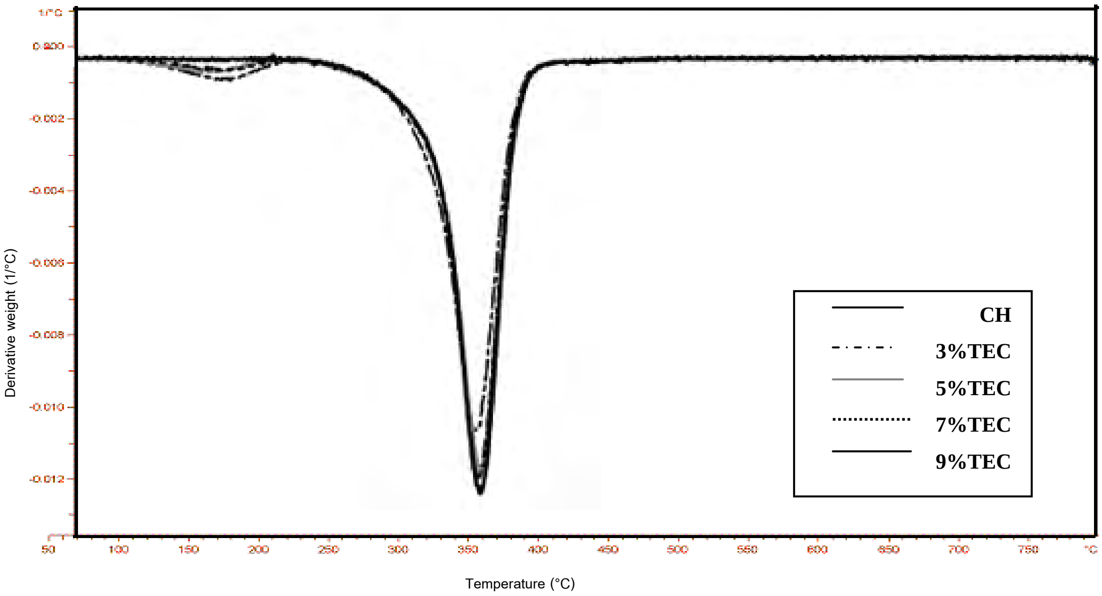
The lower thermal stability as indicated by a decrease in the onset of the degradation temperature was explained in terms of the lower crytallisition of the plasticized films. Addition of plasticizer to highly crystalline polymer reduces its crystallinity and increases degradation rate. According to the plasticization effect, plasticizer can promote a decrease in thermal stability by (1) acting as internal lubricants by reducing frictional forces between polymer chains so called “the lubrication theory” and (2) by breaking polymer-polymer interactions(e.g. hydrogen bonds and van der Waals or ionic force) so called “the gel theory” [24].

Regarding the effect of plasticizer type on thermal stability of CH and MH films, the TGA was carried out using the CH and MH films plasticized with TEC, DBP, and ESO at a constant plasticizer content of 5%w/w as shown in **Figure 4.18** and **4.19** The first stage of weight loss corresponding to the decomposition temperature of plasticizer indicated that TEC had lowest thermal stability; whereas ESO had highest thermal stability. However, considering at the second step of weight loss, it seem that there is no significant difference between the TGA curve of plasticized cellulose films with TEC and DBP, both plasticized CH and MH films with TEC and DBP had nearly the same onset of degradation temperature at 269.14 °C and 264.79 °C for CH films and at 254.13°C and 250. °C for MH films, respectively.

Comparing to the unplasticized CH and MH films, these two plasticizers noticeably decreased the thermal stability of the esterified cellulose laurate films; while this is not the case for ESO. As listed in **Table 4.5**, the addition of ESO had no influence on the second stage of weight loss. This is probably due to its higher onset of thermal degradation at the first step and its higher molecular weight compared to TEC and DBP, implying lower interaction between ESO and cellulose laurate chain y either lubrication or gel theories.

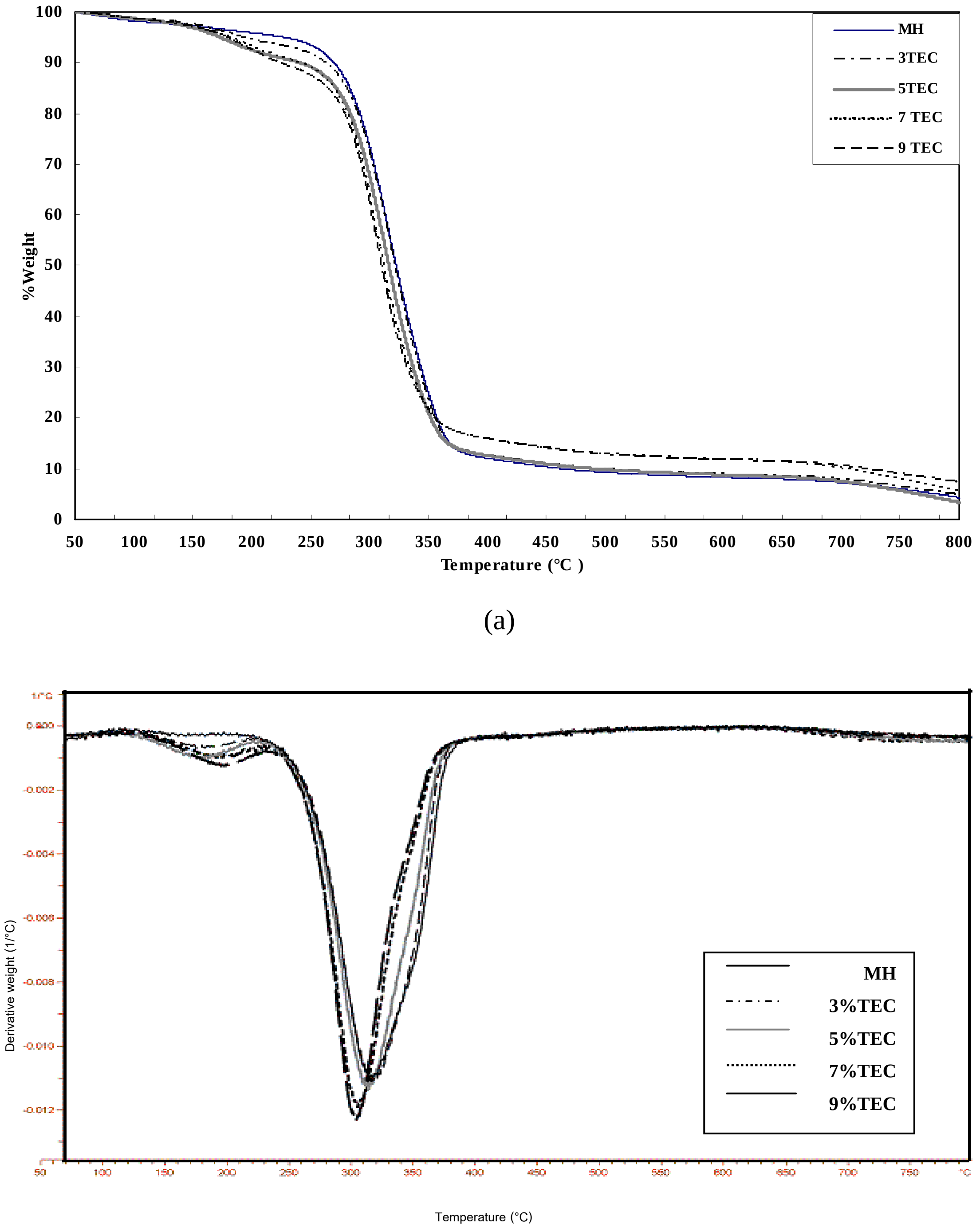


(a)



(b)

Figure 4.16 TGA(a) and DTG (b) thermograms of CH films plasticized with TEC at varying content



(a)

(b)

Figure 4.17 TGA(a) and DTG (b) thermograms of MH films plasticized with TEC at varying content

