CHAPTER II

LITERATURE SURVEY

2.1 Definition of cellulose film [11]

Cellulose film is a transparent film produced from cellulose fibers by a process that involves steeping, shredding, and converting the fibers into a viscose solution, or cellulose xanthate, which is subsequently extruded to convert it into a film. It is made in a limited range of thicknesses, between 0.00085 and 0.00016 inch, and, when rendered moisture resistant, may be used to seal documents, book leave, etc., for protection. It is a fairly flexible film of considerable strength.

2.2 Cellulose

In general, cellulose fibers can be classified into two categories: wood and nonwood. The terms of wood have two main sources: softwoods and hardwoods.

2.2.1 Wood [12]

Softwood

Wood, or trees, from the Gymnosperms, a subdivision of the division Spermatophytes (plants with seed), is known as softwoods. Gymnosperms are also called conifers or evergreens. These trees retain their needles (leaves) in winter. Most softwood fibers average from 3 to 3.6 mm in length. Some notable exceptions are three of the four southern pines—longleaf, shortleaf, and slash pines at 4.6-4.9 mm, sugar pine at 5.9 mm, western larch at 5.0 mm, sitka spruces at 5.9 mm, redwood at 7.0 mm, and baldcypress at 6.2 mm. Fiber coarseness (the mass per chain of fibers 100 meters along) is typically 18-30 mg/100 m.

Hardwood

Wood, or trees, from the Angiosperms, a subdivision of the division Spermatophytes, is known as hardwoods. Hardwood trees are also called broadleafs or deciduous. These trees lose their leaves in winter. Hardwoods have complex structure including vessel elements, fiber tracheids, libriform fibers, ray cells, and parenchyma cells. The fibers of hardwoods are on the order of 0.9-1.5 mm long, leading to smoother paper of lower strength compared to softwood fibers.

Non-wood [13]

Non-wood or agro-based fibers are derived from selected tissues of various mono- or dicotyledonous plants and are categorized botanically as grass, bast, leaf, or fruit fibers. Some non-wood fibers are classified by means of production; fibers such as sugar cane bagasse, wheat straw, and corn stalks are by-product. Other non-wood fibers are grouped as fiber plants, plants with high cellulose content that are cultivated primarily for the sake of their fibers such as jute, kenaf, flex, paper mulberry, and cotton. Some fiber plants also produce useful by-products; for example, oils from kenaf and flex seed.

2.2.2 Chemical constituents of wood

Wood is a renewable resource that consists mainly of cellulose, hemicellulose, lignin, and a small portion of terpenes, resins, and fatty acids. The breakdown of wood is 45% cellulose and 30% hemicellulose. It also contains 23% lignin, which is a resinous material that binds the cellulose fibers together. It has less than 5% substances like terpenes, resins, and fatty oils and acids [14, 15]

2.2.2.1 Cellulose [16, 17]

To describe cellulose, or in fact any of the other chemical compounds of xylem, is no easy task. Cellulose consists of anhydroglucopyranose units joined to form a molecular chain. The units are joined by ß-(1-4)-glycosidic linkages shown in Figure 2.1.
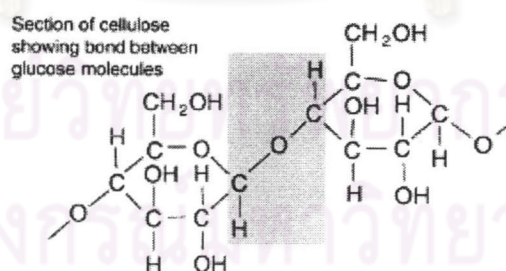

Figure 2.1 Structure of cellulose.

Cellulose is basically a "chain" of polymers, mainly glucose. In order to understand its structure, the simple necklace is a suitable analogy with each link being the glucose monomer. The glucose monomer comprises of carbon, hydrogen, and oxygen atoms (the basic building blocks of all life in the plant

kingdom). It has the chemical formulation $C_6 H_{12} O_6$, representing six units of carbon, twelve of hydrogen, and six of oxygen.

With the necklace, individual links cross through each other to form the joint. Within the cellulose chain, individual glucose monomers have chemically linked to form a cellobiose unit by a phenomenon called `condensation', eliminating one molecule of water between two adjoining hydroxyl groups at carbon 1 and 4. The linking of the cellobiose units' make-up the cellulose chain structure.

The term `the degree of polymerization (DP)' explaining the size of the cellulose chain. By dividing the molecular weigh of cellulose by the molecular weight of one glucose unit, a DP unit is obtained. Due to the abundance of hydroxyl groups along the cellulose chain, it has the tendency to form intra- and intermolecular hydrogen bonds with adjacent cellulose chain. Intramolecular bonds form between OH groups of linked glucose monomers, whereas intermolecular bonds form between OH groups of adjacent cellulose chains. Groups of cellulose chains become microfibrils, which, when on mass, make-up the cell wall layer.

Apparently, there are no direct chemical bonds between cellulose and hemicellulose, but sufficient mutual adhesion is presented through hydrogen bonds and other weaker electro-static bonds such as van der Waals forces.

2.2.2.2 Hemicellulose (Polyoses) [16]

Defining hemicellulose is just about as easy as cellulose. It is again chains of polysaccharide units. Whereas cellulose has a homopolysaccharide structure, where all the polysaccharide units are the same, hemicellouse has a hetropolysaccharide make-up. It has a DP less than cellulose and has the addition of "branches" from the main polymeric chain. The polysaccharides that make up the structure of hemicellulose can be divided into groups depending on the position in the chain. The groups are: pentoses, hexoses, hexuronic acids, and deoxy-hexoses.
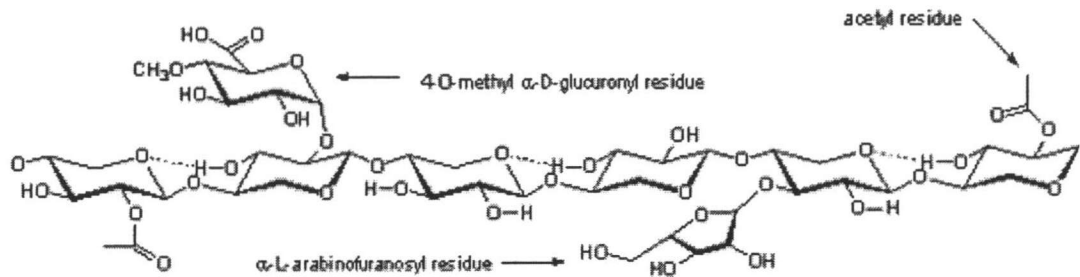
Figure 2.2 Structure of hemicellulose.

The composition and structure of hemicellulose differ in angiospermae (hardwood) and gymnospermae (softwood) tree species. The basic structure of hemicellulose found in angiosperms comprises mainly of xylose units (Xylans), linked through a similar process found in cellulose, but with acetyl units inter dispersed (Figure 2.2) and methylglucuronic acid branches. DP ranges from 100 to 200. Other units found in association with the angiospermae xylans are rhamnose and galacturonic acid.

Other hemicellulose units found in angiosperms include glucomannans which are glucose and mannose units forming chains (DP=60 to 70) which are slightly branched. However, these have very sporadic dispersion. Xylans found in gymnosperms lack acetyl groups, have arabinofuranose unit side branches, and have a higher proportion of methylglucuronic acid. The DP for gymnospermae hemicellulose is much lower, ranging from 70 to 130. Gymnosperms also contain glucomannans, but in higher quantities than angiosperms, with the additions of acetyl groups and galactose. Other hemicellulose units found in both types include glucans, galactans, and pectin.

2.2.2.3 Lignin [12, 16, 18]

Lignin is a complex polymer consisting of phenylpropane units and has an amorphous, three dimentional structure. It is found in plants. Its molecular weight in wood is very high and not easily measured. Lignin is the adhesive or binder in wood that holds the fibers together. Lignin is concentrated in the middle lamella; during chemical pulping its removal allows the fibers to separate

easily. The glass transition temperature (softening temperature) is approximately 130-150 °C. Moisture decreases the glass transition temperature slightly.

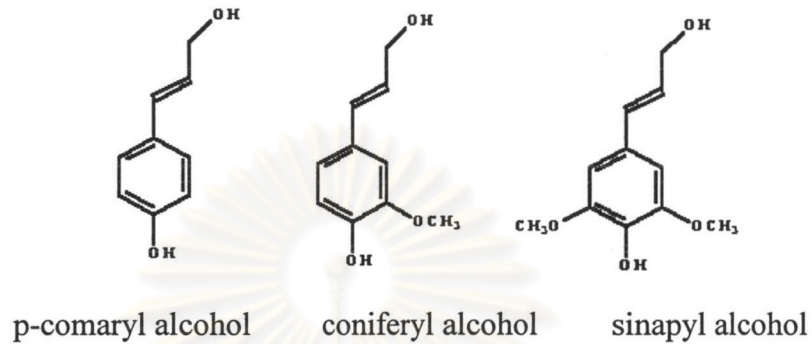There are three basic lignin monomers that are found in lignin, as shown in Figure. 2.3.

p-comaryl alcohol   coniferyl alcohol   sinapyl alcohol

Figure 2.3 Lignin precursors for plants. (Softwoods have coniferyl alcohol, while hardwoods have coniferyl and sinapyl alcohols).

Grasses and straws contain all three lignin monomers, hardwoods contain both coniferyl alcohol (50-75%) and sinapyl alcohol (25-50%), and softwoods contain only coniferyl alcohol.

Using coniferyl alcohol as an example, the first step of lignin polymerization in the plant cell wall involves formation of a free radical at the phenolic hydroxyl group, as presented in Figure 2.4.
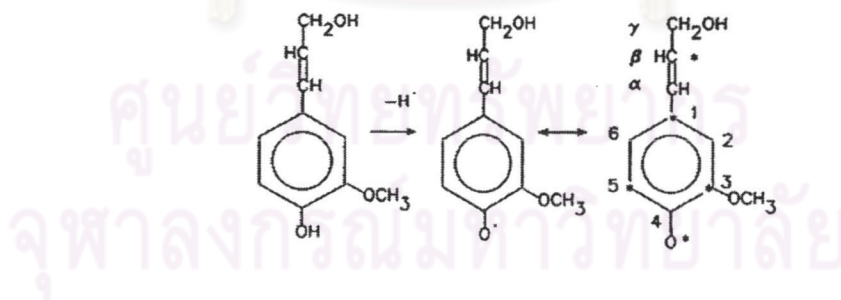

Figure 2.4 Formation of free radicals from coniferyl

This structure has five-resonance structure with the free radical occurring at various atoms as shown on the right of Figure 2.4. Carbon atoms C-1 and C-3 in soft wood and C-1, C-3 and C-5 in hardwoods do not from linkages due to steric hindrance. Carbon atoms of the propane unit are labeled from the aromatic ring outward as α, β, and γ, respectively. Carbon atoms of the aromatic ring

are labeled from the propane group towards the methoxy group from 1 to 6, respectively. Some commonly occurring lignin linkages are also shown in Figure 2.5.

