

# CHAPTER I

## INTRODUCTION

Synthetic polymers are vital to the economy and quality of life but their waste is becoming a serious ecological problem. Biopolymers can be good candidates for replacement of synthetic polymers but they have to offer comparable quality (barriers and mechanical properties, low cost, etc). These materials have the potential to reduce environmental pollution by lowering solid disposal waste and reducing the need for incineration.

Cellulose is one of the most abundant naturally occurring polysaccharides. They are produced in a sustainable way and offer many possibilities for use, because they are renewable, biodegradable, biocompatible, and derivatizable. Cellulose is found in plants as microfibrils. These form the structurally strong framework in the cell walls. Cellulose is a polydisperse linear homopolymer consisting of regio- and enantioselective  $\beta$ -1, 4- glycosidic linked D-glucose unit (so-called anhydroglucose units). The polymer contains three reactive hydroxyl groups at the C-2, C-3, and C-6 atoms, which are, in general, accessible to the typical conversions of primary and secondary alcoholic OH groups [1,2]. Commercial cellulose production concentrates on easily harvested sources such as wood or on the highly pure sources such as cotton. Cotton is one of the most important crops in Thailand and the cheap raw material of cotton production.

Modification of this polysaccharide is very interesting, because this compound is the major constituent of agricultural waste. Cellulose is converted to its organic esters, in the laboratory and commercially, for two reasons. First, cellulose is poorly soluble in common solvents and is not melt-processible because the large amounts of intra- and intermolecular hydrogen bonds in cellulose and decomposes before it undergoes melt flow. Secondly, the physical properties of cellulose can be greatly modified by derivatization. The modified properties of these cellulose derivatives give entry into a range of applications greatly expanded from those available to the parent polysaccharide[1-3].

Conversion of cellulose to its esters affords materials that are processible into various useful forms, such as three dimensional objects, fibers, and solutions to be used for coating or casting (of films or membranes, for example). It is important to gain a fundamental understanding of how structural changes are effected by cellulose esterification, the ability to predict how those changes will impact properties, and an understanding of how those property changes translate into performance and application requirements [4].

The problem in the past has been the difficulty of esterification of cellulose by conventional methods with anhydrides of carboxylic acids of chain length greater than five. These long chain anhydrides react slowly with cellulose, for both steric and polar reasons, and thus chain degradation of the cellulose competes effectively with acylation. A major stimulation for the investigation of alternative paths for polysaccharide functionalization was the discovery of a variety of new solvents. These cellulose solutions have been the subject of numerous investigations that have revealed many aspects of scientific interest. Around 20 years ago, Turbak and McCormick [4-5] independently discovered the utility of the combination of *N,N*-dimethylacetamide (DMAc) and lithium chloride (LiCl) as a solvent for cellulose. One important discovery was the fact that cellulose could be conveniently reacted in DMAc/LiCl solution with a wide range of electrophiles, using conventional acid and base catalysts, to produce a range of derivatives including cellulose esters.

The acylation of cellulose in DMAc/LiCl using carbonic acid anhydrides and the -chlorides was among the first attempts of chemical modification of the polysaccharide. The preparation of esters with long chains using the acyl chlorides, e.g. *n*-octanoic to octadecanoic was investigated. Besides the acyl chlorides for the synthesis of the simple fatty triesters, mixed triesters were obtained by conversion of cellulose in DMAc/LiCl with the fatty acid and acetic acid anhydride in the presence of HClO<sub>4</sub>[6,7].

In situ activation of the synthesis of cellulose esters from the free carboxylic acids is possible with toluenesulfonyl chloride. It was first applied for the preparation of cellulose acetates. The extension of this path on the homogeneous derivatization of cellulose with waxy carbonic acids was studied. It was shown that cellulose esters, having alkyl substituents in the range from C<sub>12</sub> (laurylic acid) to C<sub>20</sub> (eicosanoic acid), can be obtained with almost complete functionalization of the accessible OH group[7].

In general procedures, the esterification of cellulose were esterified by conventional heating method that result in long reaction time such as 30 min to 1 or 2 days. The use of microwave radiation in processing of polymers offers a number of distinct benefits over conventional processing alternatives. In the microwave field the heating process often occurs more homogeneously and thus more rapidly than with the conventional heating. The microwave heating presents some advantages, such as remarkable decrease in reaction time and in some cases, cleaner reactions and better yields have been reported. For example, C. Satge et al. [8] found that the esterification of cellulose in DMAc/LiCl with lauroyl chloride as esterifying agent and dimethylaminopyridine (DMAP) as catalyst under microwave energy resulted in a drastic drop in reaction time, i.e., 1 min irradiation was sufficient, compared with 30 min to 2 days, when conventional heating is used.

In this research, the esterification of cotton in DMAc/LiCl system was investigated by using stearic acid as a modify agent, toluenesulfonyl chloride as catalyst and pyridine as co-catalyst/medium under microwave irradiation. The effects of microwave power, reaction time, concentration of pyridine/TsCl ratio, and concentration of stearic acid and toluenesulfonyl chloride on esterification were investigated. After esterification procedure, the resulting products, cotton stearate was characterized in terms of functional group analysis, element analysis, % esterification, solubility, thermal properties and morphology. Cotton stearate films were then prepared by the casting method. Finally, the effects of %esterification of cotton stearate on the physical, mechanical, and degradable properties of cotton stearate films were investigated.