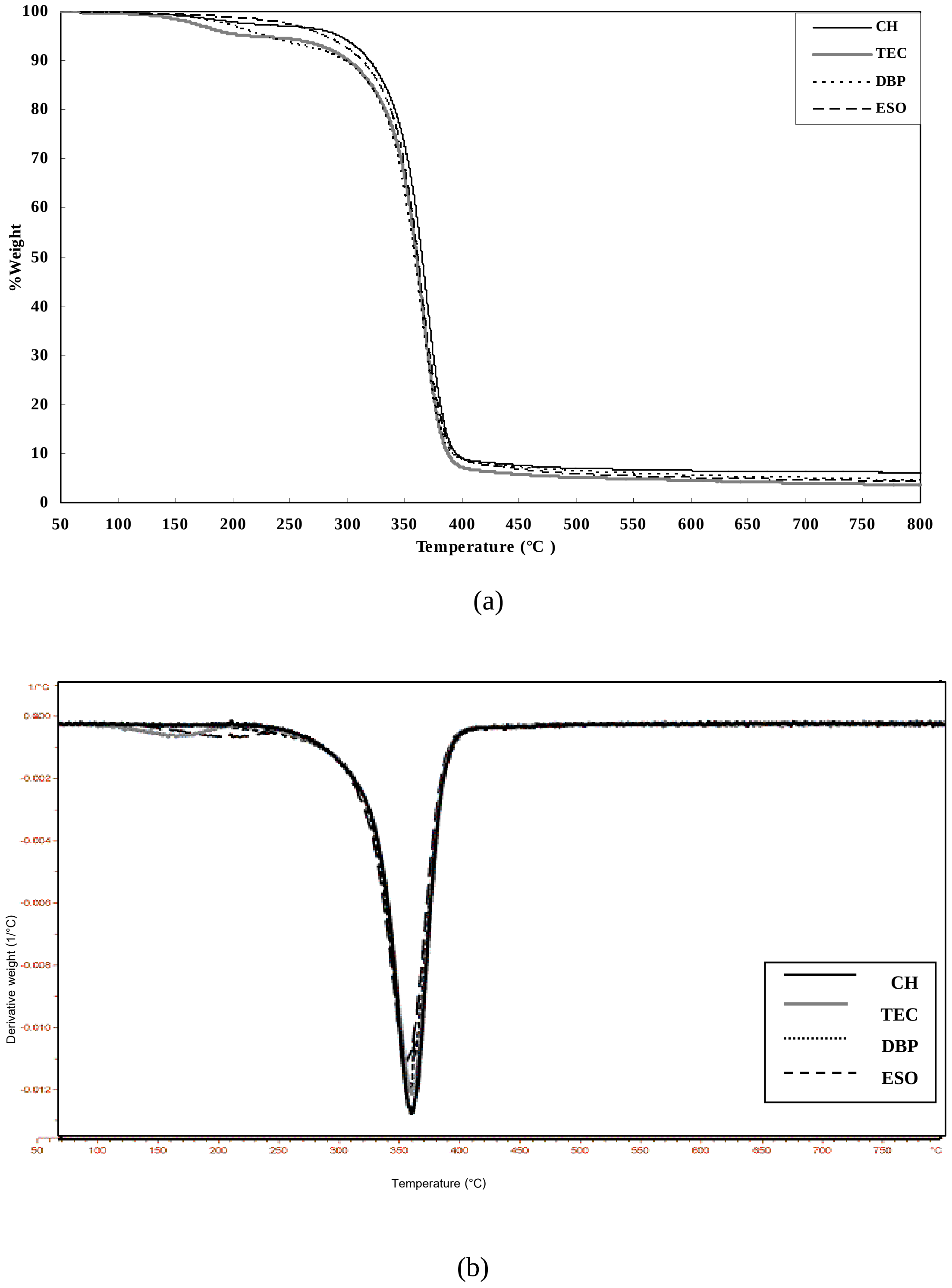
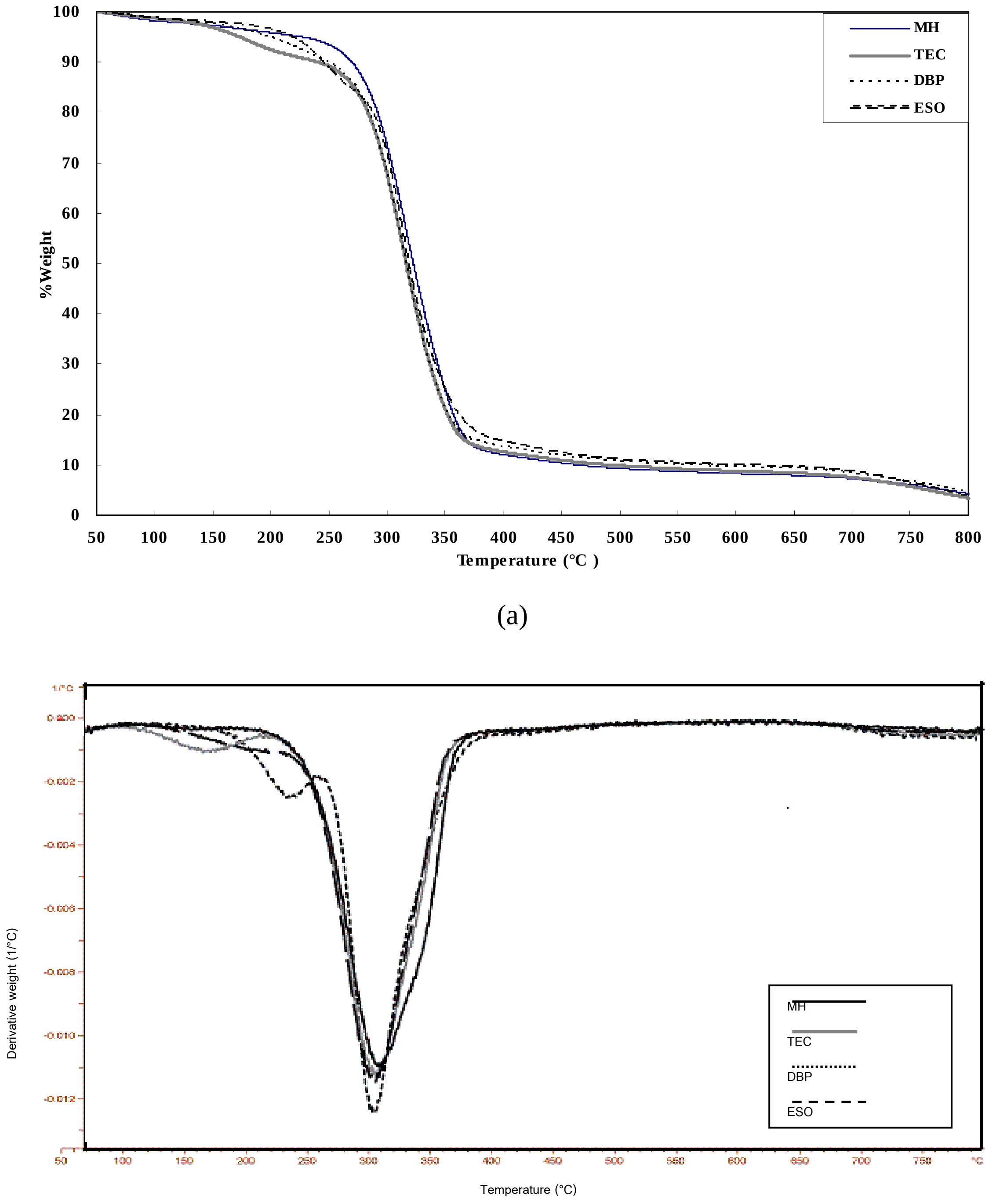


Figure 4.18 TGA (a) and (b) thermograms of CH films plasticized with 5%w/w of TEC, DBP, and ESO.



(a)

(b)

Figure 4.19 TGA (a) and (b) thermograms of MH films plasticized with 5%w/w of TEC, DBP, and ESO.

Table 4.4 TGA experimental result of CH and MH films plasticized with TEC at vary content.

Sample	plasticizer	Td(° C) (onset)		%Weight loss	
		First	Second	200 °C	300 °C
CH	0	-	292.67	2.14	5.85
	3	155.12	278.22	3.67	8.82
	5	154.34	269.14	4.56	10.16
	7	153.47	267.03	4.35	10.81
	9	155.06	254.56	6.27	13.09
MH	0	135.33	264.79	4.11	26.57
	3	154.87	250.85	5.48	27.96
	5	155.76	254.13	6.51	32.42
	7	156.45	248.22	6.79	36.78
	9	154.21	233.80	7.52	38.82

Table 4.5 TGA experimental result of plasticized CH and MH films plasticized with 5%w/w of TEC, DBP, and ESO.

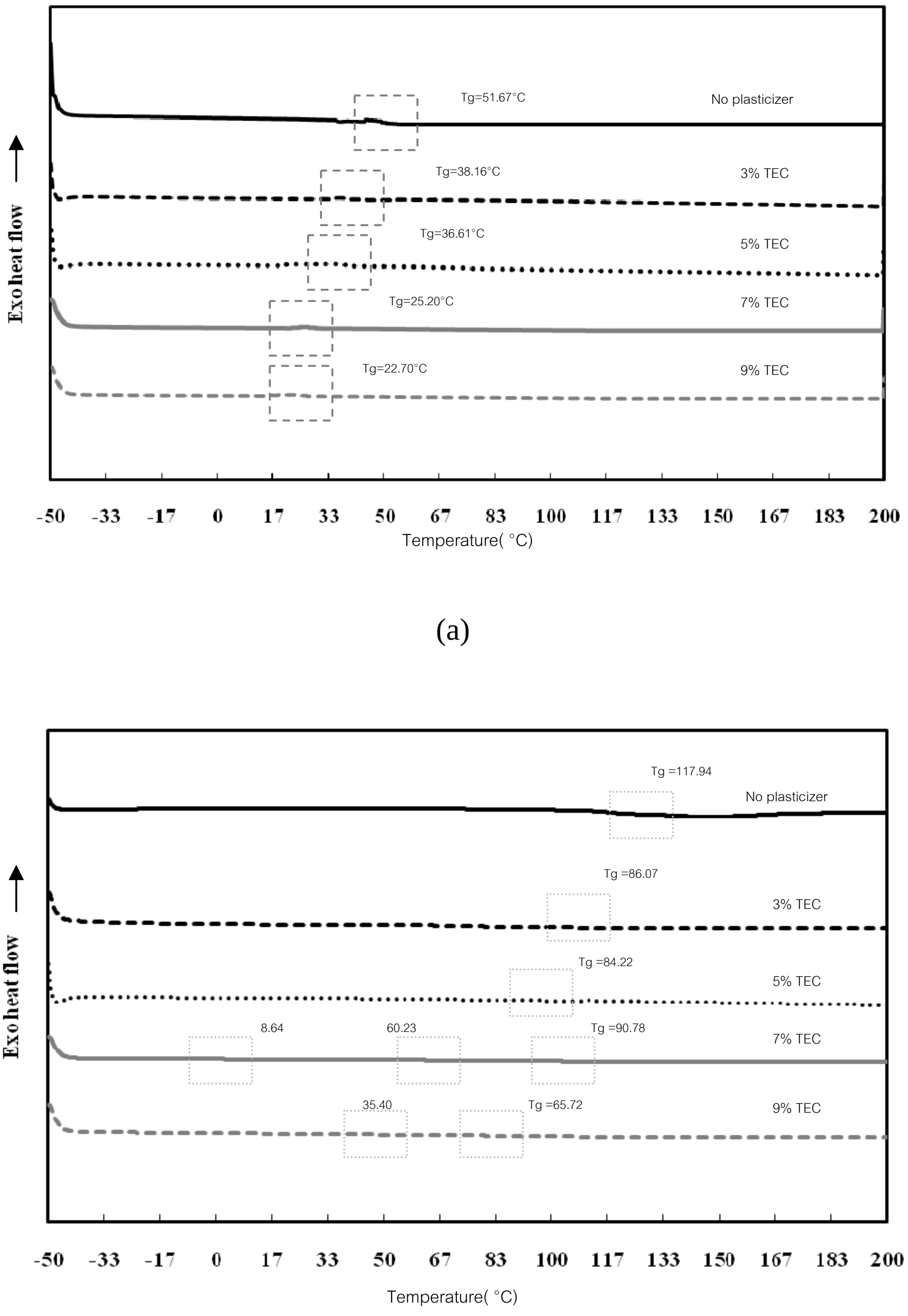
Sample	plasticizer	Td(° C) (onset)		%Weight loss	
		First	Second	200 °C	300 °C
CH	0	-	292.67	2.14	5.85
	TEC	154.34	269.14	4.56	10.16
	DBP	162.27	264.79	2.95	10.38
	ESO	-	282.33	1.28	7.57
MH	0	135.11	264.79	4.11	26.57
	TEC	155.76	254.13	6.51	32.42
	DBP	167.43	250.86	3.76	32.64
	ESO	212.09	269.20	2.77	28.80