4-o-β-aryl ether linkage   4-o-α-aryl ether linkage   C-C linkage
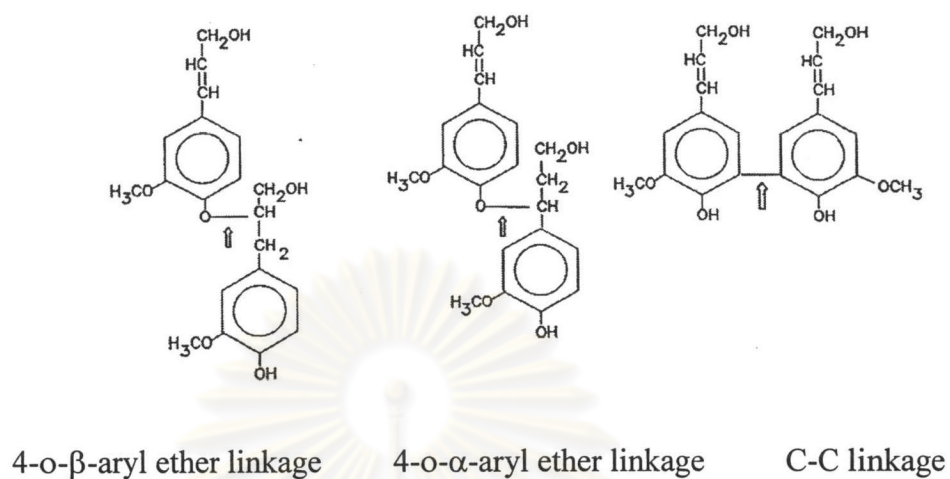
Figure 2.5 Example linkages between lignin

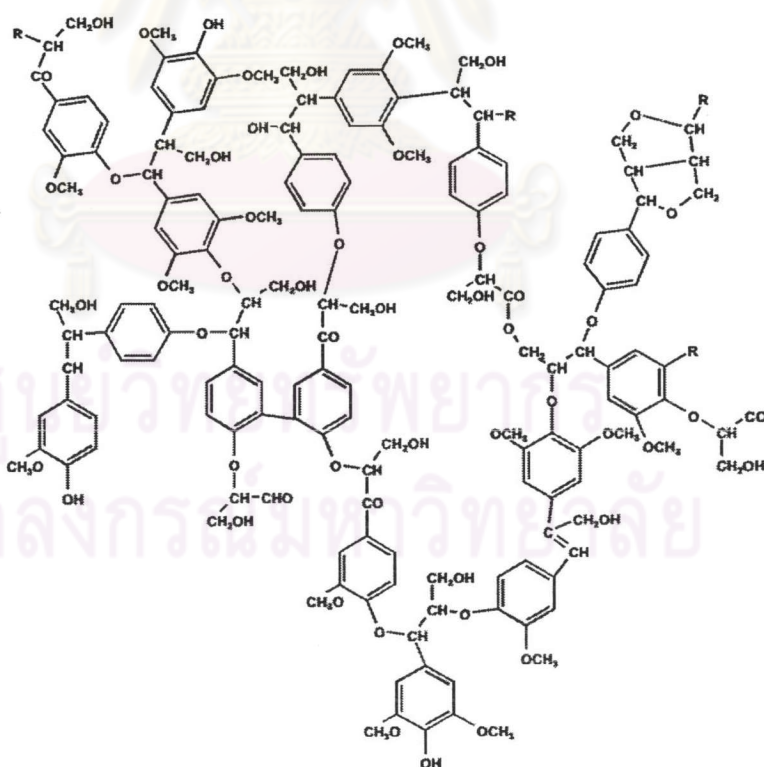A representative lignin molecule is shown in Fig 2.6

Figure 2.6 A hypothetical depiction of a portion of a softwood lignin molecule.

2.2.3 Type of cellulose and their application [19]

Type of cellulose	Application
Cellulose acetate	Extruded tape, packaging film, blister packs and premium.
Cellulose acetate butyrate	Tooth brush handles, blister packs.
Cellulose propionate	blister packs.
Ethyl cellulose	Flashlight cases and fire extinguisher components.
Cellulose triacetate	Photographic albums and photographic films base.
Cellulose nitrate	Toilet articles and industrial items fabricated from sheet, rod and tube
Cellulose laurate	Use in the production of films
Cellulose stearate	packaging film

2.3 Paper mulberry

Plants have undoubtedly played an important role throughout human history. Many examples of these important plants are known to people throughout the world including tobacco, cotton, and sugar. However, one important plant that played a very important part in shaping world history, the Paper Mulberry, *Broussonetia papyrifera*, has unfortunately now become better known as an unwelcome weed of natural areas worldwide. [20]

Paper Mulberry
Scientific Name: Broussonetia papyrifera.
Synonym: Morus papyrifera, Papyrius papyriferus
Family: Moraceae

Recommended Temperature Zone:

Heat Tolerance: Good

Sun Exposure: Full sun

Origin: Northeastern Asia

Growth Habits: Small deciduous tree, fast growing, up to 50 feet tall (15 m), 40 feet wide (12 m), somewhat untidy looking; the leaves on the young tree are lobed, up to 12 inches long (30 cm); adult trees have smaller leaves.

Watering Needs: Little water

Figure 2.7 Paper mulberry.

The Paper Mulberry is a good shade tree. In good soils and with plenty of water. It is considered invasive in Tennessee. The name "paper mulberry" comes from the fact that it yields a fine fiber from its inner bark which is, used to make paper or Polynesian tapa cloth and prepare cellulose film.

Species of paper mulberry [21]

1. Broussonetia papyrifera: the bark fibers are used for making paper, the wood is used for furniture, and the leaves, fruit, and bark are used medicinally.
2. Broussonetia kurzii: the leaves are used for cooking.
3. Broussonetia kazinoki: the bark fibers are used for making paper [Japan, Korea].
4. Broussonetia kaempferi: the bark fibers are used for making paper [Japan, Korea].

2.4 Pulp Production

2.4.1 The Pulping Process

Wood consists of three primary components: cellulose, hemicellulose and lignin. Cellulose, which is the fibrous component of wood, is used to make pulp. Lignin is the glue that holds wood fibers together. Pulping is the process which reduces wood to a fibrous mat by separating the cellulose from the lignin and hemicellulose. Pulping processes are generally classified as chemical, mechanical, or semi-mechanical. The three chemical pulping methods are known as kraft, sulfite, and soda [12, 22].

In chemical pulping, wood is cooked in a digester at elevated pressure with a solution of the appropriate chemicals, which dissolve the lignin and leave behind the cellulose. The cooking process results in emissions of a variety of hazardous air pollutants including formaldehyde, methanol, acetaldehyde, and methyl ethyl ketone.

In mechanical (or ground wood) pulping, the wood is pressed against a grinder which physically separates the fibers. Mechanical pulping, which is energy intensive, produces an opaque product which is weak and discolors easily when exposed to light.

In semi-chemical pulping, the wood chips are partially cooked with chemicals, and the remainder of the pulping is accomplished mechanically. This is process uses a combination of chemical and mechanical methods.

2.4.2 Bleaching the pulp

Bleaching is a very important step. Bleaching is used to purify and clean the pulp. Bleaching removes lignin, which affects the purity of the fiber. Fiber mills use chlorine gas and chlorine dioxide to bleach pulp, while most mechanical pulp bleaching operations use peroxide. Chlorine gas removes most of the remaining lignin, while the chlorine dioxide whitens lignin that cannot be removed. [12, 22]

-Elemental Chlorine Bleaching is the process currently in place at some existing bleaching plants, and uses chlorine and hypochlorite to brighten the pulp. When elemental chlorine and hypochlorite react with the lignin, they form chlorinated pollutants such as chloroform, dioxin and furans in the wastewater stream.

-<u>Elemental Chlorine Free Bleaching (ECF)</u> replaces chlorine with chlorine dioxide as a bleaching agent and hypochlorite in no longer used. The use of ECF bleaching results in reduced levels of chlorinated pollutants in the waste water stream.

-<u>Totally Chlorine Free (TCF) bleaching</u> uses no chlorinated bleaching agents to bleach the pulp. Instead, bleaching agents such as oxygen and peroxide are used. TCF bleaching eliminates chlorinate pollutants in the wastewater stream.

2.5 Media for cellulose functionalization

A major stimulation for the investigation of alternative paths for polysaccharide functionalization was the discovery of a variety of new solvents for polyglucans especially for cellulose with its extended supra-molecular structure. Of course, the main driving force looking for new ways to dissolve cellulose is the need to develop alternative paths for fiber spinning and related processes excluding the well documented problems of the viscose process. In addition, the use of cellulose solvents for the characterization of cellulosic material has grown in significance over the last years as well.

Dissolution of cellulose destroys the highly organized hydrogen-bonding system surrounding the single polyglucan chain. It needs to be mentioned that not only the physical dissolution of the polysaccharide (non-derivatizing solvents) is capable for alternative synthesis paths but also the functionalization after partial derivatization, i.e. after dissolving the polymer in a so-called derivatizing solvent [23, 24]. In the latter case, cellulose intermediates are formed in situ by introducing new functional groups via covalent bonds especially ester moieties of rather low hydrolytic stability. Furthermore, it is possible to isolate these intermediates or to synthesize similar compounds and to conduct subsequently the homogeneous modification starting from the polymers dissolved in an inert simple organic solvent. A clear line between these cellulose intermediates (or 'transient derivatives' as they are sometimes called) [25] and true cellulose derivatives can not be drawn. But it seems reasonable to define 'cellulose intermediates' as hydrolytically unstable cellulosics that can be either obtained by isolation from solutions of derivatizing solvents or as specifically synthesized cellulosics with substituents which are easily cleaved off during a common work-up procedure, e.g. in aqueous media. A nice example is that of

cellulose trifluoroacetates where the reaction of trifluoroacetic acid/trifluoroacetic anhydride with the polymer produces the soluble product, which can be even isolated and redissolved in common organic solvents. On the other hand, formation of cellulose acetate followed by a separate dissolution in acetone would not be classified as a cellulose solution.