4.2.3.2 Differential scanning calorymetry (DSC)

The thermal transition temperature was characterized by a differential scanning calorymetry (DSC).**Figure 4.20** shows the influence of plasticizer content on cellulose laurate films which was obtained by second heating scan from its melt state.

Glass transition temperatures of unplasticized CH and MH films were about 51.67 °C and 117.94 °C. The difference in Tg values of these two films was consistent with the Tg values of the esterified cellulose laurate powder a previously discussed that the esterified cellulose under conventional heating exhibited lower Tg value. Upon increasing the plasticizer which was TEC in this case, it can be seen that the glass transition temperature (Tg) decrease as the plasticizer content increased. With an addition of only 3 % w/w TEC, the Tg of plasticized CH and MH films was significantly lowered to 38.16 °C and 86.07°C, respectively. A possible explanation for the above phenomena is the free volume theory of plasticization that as the plasticizer concentration increases, there is an increase in the free volume of the polymer film, as thus the total volume occupied by a given number of molecules increases. The larger free volume inside the system allows enhanced molecular mobility.

However at higher TEC concentration (7-9 % w/w), the plasticized MH films exhibited several step changes which may refer to difference phases. The higher temperature specific heat increment reflected the glass transition temperature of plasticized MH films, and the lower temperature specific heat increment indicated the movement of the smaller mobile unit, such as the short chains, side groups, some groups on the side groups, and the branch chains in the cellulose molecular chain backbone.[42]



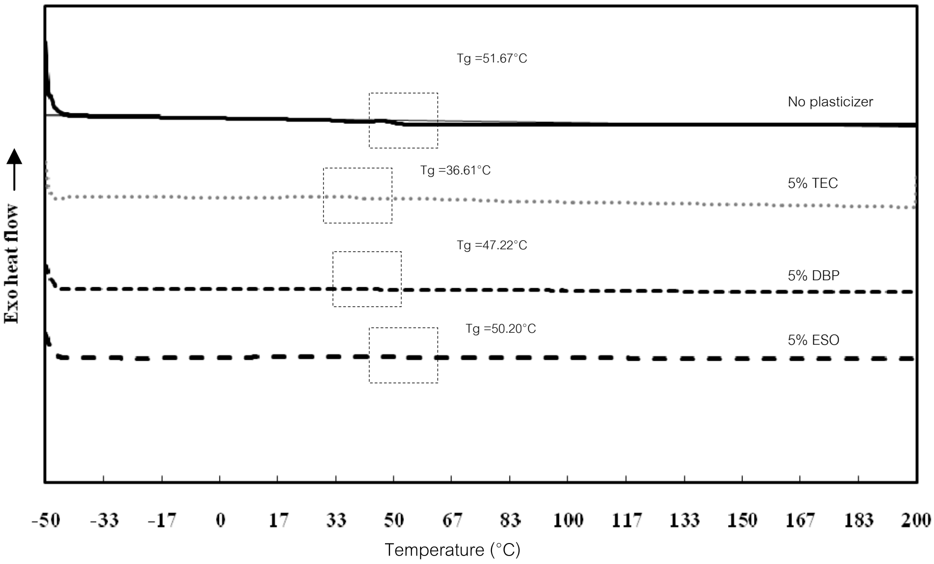
(a)

(b)

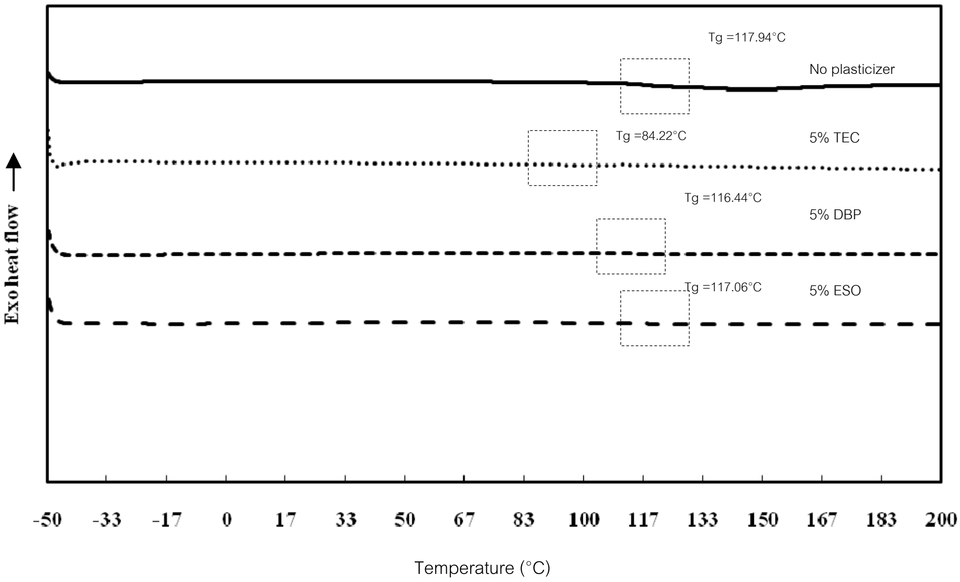
Figure 4.20 DSC thermograms (second heating scan) of plasticizer content on cellulose laurate films: (a) CH films and (b) MH films

The variation of the glass transition temperature with TEC, DBP, and ESO plasticized in cellulose laurate films is shown in **Figure 4.20**(a) and (b). The Tg of CH films plasticized with TEC, DBP, and ESO was 36.61°C, 47.22°C, and 50.20°C, respectively, while those of the MH films plasticized with TEC, DBP, and ESO were 84.22°C, 116.44°C, and 117.06°C, respectively. Comparing among three types of plasticizer, TEC values exhibit better plasticization effect than DBP and ESO by lowering the Tg value to lower extent than the other two plasticizers. In fact, it seems that the Tg of ESO plasticized cellulose laurate films was unchanged or similar to the films without a plasticizer, indicating no efficiency of ESO in term of the plasticizer for cellulose laurate film at this specific concentration. From the glass transition temperature of plasticized cellulose laurate films, it can be concluded that the efficiency of plasticizer on cellulose laurate films was higher in the order of TEC > DBP > ESO. These observations are in agreement with the mechanical properties; i.e., TEC is more efficient than DBP and ESO in increasing the %elongation of cellulose laurate films.

Higher amount of plasticizer added (greater than 5 % w/w) may result in different Tg values; in fact as shown in **Figure 4.21** greater amount of TEC added caused a significant decrease in Tg values.



(a)



(b)

Figure 4.21 DSC thermograms (second heating scan) of plasticizer type on cellulose laurate films: (a) CH films and (b) MH films.

4.2.4 Biodegradation Test

Biodegradation of cellulose laurate films was studied by soil burial test under realistic environment where soil humidity, temperature, and type and the amount of microorganisms are in less control and change with seasons. The effects of heating method and plasticizer on the degree of degradation were evaluated by measuring weight loss and physical appearance of the films surface.

4.2.4.1 Effect of heating methods

Weight loss of the films was determined at every 10 days for a period of 80 days. The results are shown in **Figure 4.22**, which illustrates the weight loss of cellulose laurate films as a function of the exposure time in soil.

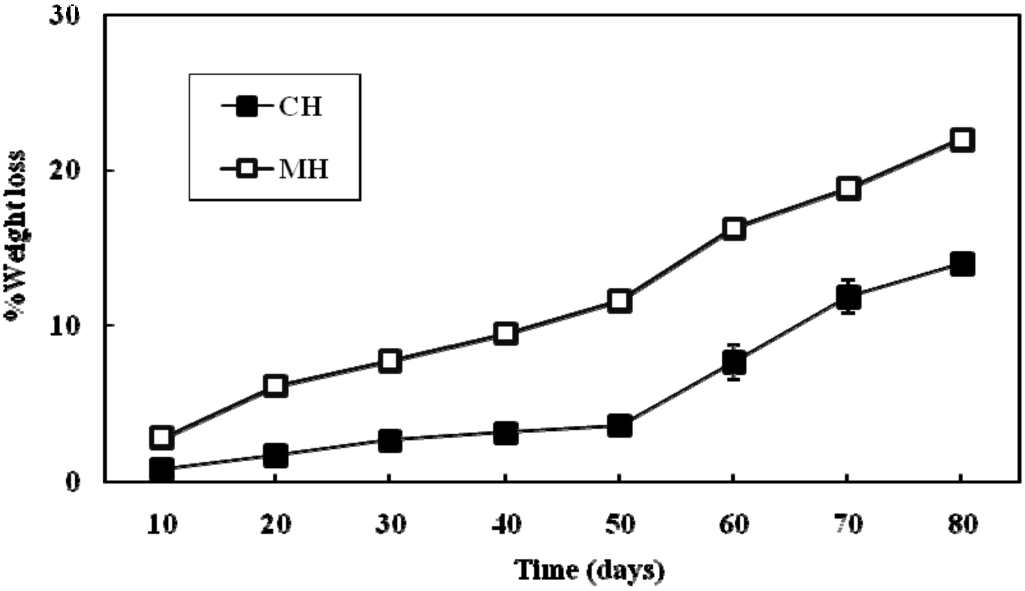


Figure 4.22 %Weight loss of CH and MH films during soil burial test

The %weight loss of cellulose laurate films increased with duration time of exposure in soil. It was slightly changed when the soil burial time was less than 30 days. Then, from 30 to 80 days, the weight loss of CH and MH films showed a significant increase. The biodegradation rate of CH films was lower than that of the MH films.

This result can be attributed to the effect of degree of substitution value that the lower biodegradability was occurred at higher levels of substitution. In this research, the degree of substitution of CH and MH films were 2.58 and 2.19, respectively; as a result the MH films with low degree of substitution exhibited greater biodegradation rate. The degree of substitution, it depends on the length of the alkyl side substituent when the alkyl side group is short, very fast degradation in noticed. The effect of the shorter side-chain length on the biodegradability was also reported by Aburto et al [37]. It seems also that the biodegradation rate increase with increases with shorter side-chain length. The bulky groups introduced by of longer side-chain length esterification are interfering with the biodegradation process, possibly by inhibiting the catalytic action of cellulose enzymes, which are responsible for the biodegradation of the cellulose film.

Moreover, besides the direct influence of DS value, the water absorption of these films were difference and should also be taking into account. As presented earlier that the water absorption of MH film was higher than that of CH film, this higher amount of water should facilitate the mechanism of biodegradation by allowing microorganisms such as bacterial and fungi to grow; thus enhancing the biodegradation of the films. In addition, the primary mechanism for the biodegradation of polymer is hydrolysis by enzyme; the MH films with low DS value can be hydrolysis easier than the CH film. The water in the soil attacks the cellulose films and splits them apart, creating smaller polymer fragment. Degradation may begin by hydrolysis, but as the polymer breaks and surface area and accessibility increase, enzymatic degradation dominates.

Microorganisms can degrade cellulose ester by producing enzymes to digest the carbon molecules of cellulose backbone and ingest them in their digestive system.

To confirm these results, the SEM micrographs of CH and MH films before and after 40 and 80 days buried in soil were demonstrated in **Figure 4.23**. It can be seen that the CH and MH films surface was becoming progressively rougher and exhibited some holes as the exposure time increased up to 80 days. The MH films had higher surface roughness with a greater amount of holes than the CH films. The holes appeared on the films surface after soil exposure verified the loss of weight due to the attack of microorganisms. As a result, the porosity and voids in the samples would enhance the breakdown of the polymer matrix into small particles, which could be further attacked by other degradation processes.

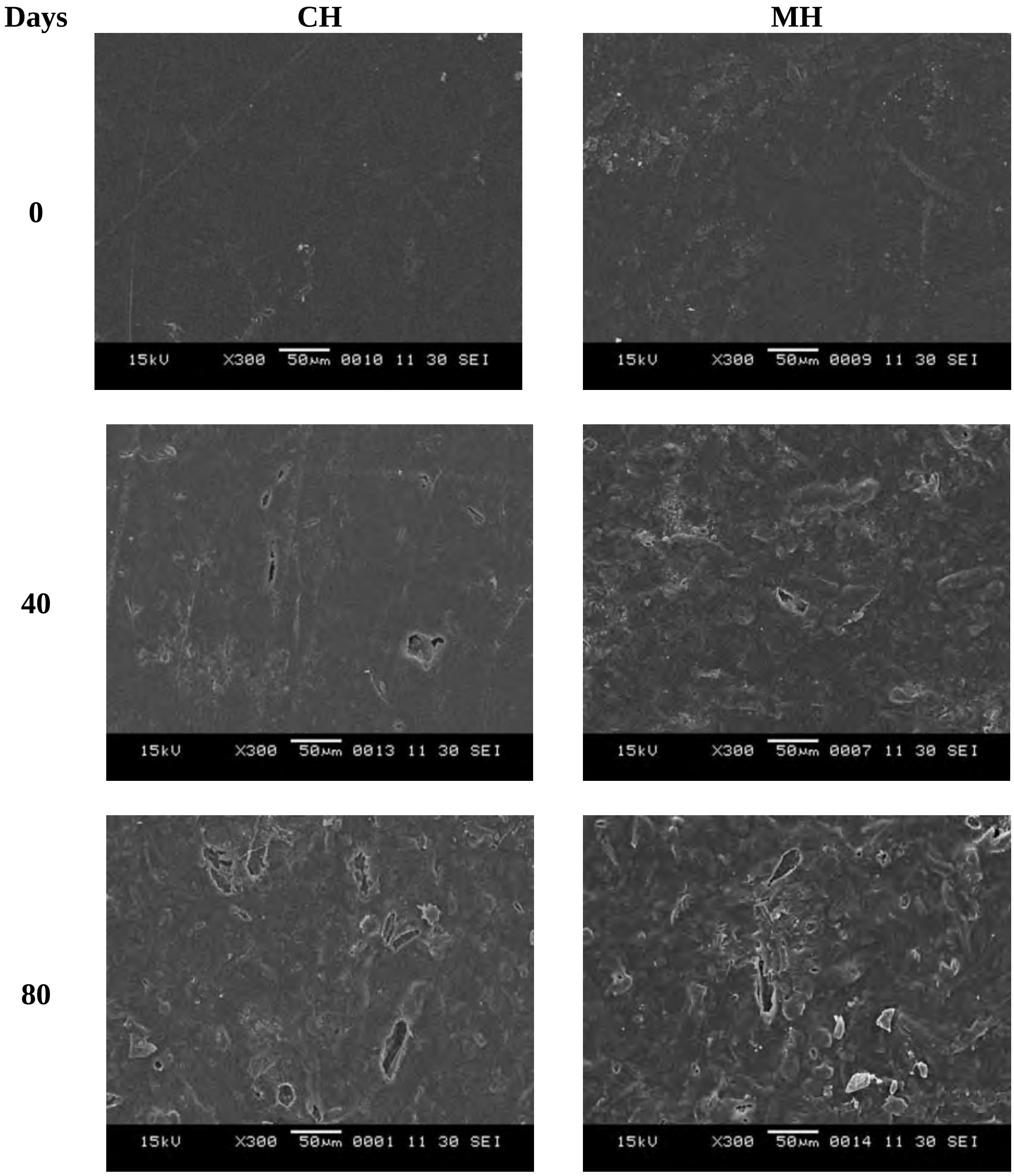


Figure 4.23 Scanning electron microscopy (SEM) showing surface morphology of the CH films and MH films before soil burial and after 40 and 80 days.

4.2.4.2 Effect of type and content of plasticizers

The effect of type and content of plasticizers on biodegradability of cellulose laurate films was studied. **Figure 4.24** showed that %weight loss of cellulose laurate films considerably increased when adding plasticizer. The effect of plasticizer on %weight loss of CH and MH films was similar that %weight loss increased as a function of exposure time and amount of plasticizer. However, difference resulted in difference degree of %weight loss.

Generally, the biodegradation of plasticizer itself leads to unsightly fungal growth in many products in a humid environment. Moreover, as a result of plasticizer degradation, over a long period of time, the remaining polymer material will suffer from an increased embrittlement and a loss of its function as a barrier against water. As the microorganism's degradation of the plasticizer creates a diffusion gradient in the bulk of the polymer mixture, the plasticizer concentration in the depth of the material will decrease. The damage of this microbial mechanism will be indirectly the water penetration into the material. Thus, the addition of plasticizer enhanced the biodegradability of cellulose laurate films. As shown, the plasticized cellulose laurate films exhibited significantly higher soil burial biodegradation than the unplasticized ones. From the literature, it was proposed that two-stage degradation took place in soil burial test: (a) the diffusion of the water into the film samples resulted in the swelling of the films and allowed the growth of microorganism on the film; (b) enzymatic and other secreted degradation caused a weight loss and disruption of the film samples.

Considering the type of added plasticizer, from the data in **Figure 4.24**, with an addition of TEC, all plasticized cellulose laurate films both CH and MH films showed substantial increase in weight loss. For example, at 80 days of exposure in soil, the CH and MH films plasticized with 9%TEC exhibited 72.23% and 74.80% of weight loss, respectively. From the result, it was shown that TEC had higher efficiency than DBP and ESO, respectively. As seen, only about 70% of weight loss was obtained after 80 days of soil burial test for the CH film plasticized with 9%ESO. The greater biodegradation of the films plasticized with TEC may be caused by its chemical structure which has a hydroxyl group that can form hydrogen bond with water leading to its higher water absorption. The water diffused into the film samples resulting in the swelling of the films and allowing the growth of microorganism on the film. As a result the microorganism growth caused degradation and weight loss in the film samples. The sample with higher TEC plasticizer contents exhibited better biodegradability due to the fact that biodegradation is naturally caused by the penetration of the microorganisms using water as a medium. The higher amount of TEC means that the higher amount of absorbed water which can facilitate the biodegradation mechanism in the cellulose laurate film.