Non-derivatizing solvents include both single and multi-component systems. Although a wide variety of these solvents were developed and investigated in recent years only a few have shown a potential for a controlled and homogeneous functionalization of polysaccharides. Limitations are high toxicity, high reactivity of the solvents leading to undesired side reaction, and the loss of solubility during reactions yielding inhomogeneous conditions by formation of gels and pastes which can be hardly mixed and even by formation of deswollen particles of low reactivity which set down in the reaction medium.

A suitable, though approximate classification of cellulose solvents is presented in Figure 2.8.
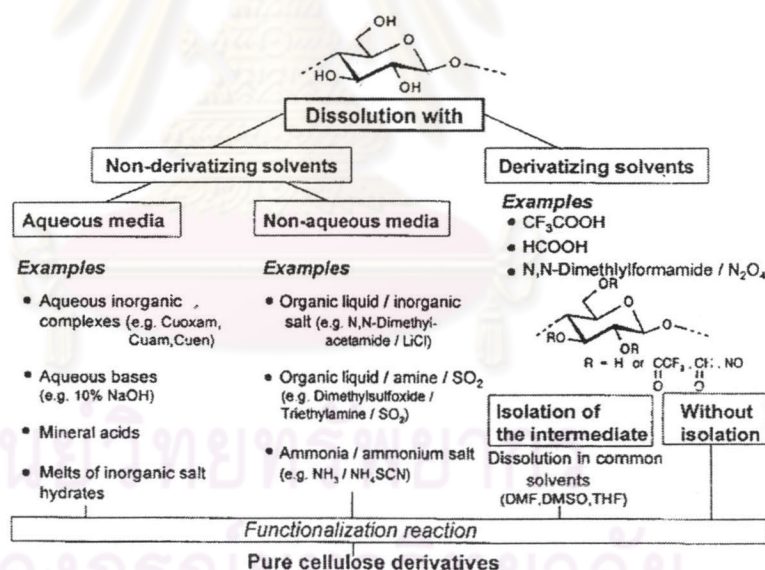
Figure 2.8 Classification of cellulose solvents suitable as medium for chemical functionalization reactions.

2.5.1 Aqueous non-derivatizing solvents

Aqueous solvents for cellulose, e.g. solutions of inorganic salts and complex compounds, were widely used for cellulose regeneration. The best-known solvents of this group are cuprammonium hydroxide (Cuam) and cupriethylenediamine hydroxide (Cuen). Regeneration of membranes from Cuam

solution provides high quality products for hemodialysis. It is even possible to dissolve the polymer in about 10% aqueous NaOH solution, however the solubility is limited to cellulose of comparably low degree of polymerization (DP) of up to 200. The application as medium for completely homogeneous functionlization reactions is just of limited interest. This is due to the high tendency of these media towards hydrolysis of reagents applied for modification, problems concerning the purification of the derivatives obtained, and their tendency to become inhomogeneous during the reaction. Thus, cellulose is already regenerated from solvent complexes by changing the pH value of the medium. Typical aqueous solvents are summarized in Table 2.1.

Table 2.1 Examples of aqueous cellulose solvents [26]

Type of compound	Solvent abbreviation	Active species
Transition metal complexes with amines or NH$_3$	Cadoxen	$[Cd(H_2N-(CH_2)_2-NH_2)_3](OH)_2$
	Cdtren	$[Cd(NH_2CH_2CH_2)_3N](OH)_2$
	Cooxen	$[Co(H_2N-(CH_2)_2-NH_2)_2](OH)_2$
	Cupren	$[Cu(H_2N-(CH_2)_3-NH_2)_2](OH)_2$
	Cuam	$[Cu(NH_3)_4](OH)_2$
	Nioxam	$[Ni(NH_3)_6](OH)_2$
	Nioxen	$[Ni(H_2N-(CH_2)_2-NH_2)_3](OH)_2$
	Pdxen	$[Pd(H_2N-(CH_2)_2-NH_2](OH)_2$
	Cuen	$[Cu(H_2N-(CH_2)_2-NH_2)_2](OH)_2$
Transition metal complexes with tartaric acid	FeTNa	$Na_6[Fe(C_4H_3O_6)_3]$
Ammonium hydroxides	TEOH	Tetraethylammonium hydroxide
	GuOH	Guanidinium hydroxide
Alkali hydroxides		NaOH,LiOH

Nevertheless, a number of modern aqueous solvents, e.g. the aqueous solution of Ni(tren)(OH)$_2$ [tren = tris(2-aminoethyl)amine], were studied in terms of the mechanism of dissolution and for their potential as medium for homogeneous etherification reactions [27]. It has been shown that the new metal complexes (Ni-tren and Cd-tren) completely dissolve cellulose by deprotonating and coordinative binding of the hydroxyl groups in the 2 and 3 positions within the AGU (anhydroglucose units) [28]. It is possible to convert cellulose dissolved in Ni-tren [concentrations of up to 10% (w/v)] in a fully homogeneous process to carboxymethyl cellulose (CMC) [29]. Structure investigations by means of ^{1}H-NMR analysis after chain degradation and HPLC analysis after complete depolymerization revealed that these products show a statistic content of the different repeating units and a distribution of the carboxymethyl functions on the level of the AGU in the order C-2 ≥ C-6 > C-3, i.e. they posses the same functionalization pattern as ethers prepared in a highly swollen state as applied for commercial production of CMC. This result clearly shows that both simple activation of cellulose with aqueous NaOH and the complete dissolution of the polysaccharide lead to reactive sites with an almost even accessibility and hence there is no particular advantage of a conversion of the dissolved polymer.

2.5.2 Non-aqueous non-derivatizing solvents

Various solvents of this group were found in the last two decades. Important examples with regard to cellulose functionalization are summarized in Table 2.2 A more detailed description of non-aqueous, non-derivatizing solvents is published elsewhere [30].

Table 2.2 Typical non-aqueous cellulose solvents

Number of components	Substance group	Examples
Unicomponent	N-Alkylpyridinium halogenide Oxides of tertiary amines	Ethylpyridinium chloride Triethylamine-N-oxide N-Methylpiperidine –N-oxide
Bicomponent	Dimethyl sulfoxide (DMSO) containing solvents	DMSO/methylamine DMSO/KSCN DMSO/CaCl$_2$
	Liquid ammnia/sodium or ammonium salts	NH$_3$/NaI (NH$_4$I) NH$_3$/NaSCN (NH$_4$SCN)
	Dipolar aprotic solvents/LiCl	DMAc/LiCl N-Methylpyrrolidone/LiCl
	Pyridine or quinoline containing systems solvent	Pyridine/resorcinol Quinoline/Ca(SCN)$_2$
	Liquid SO$_3$/secondary or tertialy amines	SO$_3$/triethyl amine
Tricomponent	NH$_3$ or amine/salt/polar solvent	NH$_3$/NaCl/DMSO Ethylenediamine/NaI/N, N-Dimethylformamide
	NH$_3$ or amine/SO$_2$ or SOCl$_2$/polar	Diethylamine/SO$_2$/DMSO

The system N, N-dimethylacetamide (DMA)/LiCl shows an enormous potential for the analysis of cellulose and for the preparation of a wide variety of derivatives. Its usefulness in analysis is due to the fact that the solvent is colorless and dissolution succeeds without or at least with negligible degradation even in case of high molecular weight polysaccharides, e.g. cotton linters or bacterial

cellulose. Thus, it was possible to investigate the dissolved cellulose by means of ^{13}C-NMR spectroscopy [31], electro spray mass spectroscopy (ESI-MS), size exclusion chromatography and light scattering techniques. Although it is the solvent of choice for these applications, a dissolution mechanism for cellulose in this solvent has still not been clearly postulated. Different solvent-polymer structures were proposed [32].

A number of modified compositions were investigated. DMA can be substituted in the solvent mixture with N-methyl-2-pyrrolidone (NMP), N, N-dimethylformamide (DMF), DMSO, N-methylpyridine or hexamethylphosphoric triamide but only NMP, the cyclic analog of DMA, was found to dissolve the polysaccharides without major degradation. In case of the preparation of bromodeoxycellulose it was useful to apply LiBr instead of LiCl as salt. The preparation of lactones and carbamates succeeds in high yields, at moderate temperatures and modest reagent concentrations in DMA/LiCl [33]. Thus, homogeneous phase carbanilation with phenylisocyanate produces a completely functionalized derivative which has been widely adopted for the determination of molecular weights in non-aqueous solvents by means of gel permeation chromatography (GPC). Furthermore, cellulose was homogeneously derivatized with pesticides using the isocyanate derivatives of, e.g. 4-amino-(1,1-dimethylethyl)-3-(methylthio)-(1,2,4)-triazine-5(4H)one (metribuzine) to obtain products with a controlled release of the bioactive compound.

The mixture 1, 3-dimethyl-2-imidazolidinone (DMI) and LiCl was found to be suitable dissolving cellulose [34]. The advantages of the nowadays commercially available DMI consist in its thermal stability and low toxicity. DMI/LiCl is able to dissolve cellulose samples with DP values as high as 1200 and concentrations of 2-10% (w/w) applying the same procedure as used for DMA/LiCl, i.e. an activation of the polymer by a heat treatment or a step-wise solvent exchange is absolutely necessary. Experimental details for a simple dissolution procedure are given in the literature [35]. ^{13}C-NMR spectra of cellulose acquired both in DMI and DMA in combination with LiCl exhibit the same chemical shifts, i.e. a comparable solvent structure may be assumed with regard to functionalization. DMI/LiCl is capable both for esterification and etherification [36]. The reactivity of the OH functions is in the order C-6 > C-2 > C-3 as found in other non-aqueous cellulose solvents, too. Thus, the methylation of cellulose in DMI/LiCl yields tris-O-methyl cellulose in a one-step procedure.