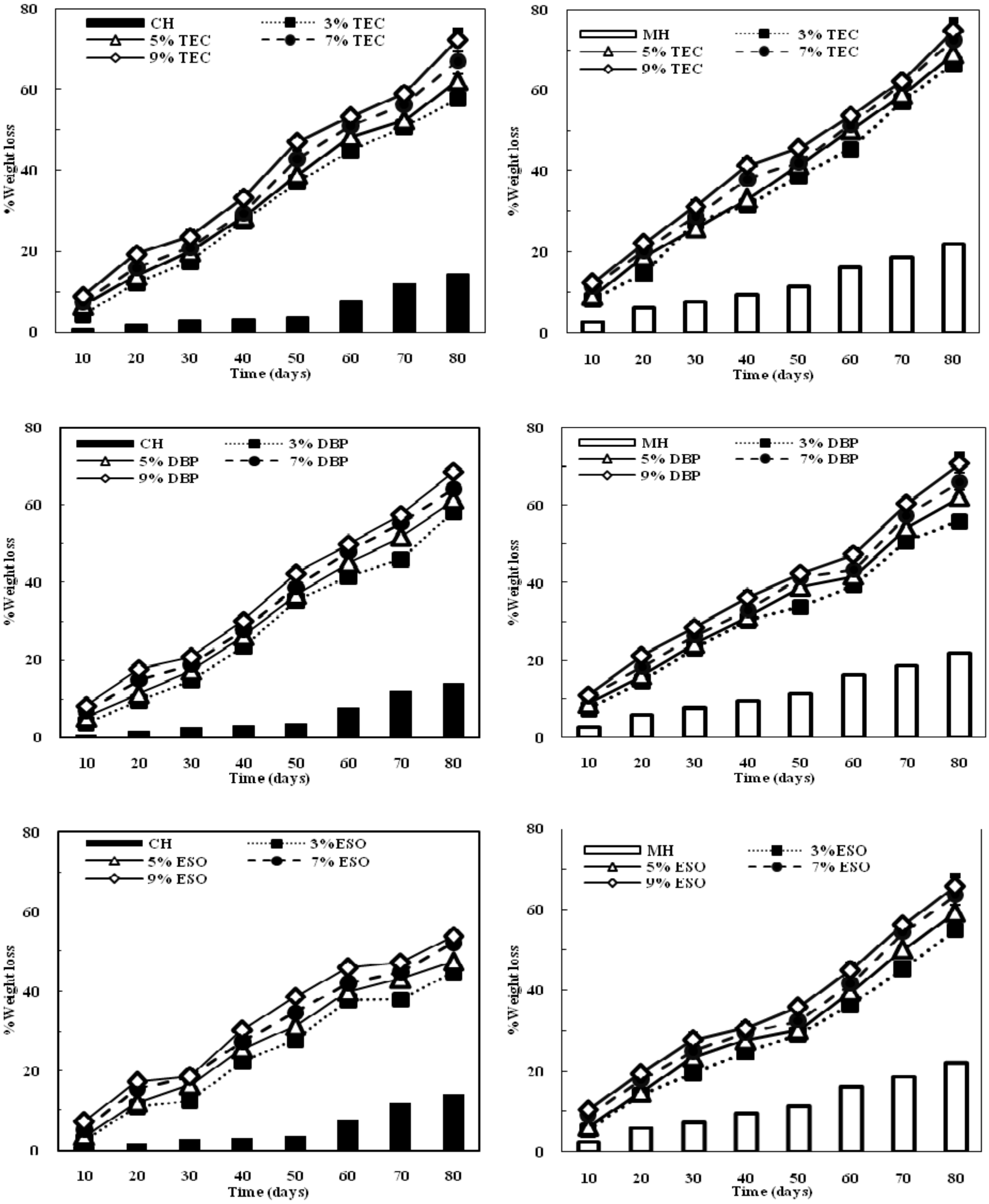
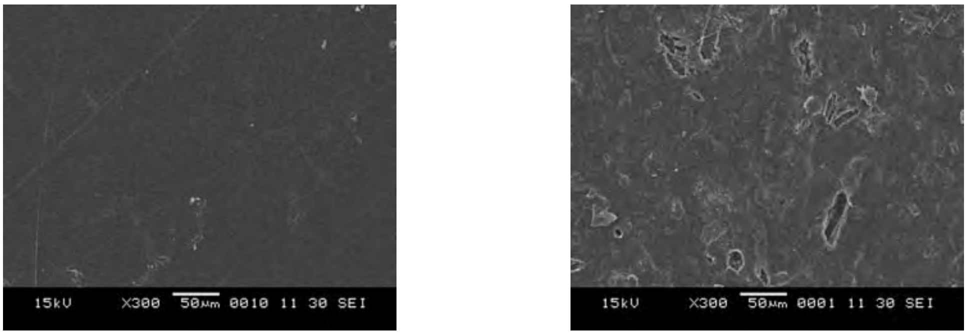


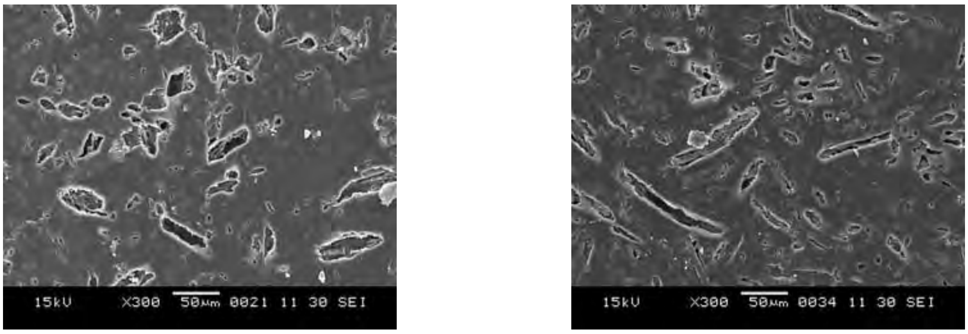
Figure 4.24 Effects of type and content of plasticizers on %weight loss of the CH films plasticized with TEC(a), DBP(c), and ESO(e) and the MH films plasticized with TEC(b), DBP(d), and ESO(f)

For the effect of plasticizer content, it can be noted that higher content of plasticizer had led to higher degradation. The dispersion of some plasticizer molecules within the chain of the cellulose films increased the ease of microorganisms to reach the cellulose molecule by increasing free volume in its structure. Hence, higher amount of water can be absorbed and the microorganisms can favorably grow; as a result, the enzymatic degradation by microorganisms increased noticeably. % weight loss of plasticized cellulose laurate films with varying plasticizer content had been investigated and it was found to be increased with increasing plasticizer content. For example, after 80 days of soil burial the % weight loss of CH film plasticized with TEC of 3%, 5%, 7% and 9%w/w was 57.54%, 62.09%, 67%, and 72.23%, respectively.

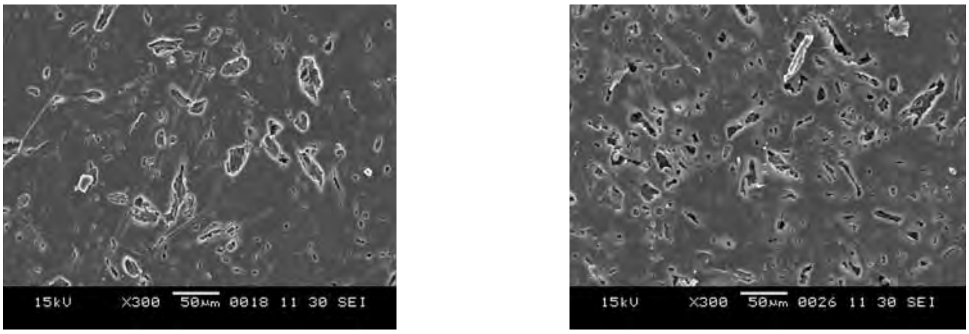
The biodegradation of the cellulose laurate films plasticized with various types and amount of plasticizer can also be verified from the SEM micrographs. As seen in **Figure 4.25** and **4.26,** the SEM micrographs of CH and MH films after 80 days of exposure in soil showed that the degradation occurs randomly at the film surface making it rough by forming cavities on it. The plasticized films exhibited better biodegradability than the unplasticized films. Which, the films plasticized with TEC showed the many number of hole more than the films plasticized with DBP and ESO. The plasticized cellulose films show cavities on the film surface increase with increasing plasticizer content. This result is similar to the result from the soil burial test and there are more holes on the film surface that can be attacked by microorganisms.



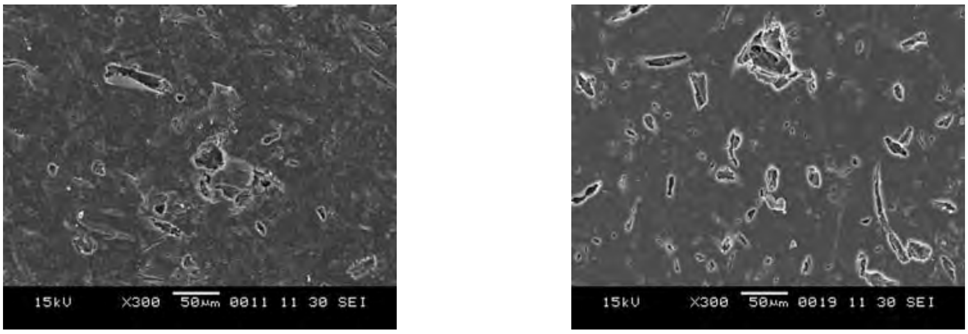
Unplasticized CH film (0 day) CH films (80 days)



5% TEC (80 days) 9% TEC (80 days)

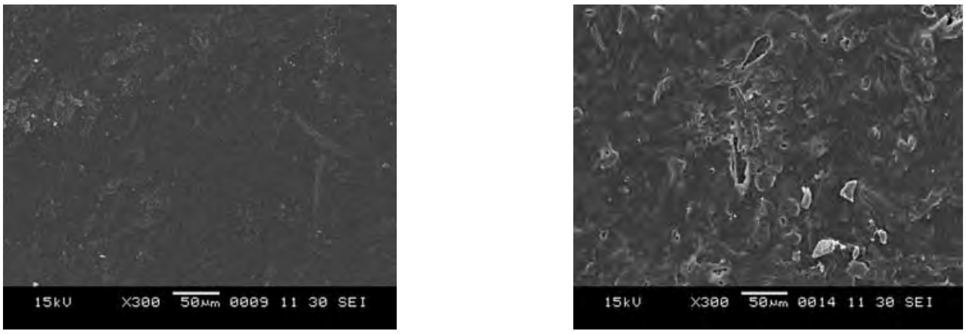


5% DBP (80 days) 9% DBP (80 days)