In case of single component solvents, N-alkylpyridinium halides and N-oxides of tertiary amines are worth mentioning. Typical structures are shown in Figure 2.9.
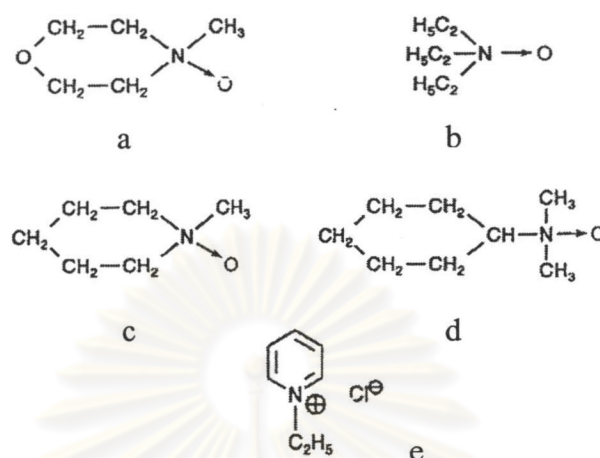

Figure 2.9 Structure of typical single component solvents of cellulose, (a) N-methyl-morpholine-N-oxide (NMNO), (b) triethylamine-N-oxide, (c) N-methyl-piperidine-N-oxide, (d) N, N-dimethylcyclohexylamine-N-oxide, (e) N-ethyl-pyridinium chloride.

The most powerful solvents in this regard are N-ethyl-pyridinium chloride (Figure 2.9(c)) and N-methylmorpholine-N-oxide (NMNO) (Figure 2.9(a)). The advantage of an easy work up procedure after modification of polysaccharides in these solvents is ruled out by the fact that most of these substances are solid at room temperature and need to be applied as melts and, on the other hand, they are highly explosive. Thus, these compounds are often diluted with common organic liquids to give appropriate reaction media. Among these additives for N-ethyl-pyridinium chloride (m.p. 118 °C) are DMF, DMSO, sulfolane, pyridine and N-methyl pyrrolidone. In this way it was possible to decrease the melting point to 75 °C and to apply the solvent for homogeneous acylation of cellulose [37].

NMNO dissolves cellulose typically as the monohydrate (about 13% water) at about 100°C. It has gained quite an enormous attention for cellulose regeneration and a new fiber spinning process based on NMNO as solvent is already industrially realized forming the so-called Lyocell fibers. Recent results were published dealing with the investigation of the interaction of cellulose with the solvent by means of ^{13}C CPMAS NMR and microscopy. In contrast to N-ethylmorpholine-N-oxide, that converts cellulose I into cellulose III but dose not

dissolve the polymer, NMNO is able to break hydrogen bonds, particularly to O-6, sufficiently to liberate individual chains and, thereby, to dissolve the polysaccharide sheets.

A novel and powerful new solvent for cellulose consists in the mixture DMSO/tetrabutylammonium fluoride trihydrate (TBAF). The advantage of DMSO/TBAF is that cellulose with a degree of polymerization as high as 650 dissolves without any pretreatment within 15 min. A remarkable finding was that only the fluoride is able to give clear solutions. If the halide is changed, no dissolution occurs. Highly resolved ^{13}C-NMR spectra of cellulose can be obtained showing all the ring carbons of the AGU and giving no hints for a derivatization during the dissolution process as shown in Figure 2.10.
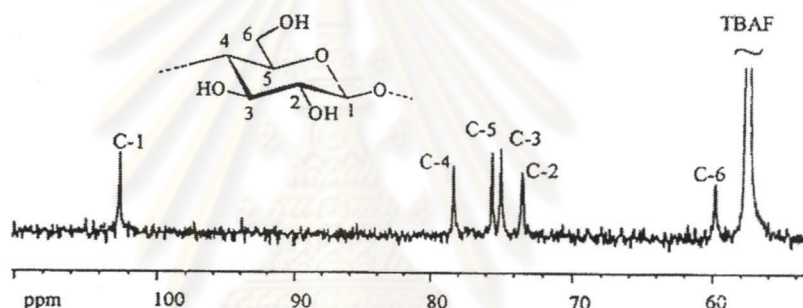

Figure 2.10 ^{13}C-NMR spectrum of cellulose (3%, w/v) dissolved in DMSO-d_6/tetrabutylammonium fluoride trihydrate.

It should be mentioned that the solutions contain a certain amount of water because TBAF is used as commercially available trihydrate and the cellulose is air-dried only.

2.5.3 Aprotic derivatizing solvents and soluble intermediates

All the solvents previously discussed show physical dissolution of the polysaccharide without derivatization of any hydroxyl group. An acceptable alternative to this route is the application of so called derivatizing solvents or the utilization of hydrolytically unstable, organo-soluble cellulose intermediates. A representative summary of such solvents and the derivatives formed in situ is given in Figure 2.11.
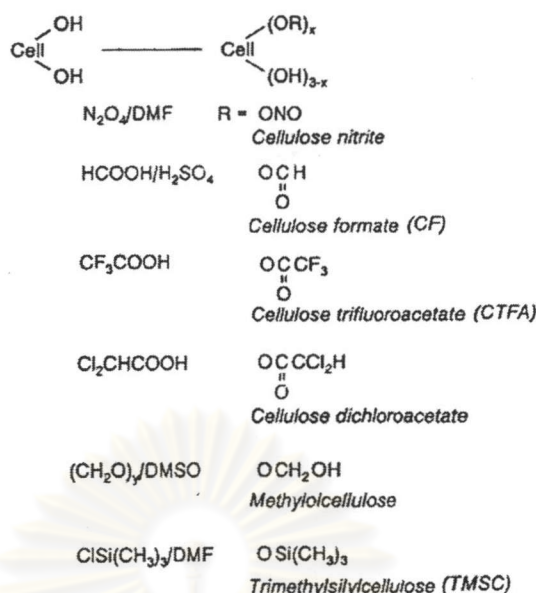
$$\underset{\text{Cell}}{\overset{\text{OH}}{\diagdown}} \overset{\text{OH}}{\diagup} \quad\longrightarrow\quad \underset{\text{Cell}}{\overset{(OR)_x}{\diagup}} \overset{}{\diagdown} (OH)_{3-x}$$

N_2O_4/DMF	R = ONO
	Cellulose nitrite
$HCOOH/H_2SO_4$	O C H, O
	Cellulose formate (CF)
CF_3COOH	O C CF_3, O
	Cellulose trifluoroacetate (CTFA)
$Cl_2CHCOOH$	O C CCl_2H, O
	Cellulose dichloroacetate
$(CH_2O)_x$/DMSO	O CH_2OH
	Methylolcellulose
$ClSi(CH_3)_3$/DMF	O $Si(CH_3)_3$
	Trimethylsilylcellulose (TMSC)

Figure 2.11 Representative examples of aprotic derivatizing solvents of cellulose and intermediates formed.

The major disadvantage of the derivatizing solvents is the occurrence of side reactions during dissolution and the formation of undefined structures. In turn, this leads to products hardly reproducible. Nevertheless, the N,N-dimethylformamide (DMF)/N_2O_4 solvent, yielding cellulose nitrite as intermediate, has found considerable interest in the synthesis of inorganic cellulose ester, e.g. cellulose sulfates despite its highly toxic nature. Although long known as solvent, the dissolution mechanism was a long lasting controversy. Golova et al. favored an addition compound of cellulose and N_2O_4, solvated by complex formation with the dipolar aprotic medium [38]. But today it is a well-accepted fact that dissolution under strictly anhydrous conditions succeeds by formation of the cellulose trinitrite [39]. In this process the first step is a heterolytic cleavage of the N_2O_4 molecule which initiates the esterification to the nitrite. If small amounts of water are present in the solvent system, the cellulose molecule is only partially derivatized in this step with a preferred conversion of the primary hydroxyl groups. Variation of the solvent components is possible. Instead of DMF, DMSO may be applied and N_2O_4 can be substituted with NOCl, nitrosyl sulfuric acid, nitrosyl hexachloroantimonate or nitrosyl tetrafluoroborate yielding solutions within the same time.

A rather interesting derivertizing solvent utilized for esterification is the mixture DMSO/paraformaldehyde. The major advantage of this system is that it dissolves cellulose rapidly and almost without degradation even in case of high molecular weight polymers. Cellulose is here dissolved by formation of

the hemiacetal, i.e. so-called methylol cellulose is obtained (Figure 2.11). ^{13}C-NMR spectroscopy revealed that the acetalization occurs preferentially at the 6 position of the AGU [40]. This methylol structure remains intact during subsequent functionalization in non-aqueous media resulting in derivatives with a pronounced substitution of the secondary OH groups as can be determined by means of GLC after complete hydrolysis of subsequently etherified cellulose. In contrast, the methylol functions can be easily removed by a treatment with water. Noteworthy is the fact that during the dissolution a growth of oligooxy methyleneoxide chains may occur. The free terminal hydroxyl groups of these chains may also be derivatized in a subsequent step. Nevertheless, the solvent was exploited for the preparation of a whole number of ethers yielding almost completely functionalized non-ionic cellulose derivatives and for the synthesis of esters via homogeneous conversion with anhydrides [41].

A much higher predictability compared with the application of the derivatizing solvents can be realized if the intermediates formed during the dissolution of the polysaccharide are isolated prior to the conversion into the final derivative (Figure 2.11). The increasing reproducibility is due to the fact that structure analysis of the intermediates is possible, on one hand. On the other, these intermediates can be dissolved in a wide variety of common organic solvents which decreases the tendency towards side reactions drastically (especially degradation). Therefore, reactive intermediates can be the starting material for a variety of highly engineered derivatives. Besides the investigation of trialkylsilyl derivatives in this regard and subsequent functionalization of the rather reactive cellulose xanthogenate, which was only of limited interest in the context of reactive intermediate compared with its wide utilization for cellulose regeneration, cellulose formats (CF) and halogenoacetic acid esters of cellulose are the most studied intermediates within this new strategy of functionalization.

The interaction of cellulose with formic acid was applied to determine the degree of disorder of the cellulose structure and the chemical accessibility of the hydroxyl groups. Moreover, solutions of cellulose in formic acid and CF were studied in terms of their hydrolytic and thermal stability and their potential for cellulose fiber preparation by regeneration [42]. This CFs are obtained by treating cellulose in a surplus of formic acid without catalyst over periods of 4-15 days or with sulfuric acid as catalyst yielding fairly degraded polymers with DS values of about 2.5. CF can be isolated from mixtures of cellulose, formic acid,

phosphoric acid and water. They are soluble in DMF and DS values of up to 1.2 are reached. The formulation takes place in the order C-6 > C-2 > C-3 as revealed by ^{13}C-NMR spectroscopy. If sulfuric acid is applied as catalyst, the reaction is completed within 15 min. The CF prepared has a DP of about 200 (DP of the starting cellulose was 600). In case of the application of partially hydrolyzed $POCl_3$ as swelling and dehydrating agent it is possible to increase the DS of up to 2.2 yielding formats soluble in DMSO, DMF and pyridine with DP values of 280 (starting from spruce sulfite pulp, DP = 680) within 4 h reaction time. These products were thermally stable of up to 280°C under anhydrous conditions. Structure analyses by mean of ^{13}C-NMR spectroscopy (Figure 2.12) and HPLC after methylation and hydrolytic degradation revealed a complete functionalization of the primary hydroxyl groups. Another interesting path for the preparation of CF samples was published by Vigo et al. [43]. It was shown that cellulose can be converted with a reagent obtained from thionyl chloride and DMF. Thereby, the formiminium compound is formed as reactive intermediate during this reaction. An appropriate work up procedure gives CF.
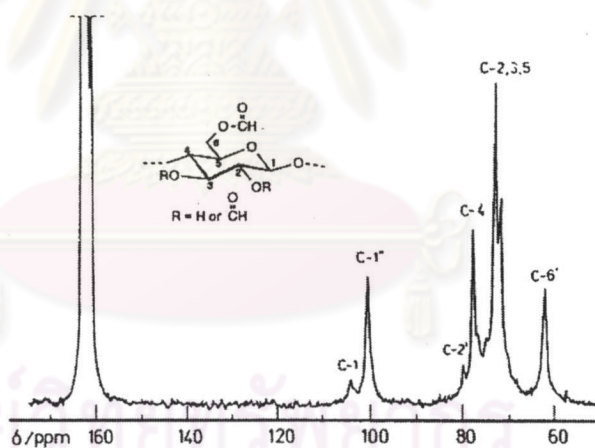

Figure 2.12 ^{13}C-NMR spectrum of cellulose formate with a degree of substitution of 2.2 (index means substituted and means influenced by a functionalization of the adjacent position).

2.6 Unconventional synthesis paths for and types of carbonic acid ester of cellulose

Ester of cellulose especially the acetate is long known derivatives of the polysaccharide. Thus, cellulose acetate (CA) was first synthesized by Schuetzenberger in 1865 and was industrially produced as early as 1900. Conventionally CAs are prepared by convension of cellulose with an excess of acetic

anhydride (10-40% above the amount needed for cellulose triacetate formation) in the presence of sulfuric acid or perchloric acid as catalyst. Two different methods are applied today to obtain the cellulose ester. The majority of the CAs (about 900,000 ton per year) is produced using a route which includes the dissolution of the products formed. On the other hand, it is possible to carry out the acetylation on the intact fiber (fiber acetylation). The products obtained in the first step are fully esterified. Usually they are partially deacetylated in an one-pot hydrolysis to give the widely applied acetone soluble 2.5 acetate (acetyl content ca. 40%; DS_{Ac} 2.4-2.6). This 'synthetic detour' is necessary because CA samples with same DS synthesized directly from cellulose are not soluble in acetone [44]. Structure analyses to elucidate the reasons for this behavior and the search for new synthesis tools for a more effective acetylation are still among the major stimulants for the work in this field.

On the other hand, there is a need for the investigation of new paths for the preparation of bulky esters (e.g. long chain or aromatic esters) of polysaccharides with a wide variety of DS values and structural features to obtain tailored highly engineered derivatives. Again it is not only the great abundance of the polysaccharide which stimulates the work but more the extraordinary structure of the cellulose backbone. Therefore, two classes of esters are desired goals. First cellulose esters with large substituents (more than 5 C-atoms or bulky moieties), low DS, and regular distribution along the polymer backbone resulting in the retention of a large portion of OH functions and, thereby, to retain desirable cellulose characteristics while the processibility is increased. Second, the complete functionalization of all OH groups may yield esters with new structure features and properties mainly determined by the type of substituent in question. Besides the application of a whole number of different new catalysts including mechanistic studies on the mode of action of these catalysts (e.g. different sulfonic acids or lewis acids like $ZnCl_2$) on the acylation mechanism and the application of the efficient 'impeller' reagents using, e.g. trifluoroacetic anhydride, the most promising approach is the esterification of the polysaccharide in solvent system using modern acylation reagents.

2.6.1 Homogeneous esterification of cellulose

2.6.1.1 Acylation in non-derivatizing solvents and new activation procedures

From the various non-derivatizing solvents discussed above N,N-dimethylacetamide (DMA) or N-methylpyrrolidone in combination with LiCl have gained special importance.

The esterification of cellulose in DMA/LiCl using carbonic acid anhydride and the –chlorides was among the first attempts of chemical modification of the polysaccharide under totally homogeneous conditions [45]. It was observed that cellulose solutions in DMA/LiCl with polymer concentrations higher than 10% (w/w) form mesophases. In this case, the conversion of the polysaccharide may be combined with a number of unreproducable effects because in the region of useable solutions of up to 15% (w/w) these anisotropic systems are not fully stable [46]. Nevertheless, the advantages of acylation in homogeneous phase in DMA/LiCl are an excellent control of the DS values and an uniform distribution of the functional groups along the polymer chains. Moreover, a selectivity of the functionalization reaction within the AGUs may appear. Thus, the reaction of cellulose with acetyl chloride in the presence of pyridine as base gives a CA with complete functionalization of the primary hydroxyl groups at DS values starting from 1.6 [47].

Especially in case of esters with aromatic functions, the use of acyl chlorides is still a convenient and effective path. 4-Phenylbenzoyl cellulose was obtained from the homogeneous esterification yielding polymers with DS values as high as 2.4. The derivatives were extensively analyzed by IR- and ^{13}C-NMR spectroscopy as well as their solution properties and mesophase formation behavior was studied by mean of viscometric and light scattering experiment. Phenylacetoxy cellulose, 4-methoxyphenylacetoxy cellulose, and p-toloylacetoxy cellulose with DS values of 1.8-1.9 could be prepared according to this procedure. Solid state ^{13}C-NMR spectroscopic studies were carried out and the derivatives were investigated towards their liquid crystalline properties. Furthermore, the introduction of bioactive substituents for controlled release systems was achieved utilizing the acid chloride of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,2-dichloropropionic acid (dalapon).

In terms of its usefulness as protective group for polysaccharides, the adamantoyl moiety was investigated recently. The remarkable

finding was that the introduction of the adamantoyl ester is most effective and selective if the carbonic acid chloride is used [48]. Alternative methods, e.g. the application of p-toluenesulfonyl chloride (Tos-Cl) or N, N carbonyldiimidazole in combination with the free acid, which are still under investigation, yield comparable results. Adamantoyl cellulose with DS values of up to 1.3 was odtained. A typical ^{13}C-NMR spectrum of a product with a DS of 0.65 is shown in figure 2.13.
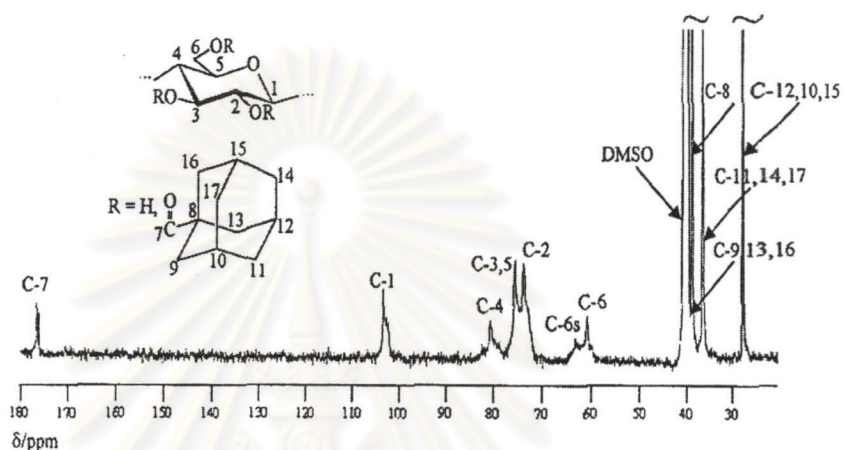

Figure 2.13 ^{13}C-NMR spectrum of adamantoyl cellulose with a degree of substitution of 0.65 (index s means substituted).

The preparation of esters with long chains using the acyl chloride, e.g. n-octanoic to octadecanoic was investigated. Besides the acyl chlorides for the synthesis of the simple fatty triester, mixed triesters were obtained by convertion of cellulose in DMA/LiCl with the fatty acid and acetic anhydride in the presence of HClO$_4$. Comparable results were published for the reaction of cellulose with acyl chloride, e.g. stearyl chloride in combination with triethylamine (TEA). The advantage of TEA in comparison with pyridine as base is the lower acidity of the hydrochloride formed resulting in a decreased tendency towards chain degradation and split-off of the ester functions introduced. Comparable homogeneous esterification reactions with long chain acid chlorides were preformed using hemicelluloses from popular chips dissolved in DMA/LiCl. DS values between 0.32 and 1.51 were accessible. It is possible to stearoylate over 75% of the hydroxyl groups in native hemicellulose via this route [49]. Even cellulose methacrylates with DS values of up to 1.3 were accessible which gellify when irradiated by UV due to the cross-linking reaction of lateral double bonds. Anhydrides of dicarbonic acids were applied for the synthesis of water-soluble carbonic acid half esters of cellulose. A

reactivity in the order phthalic anhydride > maleic anhydride > succinic anhydride was observed [50].

New and effective procedures for homogeneous acylation were studied which could be employed in large scale as well. Acetates, propionates, butyrates and mixed acetates/propionates with a stoichiometric control of the acetyl content can be obtained by reacting dissolved cellulose with the acid anhydrides, without catalyst, at 110 °C for 4 h. It was shown that the acylation of the polysaccharide occurs without degradation of the polymer [51]. A preferred acylation of the 6 position was determined by means of ^{13}C-NMR spectroscopy. Both the negligible effect on the DP and the stoichiometric conversion of the polysaccharide make this synthesis path a very reliable and reproducible process.