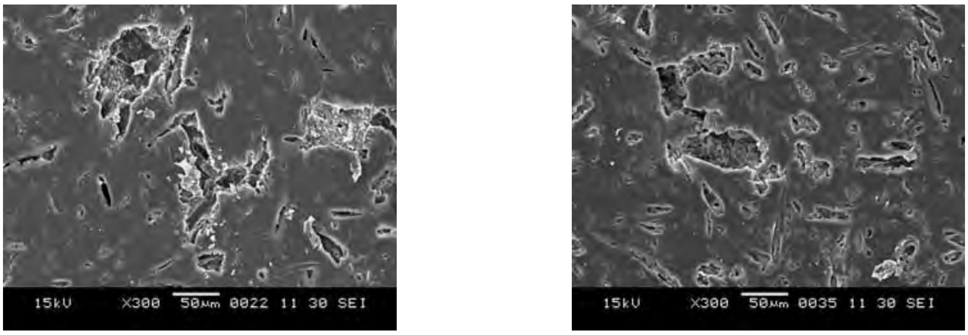


5% ESO (80 days) 9%ESO (80 days)

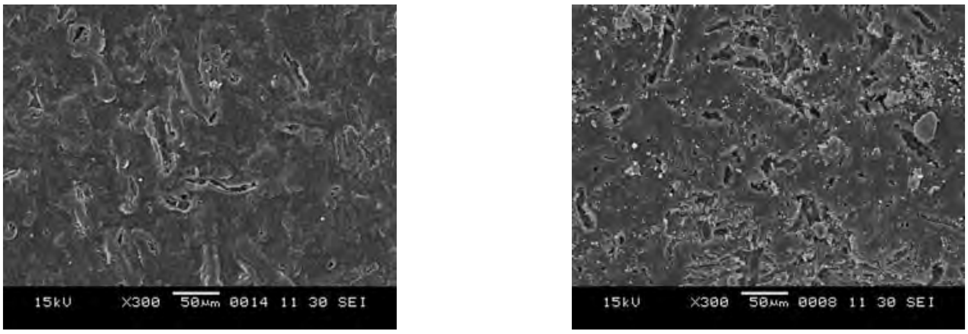
Figure 4.25 SEM images of unplasticized CH films before and after soil burial test and CH films plasticized with TEC, DBP, and ESO at 0%, 5% and 9%w/w after 80 days



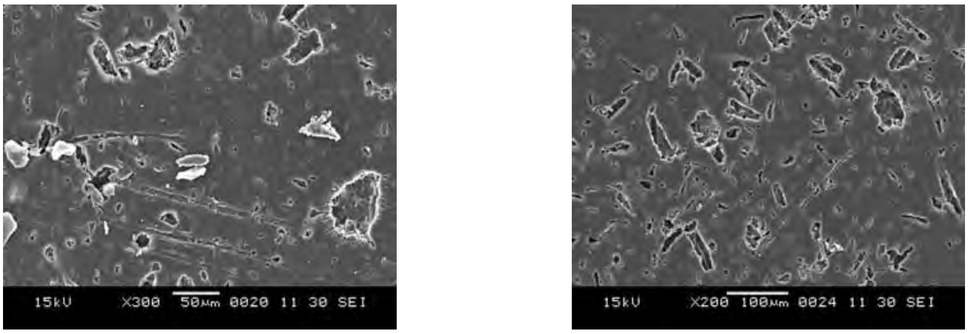
Unplasticized MH film (0 day) MH films (80 days)



5% TEC (80 days) 9% TEC (80 days)



5% DBP (80 days) 9% DBP (80 days)



5% ESO (80 days) 9%ESO (80 days)

Figure 4.26 SEM images of unplasticized MH films before and after soil burial test and MH films plasticized with TEC, DBP, and ESO at 0%, 5% and 9%w/w after 80 days

CHAPTER V

CONCLUSIONS

The esterification of cotton in DMAc/LiCl system was investigated by using lauroyl chloride as an esterified agent and DMAP as catalyst under conventional and microwave heating methods. Then, the cellulose laurate powder from both heating methods was converted into plastic film by casting method. Three types of plasticizer, triethyl citrate (TEC), dibutyl phthalate (DBP), and epoxidized soy bean oil (ESO), were used as an additive at a concentration of 3%, 5%, 7%, and 9% (w/w) of dry cellulose laurate.

The properties of cellulose laurate powder were characterized in terms of chemical structure, morphology, and thermal properties. The effects of plasticizers on the physical, thermal, mechanical, and biodegradable properties of plasticized cellulose laurate film were evaluated. The influence of heating methods (i.e., conventional heating vs. microwave heating) on the properties of plasticized cellulose laurate films was also compared. The results can be summarized as follows:

1. The optimum condition for esterification reaction of cellulose laurate was chosen from the maximum value of %WI and degree of substitution without the degradation of cellulose. The appropriated condition which yielded the maximum DS value and suitable % weight increase (%WI) for conventional heating and microwave heating were at 60°C for 12 hr (DS=2.58) and was 240 watt at 90 (DS=2.19), which yielded the %WI of esterified cellulose as 128% and 75%, respectively.

2. The infrared analysis before and after esterification of cellulose proved that chemical changes had occurred in the cellulose structure. After modification, cellulose laurate showed the existence of the ester carbonyl group stretching at 1746 cm^{-1}(C=O). The occurrence of strong intensities of two peaks at 2924 and 2853 cm^{-1} in the cellulose laurate spectra was attributed to the methyl and methylene C-H stretching associated with the lauroyl substituent. The decrease in the intensity of strong band at 3345 $cm^{-1}$of the hydroxyl group indicated the substitution of long chain fatty acid chloride on the cellulose structure.

3. The ^{1}H-NMR spectra of cellulose laurate showed peaks between 0.9 and 2.3 ppm, corresponding to the alkyl groups of lauric chain, and peaks of the anhydroglucose unit of cellulose between 3.5 and 5.5 ppm.

4. The degradation temperature (Td) of cellulose laurate powder started to decompose at a temperature substantially lower than the unesterified cellulose. The onset of degradation temperature of the esterified cellulose under conventional and microwave heating methods occurred around 261°C and 266°C, respectively. While the thermal decomposition temperature of unsesterified occurred at 312 °C. This behavior was probably attributed to the acyl substitution of long chain aliphatic on hydroxyl groups of cellulose.

5. The DSC thermograms of unesterified cellulose reveals distinct transition that occurring at a temperature at 100.47 °C, while the second order-transition temperature of esterified cellulose under conventional and microwave were 46.82 °C and 78.23°C,respectively. The second-order transition found in thermal transition of esterified cellulose was designated as Tg of cellulose laurate that occurred from long-chain substitution of lauroyl chloride at hydroxyl groups of cellulose, causing an increase in amorphous region and a decrease in the crystalline structure of cellulose. After esterification, the Tg decrease due to increased spacing between cellulose chains

and dilution of secondary bonding, increasing the mobility of cellulose chains so called a plasticization effect.

6. SEM micrograph of hydrolyzed cellulose appeared as a short fiber shape with a smooth surface. After esterification, its size become bigger, having some agglomeration and rough surface. The difference in morphology between unesterified and esterified cellulose was resulted from the acyl substitution of lauroyl chloride leading to an aggregation of acyl group on the cellulose surface.

7. The physical appearance of unplasticized CH film was homogeneous, transparent, and brittle. While the unplasticized MH film was opaque, rigid, and brittle and had some white spots spreaded on the film surface. The CH films contained less insoluble particles compared to MH films. The transparent and homogeneous of CH films structure resulted from the better solubility of CH powder in chloroform solvent.

8. The crystallinity of cellulose laurate films comparing between the MH and CH films found that the MH had higher crystallinity than the CH films.Addition plasticizer,the result showed that the plasticizing effect of both CH and MH was seemingly similar. Comparing to the unplasticized cellulose laurate films, the X-ray pattern of plasticized cellulose laurate films show the slightly lower peak at 22.8° than unplasticized cellulose laurate film. After plasticization, all plasticized CH and MH films were a homogeneous and had smooth surface. Particularly, they were softer compared to the unplasticized films. The homogeneous films structure resulted from both compatibility of the plasticizer with the polymer and the suitability of chloroform as a solvent for both polymers.

9. Water absorption of the plasticized and unplasticized CH films gave lower %water absorption than the plasticized and unplasticized MH films. the %water absorption of unplasticized CH film was 4.53% whereas that of unplasticized MH

film was 8.29%. The effect of plasticizer, the water absorption values of both CH and MH films increased with increasing of plasticizer content. The CH and MH films plasticized with TEC can absorb water as high as 13.66% and 17.55%, respectively. This is because TEC is hydrophilic and has a free hydroxyl group that can form hydrogen bondings with water, while DBP and ESO are insoluble water

10. The result on mechanical properties showed that the CH films showed better mechanical properties than the MH films. The CH films exhibited significant higher tensile strength and %elongation at break including lower Young's Modulus compared with the MH films. The mechanical properties of the cellulose laurate films were dependent on degree of substitution. The higher substitution of acyl substituent reduced the crystalline region or increased the amorphous region. The substitutions acted as the internal plasticizer for cellulose laurate films.

The addition of plasticizer in cellulose laurate, it was found that type and content of plasticizer had effects on the mechanical properties, which led to decrease in tensile strength and Young's Modulus and improves elongation at break value of films. The cellulose laurate films contain TEC had more %Elongation at break values than the films plasticized with ESO and DBP. The results from the elongation at break of plasticized CH and MH films indicated that the flexibility of the films increased in the order of TEC>ESO>DBP. The films plasticized with TEC was found to be a more efficient plasticizer than DBP and ESO respectively. The suitable concentration of TEC was 5 %(w/w).