A highly efficient and sophisticated method is the conversion of cellulose dissolved in DMA/LiCl with diketene shown in figure 2.14.
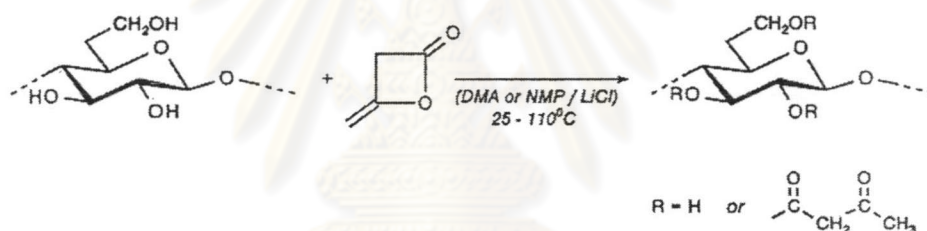

Figure 2.14 Reaction scheme illustrating the acylation of cellulose with diketene yielding cellulose acetoacetate in one-step under homogeneous condition.

or with a mixture of diketene/carbonic acid anhydrides. Via this route it is possible to prepare both pure acetoacetates or mixed acetoacetate/carbonic acid esters of cellulose (especially with acetyl and propionyl moieties). The reaction with diketene is a very useful alternative to the conversion of cellulose with tert-butyl acetoacetate which is not able to yield products with high DS values in predictable processes. The reactive intermediate in both cases is acetylketene. The reaction can be as well be carried out in NMP/LiCl. Acetoacetylation with diketene occurs very rapidly at temperature of 100-110 °C. Thus, a complete derivatization was observed within 30 min. Conversion of the polymer with mixtures of diketene/carbonic acid anhydrides revealed the same efficiency and predictability as discussed for the pure ester. Mixed acetoacetate-acetates, propionates and butyrates were obtained without catalysts. This

derivatization imparts the polymers solubility ranging from water to THF depending on the DS of the products. The DP is just negligibly affected during the reactions. The glass transition temperature (T_g) of the cellulose acetoacetates shows no correlation with the DP of the derivative but is strongly influenced by the DS values.

Besides the application of carbonic acid chlorides and anhydride for acylation, a number of very efficient reagents for the in situ activation of the carbonic acids were applied which can be used without degrading the polysaccharide backbone during the reaction. Starting from the free acid overcomes a number of disadvantages connected to the acylation with the derivatives. Whereas acid chlorides are most reactive, they are collectively insoluble (except acetyl chloride) in the solvent system when TEA is present as base. In case of carbonic acid anhydrides which permit a homogeneous conversion, problems arise from their limited commercial availability and the inherent inefficiency because only half of the reagent becomes incorporated into the product. This makes the use of the free acid combined with suitable activation a desirable tool.

In situ activation of the carbonic acids is possible with Tos-Cl. It was first applied for the preparation of cellulose acetates. During the reaction the mixed p-toluenesulfonic/carbonic acid anhydride is formed which represents the reactive species shown in figure 2.15.
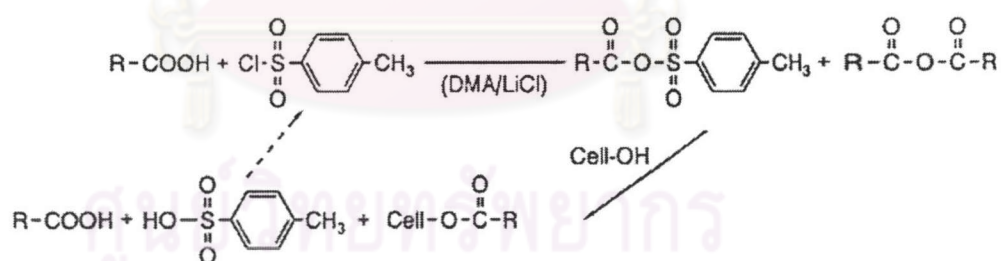

Figure 2.15 Acylation of cellulose dissolved in DMA/LiCl using in situ activation of the carbonic acid by forming the mixed carbonic/p-toluenesulfonic acid anhydride.

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_{12} (laurylic acid) to C_{20} (eicosanoic acid), can be obtained with almost complete functionalization of the accessible OH groups (DS values 2.8-2.9) [52]. The esters were examined in terms of their thermal characteristics by means of the differential scanning calorimetry (DSC)

and dynamic mechanical thermal analysis (DMTA) leading to the result that the ester moiety transition temperature is increased by 10 °C per C-atom of the ester moieties. Beside the preparation of waxy carbonic acid esters of cellulose, the method was applied for the introduction of fluorine-containing substituents e.g. 2,2-difloroethoxy-, 2,2,2-trifluoroethoxy-, and 2,2,3,3,4,4,5,5-octafluoropentoxy functions. The goal of this functionalization was a stepwise increase of the hydrophobicity of the products.

A method, which have gained limited interest up to now, is the acylation of cellulose with the free carbonic acid using N,N-carbonyldiimidazole as activating reagent. Its use for the preparation of the adamantoyl esters of cellulose in DMA/LiCl has been investigated. The derivative has DS value of up to 1.4. The reagent is also very efficient for the subsequent homogeneous esterification of cellulose intermediates in pyridine or DMF

Very recently the conversion of cellulose in DMI/LiCl was studied and the results were compared with those of the homogeneous acetylation of the polymer in DMA/LiCl. The reaction was carried out with acetic anhydride and pyridine as a base. CA with a DS value of 1.4 was accessible showing a same distribution of substituents as products obtained in DMA/LiCl (reactivity: C-6 > C-2 > C-3). The solvent is especially efficient for etherification reactions.

Another solvent for cellulose recently found is the mixture of DMSO/TBAF. The system studied in terms of its usefulness for homogeneous acylation reactions contained 2.9% cellulose and 16.6% TBAF. In a first series of experiments, the dissolved cellulose was treated with acetic anhydride. It was possible to obtain cellulose acetate with a DS of 0.83. The fairly high DS is quite remarkable because the solvent DMSO/TBAF contains a rather high amount of water. An alternative to the esterification with an acid anhydride is the tranesterification with carbonic acid esters which is an uncommon method in cellulose chemistry in contrast to starch modification. Especially the use of vinyl acetates and its higher homologeneous is a very interesting path because the formation of the acetic aldehyde during the reaction shifts the equilibrium towards the product site. Thus, it is possible to obtain cellulose acetates with DS values of 2.7 by applying 10 mol reagent per mol AGU over 70 h at 40 °C. Moreover, the $DS_{Acetate}$ can be directly controlled by the amount of reagent. Even long chain alkyl esters can be synthesized via this route. The one-step synthesis of cellulose butyrates, laureates and in addition the preparation of

benzoates was carried out showing that fatty acid esters of cellulose with DS values as high as 2.6 (in case of the laureate) are accessible (Table 2.3).

Table 2.3 Condition and results of the acylation of cellulose (Avicel, 2.9%) dissolved in dimethyl sulfoxide/tetrabutylammonium fluoride trihydrate (16.6%) at 40 °C for 70 h (DS, degree of substitution calculated from ^{1}H-NMR spectra)

Acylation mixture				Cellulose ester		
Compound	Molar ratio[a]	Catalyst[b] (mg)	DS	Partial-DS at O-6	O-2/3	δ (C=O)[c] (ppm)
Vinyl acetate	2.3	-	1.04	0.49	0.55	169.1-169.9
Vinyl acetate	2.3	20	1.07	0.52	0.55	169.2-170.0
Vinyl acetate	1.5	20	0.63	0.39	0.24	169.4-170.2
Vinyl acetate	10.0	20	2.72	0.98	1.74	169.3-170.1
Vinyl butyrate	2.3	-	0.86	-	-	171.4-172.5
Vinyl laurate	2.3	-	1.47	-	-	171.6-172.7
Vinyl laurate	10	-	2.60	-	-	171.5-172.6
Vinylbenzoate	2.3	-	0.95	-	-	164.9

[a]Mol acylation agent per mol anhydroglucose unit.

[b]Mixture of KH_2PO_4 and Na_2HPO_4 yielding a pH value of 7.1 in water.

[c]Chemical shift of the ester carbonyl peak taken from the ^{13}C-NMR spectra, group of peaks.

2.6.1.2 Acylation of cellulose in derivatizing solvents

The solvents DMSO/paraformaldehyde (PF), chloral/DMF/pyridine, TFA, and DMF/N_2O_4 were investigated as reaction medium for the homogeneous conversion of cellulose.

A variety of methods were studied for homogeneous esterification of polysaccharide dissolved in DMSO/PF. The polymer can be converted with a number of carbonic acid anhydrides in the presence of pyridine at low temperature. Among the acylating reagents are aliphatic compounds, e.g. acetic and butyric anhydride, aromatic acid derivatives like phthalic anhydride and even unsaturated species like methacrylic and maleinic anhydrides. The DS values reached are usually in the range from 0.2 to 2.0, except acetylation where DS values of up to 2.5 were realized. By means of ^{1}H- and ^{13}C-NMR spectroscopy it was shown that the hydroxyl groups of the methylol chains are preferentially acetylated with the carbonic acid anhydrides. Acylation with acetyl chloride or with the free acid succeeded just to

a limited extent. Furthermore, introduction of acetyl groups by tranesterification has been achieved with methylene diacetate and ethylene diacetate yielding polymers with high DS values (acetyl content 22%). For this purpose, the cellulose dissolved in DMSO/PF is treated with the reagents in the presence of sodium acetate at 90 °C. Moreover, the reaction of cellulose with acetic anhydride in the presence of potassium acetate was investigated. An interesting observation was that the DMSO in the solvent system can be substituted with DMF or DMA [53]. Quite recently this solvent has found some interest again. Homogeneous esterification with trimethylacetic anhydride (TMAA), trimellitic anhydride (TMA) and phthalic anhydride (PA) in DMSO/PF using high α- cellulose pulps of fast growing plant species was described. The corresponding esters are prepared by treating the solutions of cellulose with TMA and PA in the presence of pyridine for 8 h at 80-100 °C. The trimellitic acid ester is obtained after 1 h at room temperature. DS values between 2.4 and 2.6 are accessible. The esters were studied in terms of their thermal behavior. They are versatile compounds because of their elastomeric and thermoplastic properties and can be used for the preparation of films, membranes and film coatings of medical tablets.

Esters of carbonic acids can be obtained both with anhydrides and chlorides of carbonic acids in the presence of an appropriate base, e.g. pyridine. A variety of acid chlorides was applied for the esterification including caprionyl-, caproyl-, lauryl-, palmitoyl-, and stearyl chloride. The reaction succeeds via tranesterification of the cellulose nitrite formed during dissolution of the polymer. The conversion with acetic anhydride yields cellulose acetates with DS values of up to 2. In case of the preparation of derivatives with DS values of about 0.5, the tranesterification is rather selective at position 2 of the AGU (anhydroglucose units) as can be concluded from ^{13}C-NMR spectra. Comparable results were obtained for acetylation of cellulose in the derivatizing solvent chloral/DMF/pyridine. Treatment of the dissolved cellulose with acetyl chloride or acetic anhydride yields polymers with DS values of up 2.5.

A suitable alternative to esterification reaction in the multicomponent systems. Cellulose is partially trifluoroacetylated in the dissolved state (DS$_{CTFA}$about 1-1.5). Solutions of CTFA in a surplus of TFA were used for subsequent esterification in a number of studies. Thus, Emelyanov et al. investigated the acylation after treatment of cellulose for 24 h with TFA [54]. Anhydrides of

acetic-, propionic-, 3-nitrophthalic acid and a variety of aliphatic, aromatic and unsaturated acid chlorides, e.g. acetyl-, acryl-, cinnamoyl-, benzoyl-, and 4-nitrobenzoyl chloride, as well as free acids like benzoic acid in combination with TFAA were applied as acylation reagents. The course of reaction was followed by IR spectroscopy leading to the conclusion that partial tranesterification occurs during acylation. Isolation in aprotic media yields mixed esters with almost complete functionalization. After reaction for several hours at 50 °C the DS of trifluoroacetyl function is usually at about 1.4 and the amount of the second acyl component ranges from DS 0.5 to 1.6. Comparable results were obtained by Salin et al. In this study cellulose esters with DS values in the range from 2.9 to 3.0 were prepared by reacting cellulose in TFA with carbonic acid anhydride (C_2-C_{10}) at 60 °C. These esters were studied in terms of their viscosity in solution and T_g dependent on the acyl moiety. Furthermore, the preparation of mixed esters of cellulose in TFA was investigated using mixtures of acetic anhydride and aliphatic acids. Its was stated that method yields polymers with DS higher than 2.8 with DS_{Acetyl} between 1.3 and 1.7.

2.6.1.3 Esterification of organo-soluble cellulose intermediates

A rather new way of homogeneous esterification of polysaccharides is the application of soluble, regenerable intermediates. An important advantage compared to the functionalization reactions in derivatizing solvents is that acylation with highly reactive can be performed in inert common organic solvents avoiding side reactions. Important intermediates are the trifluoroacetates, formates, and dichloroacetates as well as trialkylsilyl derivatives of cellulose of various DS values [55]. These compounds can be subsequently esterified in homogeneous phase with carbonic acid chlorides and anhydrides or with the free acid after in situ activation. Usually the substituent introduced in the first step remains at the polymer backbond during the subsequent functionalization and is cleaved off during the work up procedure in protic media eventually catalyzed by changing the pH values to acidic or basic conditions. In case of the trialkylsilyl cellulose derivatives the application of fluoride ions for deprotection is a suitable method as well [56]. Typical examples of homogeneous esterification reaction carried out via intermediates are given in Table 2.4.

Table 2.4 Examples of subsequent reactions on cellulose intermediates isolated under aprotic conditions with different degree of substitution (DS)

Cellulose intermediate/DS	Reagents	Cellulosic products (after work-up)
Cellulose trifluoroacetate/1.5	Pyridine/ SO_3	Cellulose sulfate
	N, N carbonyldiimidazole/4-nitrobenzoic acid	Cellulose-4-nitrobenzoate
	4-Nitrobenzoic acid/tosyl chloride	Cellulose-4-nitrobenzoate
	Palmitoyl chloride/tosyl chloride	Cellulose palmitate
	NaOH/sodium monochloroacetate (SMCA)	CMC
Cellulose formate/2.2	Pyridine/SO_3	Cellulose sulfate
	DMF/ SO_3	Cellulose sulfate
	NaOH/(SMCA)	CMC
Cellulose dichloroacetate/1.6	Pyridine/ SO_3	Cellulose sulfate
	Phenyl isocyanate	Cellulose phenylcarbamate
Trimethylsilyl cellulose/1.6	3, 4 Dinitrobenzoyl chloride	Cellulose-3, 4-dinitrobenzoate
Trimethylsilyl cellulose/2.5	4-Nitrobenzoyl chloride	Cellulose-4-nitrobenzoate
Trimethylsilyl cellulose/1.1	NaOH/(SMCA)	Carboxylmethyl cellulose

Besides the preparation of inorganic esters and carbamates via cellulose intermediates (CTFA, CF and cellulose dichloroacetates), the synthesis of carbonic acid esters was extensively studied. In addition to the conversion with aromatic acids, e.g. 4-nitrobenzoic acid, 4- nitrocinnamic acid, and long chain fatty acids (palmitic acid), the synthesis of spacer modified unsaturated ester (e.g. N-cinnamoyl-11-aminoundecanoic acid) was investigated. For the first time it was shown that N,N-carbonyldiimidazole and chloromethylene-dimethyliminium chloride

(CDIC) can be used for the in situ activation of the carbonic acids which is a new tool for cellulose derivatization (Figure 2.15) [57, 58].

The rather uncommon activation with CDIC was exploited for the synthesis of cellulose-4-nitrobenzoates starting from CTFA (DS_{CTFA} of 1.5) dissolved in DMF and yields polymers with $DS_{Nitrobenzoate}$ of 0.5 soluble in DMSO. The reaction with N, N-carbonyldiimidazole is an efficient and mild process [59]. Thus, the activation of the carbonic acid is carried out at room temperature in DMF. The esterification succeeds at 60°C. Products with DS values of up to 0.9 can be obtained from cellulose trifluoroacetate (DS_{CTFA} of 1.5). The trifluoroacetyl function is usually removed during the work up procedure in aqueous media. Therefore, a rather pure final product is isolated having a pattern of functionalization in verse to the intermediate applied as revealed by ^{13}C-NMR spectroscopy. Thus, the ester function introduced in the first step may serve as protective group, i.e. a defined distribution of substituents can be realized. It was observed that for the preparation of the aliphatic esters the Tos-Cl in situ activation yields the highest DS values. In contrast, for the preparation of aromatic esters like the nitrobenzoates utilization of N, N-carbonyldiimidazole is the method of choice. Note worthy in this regard is the synthesis of cellulose sulfuric acid half ester via CTFA showing a very selective O-3 sulfation [60].

2.6.2 New methods for heterogeneous esterification

Besides the homogeneous esterification, new paths were developed for heterogeneous processes. It must be pointed out that heterogeneous processes (at least at their initial stages) are still frequently used. All large-scale processes are exclusively carried out heterogeneous which, however, is not a topic of this paper. Comprehensive review articles appeared elsewhere [61].

A very efficient method for cellulose esterification under heterogeneous reaction conditions is the so-called 'impeller' method. The carbonic acids used are converted to reactive mixed anhydrides during these reactions. Chloroacetyl-, methoxyacetyl-, and most important trifluoroacetyl moieties are used as impellers [62]. Tri-O-propionates and tri-O-butyrates of cellulose can be obtained in this way [63] which were part of a series of DSC studies including also

regioselectively substituted mixed cellulose ester (e.g. titanium-(IV)-alkoxid compounds like titanium-(IV)-isopropoxide shown in Table 2.5.

Table 2.5 Long-chain cellulose esters synthesized by titanium (IV) isopropoxide-catalyzed reaction in N, N-dimethylacetamide (AGU, anhydroglucose unit)

Carbonic acid anhydride	Equivalent per AGU	Time (h)	Temp. ($^\circ$C)	DS (^{1}H-NMR)	M_n 10^3	M_w 10^3	T_g ($^\circ$C)
Acetic/hexanoic	2.00/2.00	9	155	1.91/0.75	40	164	149
Acetic/hexanoic	1.00/3.00	9	155	1.38/1.36	35	113	122
Acetic/hexanoic	0.00/4.50	6	155	0.12/2.39	33	245	119
Acetic/nananoic	2.00/2.00	11	145	2.03/0.70	44	177	129
Acetic/lauric	3.50/1.00	12	140	2.40/0.20	96	295	165
Acetic/palmitic	2.00/2.00	12	145	2.06/0.42	33	125	156
Acetic/hexanoic	0.00/3.00	7	140	0.00/2.73	23	61	104
Acetic/nonanoic	3.00/1.00	8	145	2.44/0.26	43	220	161
Acetic/nonanoic	1.00/3.00	13	155	1.59/1.11	44	182	118
Acetic/nonanoic	0.00/4.00	13	160	1.11/1.35	31	200	110

It was shown that the catalyst can be applied for the preparation of partially esterified cellulose derivatives if an appropriate solvent is used. Furthermore, the esterification of cellulose with acetyl chloride at elevated temperatures and in vacuum using 1,4-dioxan/pyridine as reaction medium is known. Vacuum is applied to remove the liberate HCl during the reaction [64].

Acylation of the polymer is also possible by conversion of cellulose suspended in pyridine or DMF using sulfonic acid chlorides as activating agent. Thus, it was demonstrated that CA can be obtained in a wide range of DS values by treatment of the polysaccharide with acetic acid in the presence of Tos-Cl or methanesulfonyl chloride. Highly efficient is the reaction with the alkali or alkaline earth salt of acetic acids in combination with Tos-Cl [65]. These methods were extended for the preparation of aromatic cellulose ester, e.g. nitro-, chloro-, methyl-, methoxy-benzoyl esters and 4-azido-benzoyl ester. On the other hand, it is possible to carry out tranesterification reactions. For this procedure it was shown that a certain combination of reagent and solvent leads to a modified distribution of the ester functions within the AGU.

The classical method to prepare cellulose ester, i.e. converting the polymer suspended in pyridine with carbonic acid chlorides, is still an important procedure even to synthesize cellulosics with unconventional functional groups and hence with new properties. For example, products containing photo reactive moieties like stilbene-4-carboxylate-, cinnamoyl-, 2-methylstilbene-5-carboxylate, and p-phenylazobenzoate functions were synthesized recently.

2.7 Microwaves Energy

Microwaves are a form of electromagnetic energy. Microwaves, like all electromagnetic radiation, have an electrical component as well as a magnetic component. The microwave portion of the electromagnetic spectrum is characterized by wavelengths between 1 mm and 1 m, and corresponds to frequencies between 300 MHz and 300 GHz. Typically, household microwave oven uses it is important to recognize that the energy delivered by microwaves is insufficient for breaking covalent chemical bonds. This information can help to narrow speculation on the mechanisms for enhancement in specific reactions. Fixed frequency of 2,450 MHz (2.45 GHz) [66, 67].