11. The decomposition temperature (Td) of plasticized cellulose laurate films. the plasticizer content affected the amount of first stage of weight loss. Upon increasing the TEC content, weight loss of the films at 200 °C was increased. These results confirm that the first step of weight loss must be due to the decomposition of TEC. This thermal behavior was similarly found in both plasticized CH and MH

films. Considering the second step of weight loss, it was found that the thermal stability of both CH and MH films decreased as increasing plasticizer content, although with different magnitude. Regarding the effect of plasticizer type on thermal stability of CH and MH films, Comparing to the unesterified CH and MH films, These two plasticizers (TEC and DBP) noticeably decreased the thermal stability of the esterified cellulose laurate films; while this is not the case for ESO.

12. Glass transition temperatures of unplasticized CH and MH films were about 51.67 °C and 117.94 °C. The difference in Tg values of these two films was consistent with the Tg values of the esterified cellulose laurate powder. The esterified cellulose under conventional heating exhibited lower Tg value. Upon increasing the plasticizer which was TEC in this case, it can be seen that the glass transition temperature (Tg) decrease as the plasticizer content increased. With an addition of only 3 % w/w TEC, the Tg of plasticized CH and MH films was significantly lowered to 38.16 °C and 86.07°C, respectively. Comparing among three types of plasticizer, TEC values exhibit better plasticization effect than DBP and ESO by lowering the Tg value to lower extent than the other two plasticizers.

13. The degradability of cellulose laurate films was examined by soil burial test. The %weight loss of cellulose laurate films increased with duration time of exposure in soil. The biodegradation rate of CH films was lower than that of MH films as a result the MH films with low degree of substitution exhibited greater biodegradation rate. The degree of substitution, it depends on the length of the alkyl side substituent when the alkyl side group is short, very fast degradation in noticed. The biodegradation rate increase with increases with shorter side-chain length. Moreover, the water absorption of MH film was higher than that of CH film, this higher amount of water should facilitate the mechanism of biodegradation by allowing microorganisms such as bacterial and fungi to grow; thus enhancing the biodegradation of the films.

The addition of plasticizer in the films enhanced the biodegradability of cellulose laurate films when compared with the unplasticized cellulose laurate films. The films plasticized with TEC had higher biodegradation rate than the films plasticized with DBP and ESO, respectively. These result are in agreement with SEM micrographs, the plasticized films exhibited better biodegradability than unplasticized films as evidenced by a greater amount of holes and cavities. Comparing among three types of plasticizer, the films plasticized with TEC showed many number of holes than the films plasticized with DBP and ESO. In addition, the cavities on the plasticized cellulose laurate films surface increased with increasing plasticizer content.

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APPENDICES

APPENDIX A

A1 The degree of substitution (DS) and %weight increase (WI) of modified cellulose under conventional heating

Sample No.	Temperature (°C)	Time (hr)	DS	%WI
1	30	4	1.10	34
2		8	1.72	47
3		12	1.78	51
4		16	1.94	73
5		20	1.84	62
6	60	4	1.95	59
7		8	2.34	63
8		12	2.58	122
9		16	2.29	98
10		20	2.24	92
11	80	4	2.25	67
12		8	2.53	128
13		12	2.4	114
14		16	1.82	60
15		20	-	48

A2 The degree of substitution (DS) and %weight increase (WI) of modified cellulose under microwave heating

Sample No.	Watt	Time (min)	DS	%WI
1	80	60	0.76	17
2		90	1.05	30
3		120	1.61	25
4		150	1.91	49
5		180	1.89	34
6	160	60	2.05	28
7		90	1.75	41
8		120	2.07	69
9		150	2.18	55
10		180	2.12	37
11	240	60	2.14	44
12		90	2.19	75
13		120	2.16	66
14		150	1.97	41
15		180	1.66	20
16	320	60	2.05	42
17		90	1.99	53
18		120	1.89	48
19		150	-	32
20		180	-	10

A3 The effect of plasticizer on water absorption values of CH films are tabulated in table

Type of plasticizer	Conc. of plasticizer/%	Water absorption (%)
CH	0	4.534 ± 0.35
TEC	3	11.126 ± 0.56
	5	12.093 ± 0.16
	7	13.712 ± 0.08
	9	14.715 ± 0.36
DBP	3	6.978 ± 0.18
	5	9.226 ± 0.55
	7	10.431 ± 0.04
	9	11.481 ± 0.54
ESO	3	8.591 ± 0.36
	5	9.770 ± 0.46
	7	10.819 ± 0.31
	9	12.134 ± 0.11

A4 The effect of plasticizer on water absorption values of MH films are tabulated in table

Type of plasticizer	Conc. of plasticizer/%	Water absorption (%)
MH	0	8.297± 0.49
TEC	3	13.091± 0.57
	5	15.467± 0.03
	7	16.620± 0.25
	9	17.552± 0.43
DBP	3	9.263± 0.48
	5	11.601± 0.31
	7	12.892± 0.62
	9	14.361± 0.04
ESO	3	9.991± 0.75
	5	12.839± 0.08
	7	13.252± 0.12
	9	14.813± 0.27

A5 The effect of plsticizer on tensile properties of CH andMH film

Sample	Plasticizer (%)	Tensile properties (Mpa)						
		1	2	3	4	5	Average	SD
CH	0	7.76	7.06	6.62	9.00	8.19	7.73	0.94
TEC	3	5.72	5.85	5.67	5.83	5.90	5.79	0.08
	5	5.87	5.59	6.39	6.15	6.52	6.10	0.34
	7	4.03	4.65	5.06	4.74	5.61	4.82	0.52
	9	3.31	3.93	2.78	3.08	3.84	3.39	0.44
DBP	3	4.91	5.45	5.49	5.72	5.32	5.38	0.30
	5	4.87	4.75	4.70	5.02	4.40	4.75	0.23
	7	4.14	4.24	4.70	4.40	4.36	4.37	0.21
	9	3.36	3.11	3.05	2.96	2.98	3.09	0.16
ESO	3	5.50	5.31	5.49	5.21	5.09	5.32	0.18
	5	5.58	5.78	6.25	5.91	6.27	5.96	0.30
	7	5.52	5.12	5.29	5.04	5.42	5.28	0.20
	9	4.62	3.93	3.33	3.27	3.61	3.75	0.55

Sample	Plasticizer (%)	Tensile properties (Mpa)						
		1	2	3	4	5	Average	SD
MH	0	5.270	5.100	4.821	5.180	5.148	5.104	0.17
TEC	3	6.289	4.968	4.463	4.335	4.917	4.994	0.69
	5	4.704	4.773	4.911	5.173	5.045	4.921	0.17
	7	4.092	3.496	3.995	4.127	4.053	3.953	0.23
	9	3.701	3.580	3.263	3.890	3.637	3.614	0.20
DBP	3	4.062	4.518	4.507	4.769	4.950	4.561	0.34
	5	4.827	4.842	5.362	4.165	5.263	4.892	0.47
	7	3.965	4.433	3.814	3.316	4.351	3.976	0.45
	9	3.803	3.234	3.613	3.347	3.429	3.485	0.23
ESO	3	4.558	4.501	4.214	4.332	4.729	4.467	0.20
	5	4.609	4.830	4.571	4.486	4.401	4.579	0.16
	7	3.830	3.771	4.152	3.943	3.814	3.902	0.15
	9	3.969	3.603	3.787	3.382	3.391	3.626	0.25

A6 The effect of plsticizer on Young’s modulus of CH and MH film.

Sample	Plasticizer (%)	Young's Modulus (Mpa)						
		1	2	3	4	5	Average	SD
CH	0	432.30	344.52	345.91	382.01	484.24	397.80	60.09
TEC	3	254.12	316.01	252.63	285.01	278.20	277.19	26.00
	5	269.42	269.81	244.33	375.80	266.71	285.21	51.74
	7	179.84	202.94	227.78	369.47	250.12	246.03	73.87
	9	214.20	300.36	274.61	184.45	272.38	249.20	48.00
DBP	3	233.52	271.14	262.02	286.54	253.68	261.38	19.77
	5	202.05	295.97	347.18	227.37	216.45	257.80	61.62
	7	214.03	207.51	229.38	263.65	220.58	227.03	22.01
	9	264.39	214.83	194.09	187.20	206.57	213.42	30.45
ESO	3	319.76	260.59	289.52	224.29	225.18	263.87	41.40
	5	216.93	228.16	235.26	236.38	376.92	258.73	66.52
	7	204.90	222.50	209.35	207.76	220.55	213.01	7.96
	9	272.15	262.59	209.53	180.72	247.13	234.42	38.35

Sample	Plasticizer (%)	Young's Modulus (Mpa)						
		1	2	3	4	5	Average	SD
MH	0	892.54	706.92	941.55	568.65	625.20	746.97	163.77
TEC	3	623.78	493.04	371.28	401.92	485.89	475.18	98.33
	5	405.16	424.64	478.76	430.47	445.28	436.86	27.48
	7	383.34	321.39	417.79	377.54	436.93	387.39	44.29
	9	345.60	320.16	309.12	423.21	339.51	347.52	44.78
DBP	3	527.54	547.60	490.52	472.86	676.24	542.95	80.14
	5	421.31	571.66	402.83	415.51	472.54	456.77	69.49
	7	402.14	422.57	435.95	408.97	451.16	424.15	19.91
	9	430.96	283.83	435.17	366.23	330.47	369.33	65.12
ESO	3	405.25	404.67	399.32	352.27	452.53	402.80	35.52
	5	344.31	517.68	443.80	377.29	410.17	418.65	66.61
	7	279.99	315.81	332.29	361.27	374.12	332.69	37.40
	9	399.09	357.35	365.89	317.10	363.03	360.49	29.23

A7 The effect of plasticizer on % elongation at break of CH and MH film.

Sample	Plasticizer (%)	%Elongation at break						
		1.00	2.00	3.00	4.00	5.00	Average	SD
CH	0	7.84	6.38	6.15	7.95	5.70	6.80	1.03
TEC	3	11.77	11.65	11.02	9.60	10.38	10.88	0.91
	5	14.08	13.82	13.69	14.99	16.27	14.57	1.08
	7	8.60	12.13	13.01	10.91	10.75	11.08	1.67
	9	4.31	4.97	3.84	5.06	5.54	4.74	0.67
DBP	3	6.77	7.41	7.54	7.62	7.41	7.35	0.34
	5	9.18	9.63	7.82	5.02	6.17	7.57	1.96
	7	8.94	9.35	9.69	10.12	8.21	9.26	0.73
	9	4.94	4.23	4.27	3.84	4.12	4.28	0.41
ESO	3	9.16	9.32	9.11	8.88	7.88	8.87	1.14
	5	10.55	11.27	15.20	13.20	10.14	12.07	2.11
	7	13.79	12.43	11.29	12.46	9.33	11.86	1.67
	9	6.52	5.10	3.48	5.06	4.24	4.88	1.14

Sample	Plasticizer (%)	%Elongation at break						
		1	2	3	4	5	Average	SD
MH	0	1.708	1.903	1.835	1.856	2.044	1.869	0.12
TEC	3	3.138	3.140	3.296	3.108	3.166	3.170	0.07
	5	3.522	3.555	3.515	4.200	4.024	3.763	0.32
	7	3.000	2.976	3.109	3.091	3.065	3.048	0.06
	9	2.927	2.966	2.743	2.600	2.863	2.820	0.15
DBP	3	2.205	2.225	2.361	2.271	2.338	2.280	0.07
	5	3.261	3.251	3.535	3.425	3.204	3.335	0.14
	7	2.526	2.314	2.578	2.336	2.710	2.493	0.17
	9	2.679	2.537	2.452	2.462	2.425	2.511	0.10
ESO	3	3.293	3.389	3.040	3.286	3.238	3.249	0.13
	5	3.880	3.807	3.606	3.535	3.619	3.689	0.15
	7	3.052	3.191	3.338	3.071	2.827	3.096	0.19
	9	2.704	2.818	2.854	2.947	2.649	2.794	0.12

A8 The unplasticized CH and plasticized CH films before and after soil burial test

Sample	Plasticizer (%)	Soil burial time (day)							
		10	20	30	40	50	60	70	80
CH	0	0.77±0.16	1.71±0.33	2.64±0.23	3.13±0.30	3.61±0.44	7.68±1.13	11.89±1.05	14.04±0.68
TEC	3	4.02±0.76	11.93±0.41	17.20±0.33	27.33±0.51	37.14±0.54	44.70±0.72	50.75±0.93	57.54±0.76
	5	6.58±0.81	13.88±0.17	19.77±0.20	28.43±0.19	38.91±0.88	48.30±0.48	52.43±0.70	62.09±1.83
	7	7.33±0.60	15.88±0.61	20.77±0.93	29.28±0.14	42.77±2.06	51.03±0.94	56.22±1.36	67.00±2.30
	9	8.81±0.14	19.17±0.08	23.45±1.18	33.15±1.32	47.02±0.34	53.34±1.14	58.88±0.52	72.23±2.43
DBP	3	3.77±0.53	9.33±1.12	14.82±0.63	23.57±0.65	35.34±0.39	41.72±1.07	46.06±0.28	58.21±0.26
	5	5.07±1.21	11.24±0.75	17.25±0.77	26.20±0.07	36.80±0.84	45.09±0.90	51.79±1.89	61.32±0.50
	7	6.81±0.11	14.88±0.72	18.94±0.85	27.83±1.07	38.73±1.07	48.12±0.39	55.34±0.45	64.24±1.35
	9	8.13±0.53	17.71±1.11	20.80±0.82	30.09±1.00	42.35±3.03	49.92±0.03	57.48±1.39	68.62±0.68
ESO	3	2.52±0.16	10.92±0.51	12.35±1.26	22.27±0.99	27.96±1.39	37.62±0.69	37.94±0.69	44.72±1.32
	5	3.52±0.65	12.02±0.74	16.29±0.58	25.45±0.47	31.19±0.80	39.74±1.01	43.12±0.49	47.53±0.88
	7	5.30±0.13	15.34±0.60	18.55±0.71	27.23±0.37	34.64±1.01	42.12±0.82	44.90±0.18	52.19±0.42
	9	7.22±0.76	17.28±1.25	18.64±0.57	30.20±0.57	38.66±0.85	45.94±1.63	47.29±1.05	53.75±0.69

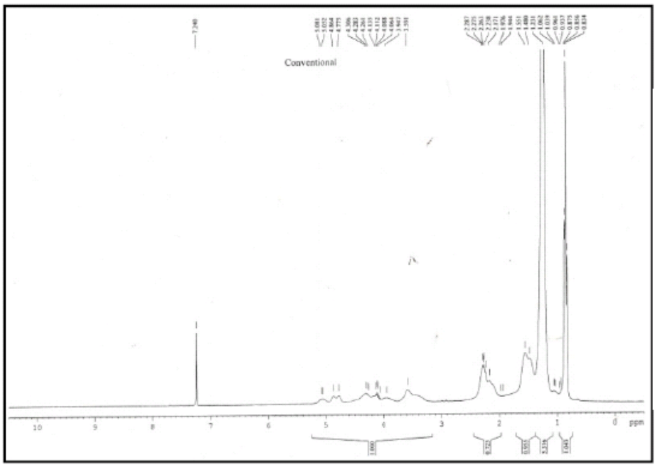
A9 The unplasticized MH and plasticized MH films before and after soil burial test

Sample	Plasticizer (%)	Soil burial time (day)							
		10	20	30	40	50	60	70	80
MH	0	2.76±0.37	6.13±0.53	7.73±0.37	9.49±0.32	11.58±0.46	16.25±0.58	18.84±0.72	22.01±0.58
TEC	3	8.32±1.00	14.70±0.72	27.61±5.20	31.51±0.37	38.89±0.92	45.49±1.57	57.32±0.36	66.47±1.35
	5	9.13±1.14	18.92±0.84	25.88±0.60	33.25±1.27	41.46±0.87	50.19±0.23	58.99±0.97	68.94±1.09
	7	11.58±0.33	20.44±0.46	28.90±1.32	38.05±0.65	42.20±0.96	51.48±0.66	61.62±0.43	72.48±0.36
	9	12.45±0.34	22.13±0.14	31.26±0.65	41.46±1.20	45.69±0.93	53.77±0.88	62.36±0.48	74.80±0.28
DBP	3	7.37±0.72	14.61±1.31	23.06±0.29	30.28±0.29	33.81±0.18	39.40±0.17	50.72±1.26	56.03±2.12
	5	8.80±0.35	16.12±0.66	24.20±1.23	31.23±0.40	38.92±1.08	41.80±0.18	54.02±0.85	62.10±1.12
	7	10.62±0.17	18.33±0.88	26.44±0.82	33.07±1.08	41.41±0.49	43.56±0.82	57.37±0.93	66.19±0.75
	9	11.08±0.28	21.27±0.59	28.53±1.10	36.23±0.90	42.48±0.50	47.39±1.15	60.46±0.97	70.80±0.28
ESO	3	5.45±0.36	14.06±0.89	19.40±0.16	24.55±0.20	29.04±1.33	36.41±1.49	45.27±0.88	54.84±0.35
	5	6.31±0.44	14.78±0.62	23.38±0.95	27.62±1.13	30.27±0.52	39.73±0.69	50.25±0.37	59.35±0.23
	7	9.12±0.39	17.92±1.00	24.93±0.42	29.55±0.48	32.53±1.01	41.79±0.81	54.45±0.42	63.63±1.51
	9	10.47±0.59	19.44±1.41	27.81±1.09	30.60±0.75	35.98±1.02	45.10±0.33	56.38±0.82	65.88±1.35

APPENDIX B

Determination of degree of substitution

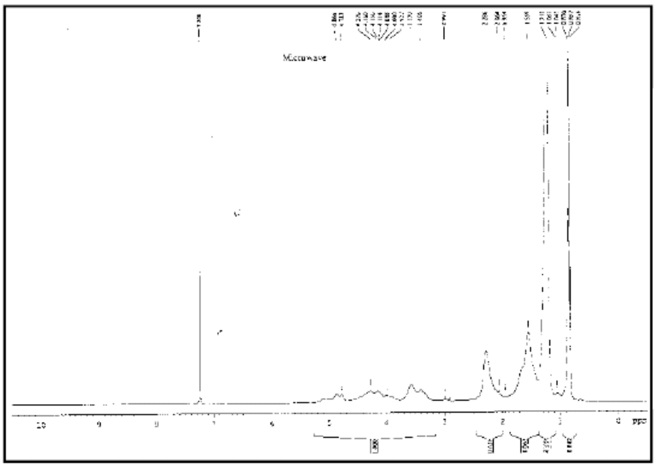
Example



Conventional heating:

$$DS = \frac{10(1.043)}{3(1) + 1.043}$$

$$= 2.58$$



Microwave heating:

$$DS = \frac{10(0.842)}{3(1) + 0.842}$$

$$= 2.19$$

BIOGRAPHY

Miss Panita Hongphruk was born in Songkhla, Thailand, on August 25th, 1982. She received her Bachelor Degree of Science majoring in Polymer, Faculty of Science, Prince of Songkla University in 2005. She started the job as a process engineer at SGMP, Co, Ltd during 2005-2006. After that, she started as a graduate student in Department of Materials Science, with Master Degree in the filed of Applied Polymer Science and Textile Technology at Chulalongkorn University in 2007 and completed the program in 2009.