- Microwaves Can Interact with Matter

One can broadly characterize how bulk materials behave in a microwave field. Materials can absorb the energy (e.g. water, carbon), they can reflect the energy (e.g. metal), or they can simply pass the energy (e.g. glass, PP). It should be noted that few materials are either pure absorbers, pure reflectors, or completely transparent to microwaves. The chemical composition of the material, as well as the physical size and shape, will affect how it behaves in a microwave field.

Microwave interaction with matter is characterized by a penetration depth. That is, microwaves can penetrate only a certain distance into a bulk material. Not only is the penetration depth a function of the material composition, it is a function of the frequency of the microwaves. If the penetration depth of material is less than sample size, it is considered as a "surface heating". On the contrary, a "volumetric heating" will occur in a bulk material when the penetration depth is larger than a sample size.

- Two Principal Mechanisms for Interaction with Matter

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

Dipole interactions occur with polar molecules. The polar ends of a molecule tend to align themselves and oscillate in step with the oscillating electrical field of the microwaves. Collisions and friction between the moving molecules result in heating. Broadly, the more polar a molecule, the more effectively it will couple with (and be influenced by) the microwave field.

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

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

2.7.1 Microwave Heating Differs from Conventional Means

- Conventional heating methods [66, 67]

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 the 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 reactants 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.

- Microwave Heating

Microwave heating occurs somewhat differently from conventional heating. First, the reaction vessel must be substantially transparent to the passage of microwaves. The selection of vessel materials is limited to fluoropolymers and only a few other engineering plastics such as polypropylene, or glass fiber filled PEEK (poly ether-ether-ketone). Heating of the reaction mixture does not proceed from the surface of the vessel; the vessel wall is almost always at a lower temperature than the reaction mixture. In fact, the vessel wall can be an effective route for heat loss from the reaction mixture.

Second, for microwave heating to occur, there must be some component of the reaction mixture that absorbs the penetrating microwaves. Microwaves will penetrate the reaction mixture, and if they are absorbed, the energy will be converted into heat. Just as with conventional heating, mixing of the reaction mixture may occur through convection, or mechanical means (stirring) can be employed to homogeneously distribute the reactants and temperature throughout the reaction vessel.

- Microwave Effect

To understand how microwave heating can have effects that are different from conventional heating techniques, one must focus on what in the reaction mixture is actually absorbing the microwave energy. The simple fact is that materials or components of a reaction mixture can differ in their ability to absorb

microwaves. Differential absorption of microwaves will lead to differential heating and localized thermal inhomogeneities that cannot be duplicated by conventional heating techniques.

To illustrate the consequences, several examples are presented wherein we consider microwave absorption by a bulk solvent and/or by the minor concentration of reactants in the solvent are considered.

Example 1: Solvent and reactants absorb microwaves equally

If the bulk solvent and reactants absorb microwaves equally, then energy transfer and heating will occur to the allowed depth of penetration into the bulk mixture. Homogeneous reaction conditions can be established with thorough mixing, and at equilibrium (chemical and thermal), the temperature of the reactants will be the same as that of the bulk solvent. In this case, reaction rates can be increased by increasing the temperature of the reaction mixture. This can easily be achieved using closed-vessel microwave techniques, using the same reaction chemistry and solvent. Alternatively, using conventional heating techniques, higher reaction temperatures can be achieved in a closed reactor system, or by using a higher-boiling solvent in an open vessel.

Example 2: Solvent absorbs microwaves, reactants much less so

If the bulk solvent absorbs microwaves, but the reactants do not absorb (or absorb to a lesser extent than the solvent), then energy transfer and heating of the solvent will occur to the allowed depth of penetration. The bulk solvent will, in turn, heat the reactants by conduction. Homogeneous reaction conditions can be established with thorough mixing, and at equilibrium the temperature of the reactants will be the same as that of the bulk solvent. This case is little different from conventional heating techniques. Reaction rates can be increased by increasing the temperature of the reaction mixture. Using closed-vessel microwave techniques, as previously described. In conventional heating techniques, higher reaction temperatures can also be achieved in a closed-vessel reactor system, or by using a higher-boiling solvent in an open vessel.

2.8 Degradation of Cellulose

Cellulose is a long-chain carbohydrate with no crosslinking. The large number of hydroxyl groups in each molecule results result in a lot of hydrogen bonds and a consequent strong attraction between the chains. Therefore, cellulose is not thermoplastic and, therefore, can not be extruded. Cellulose films are not edible. Modification can solve this problem. Cellulose ethers (methyl cellulose (MC), carboxymethyl cellulose (CMC)) are edible. These films have moderate strength, are flexible and transparent and resistant to oils and fats [68]. There are six broad categories of degradation of cellulose: acid, alkaline hydrolysis, thermal, oxidative, radiative, and biological degradation [69]. Some details of each category are presented as follows.

2.8.1 Degradation by Acid Hydrolysis

Degradation in acidic medium is based on the hydrolysis of the b-glucosidic linkages between the glucose base units. The reaction depends strongly on pH and already proceeds at a remarkable rate at low pH and temperatures well under 100 °C. Initially the acetal oxygen of the glucosidic linkage is protonated. Through heterolysis, an intermediate carbonium ion is formed, causing chain splitting. The carbonium ion finally reacts with water, which reforms the proton. Figure 2.16 illustrates the degradation by acid hydrolysis of cellulose.
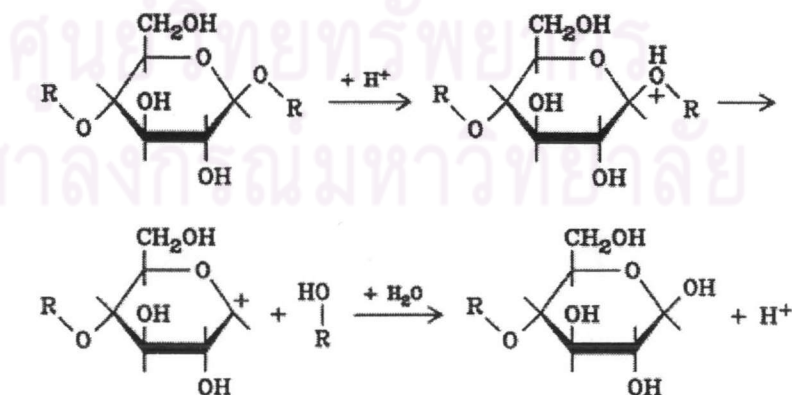

Figure 2.16 Degradation by acid hydrolysis.

2.8.2 Degradation in Alkaline Media

Hydrolysis of the b-glucosidic linkages in alkaline media occurs at a significant rate only at temperatures above 150 °C. It is most probable that chain splitting proceeds by way of the 1, 2-anhydro configurations, as shown in Figure 2.17.
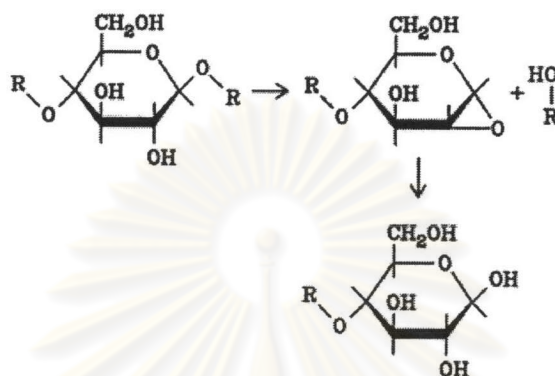

Figure 2.17 Degradation in Alkaline Media.

Acidic as well as alkaline hydrolysis of the glucosidic bond is remarkably enhanced (b-elimination) by oxidative changes at the C–2, C–3, or C–6 carbons leading to carbonyl groups. An example of this chain-splitting reaction, which can even occur at moderate temperatures, is shown in Figure 2.18.
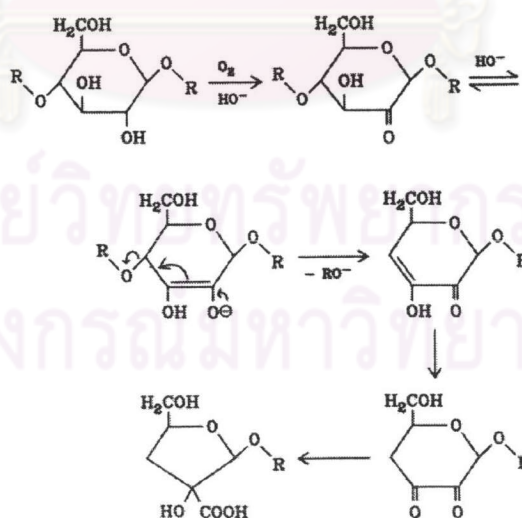

Figure 2.18 Degradation in Alkaline Media of the glucosidic bond.

2.8.3 Oxidation Reactions

The hydroxyl groups and the aldehydic end groups participate in the oxidation reactions of cellulose. These reactions form aldehyde, ketone, and carboxyl groups. Extensively oxidized and degraded products are designated as oxycelluloses. Some oxidizing agents show specific action. They attack only specific functional groups, forming defined oxidation products. Other oxidants react nonspecifically with all types of oxidizable groups in the cellulose molecules. Under special conditions hypoiodite and chlorite attack only the aldehyde end group on C–1, oxidizing it to form a carboxylic group. Another oxidant with specific action is periodate, which attacks the glycol configuration on the carbon atoms C–2 and C–3, thus causing ring-splitting and forming a dialdehyde structure is shown in Figure 2.19.
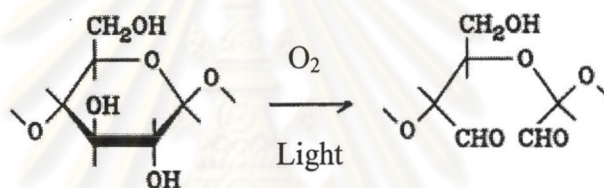

Figure 2.19 Oxidation Reactions.

2.8.4 Thermal Degradation

A numbers of different thermal degradation reactions are known to occur with cellulose at different temperatures. Degradation at lower temperatures (as in aging of cellulosic materials) is often predominantly thermo-oxidative and/or hydrolytic. As expected, aging of cellulose is, thus, usually a function of humidity, light, oxygen availability, etc., in addition to temperature. At higher temperatures (>200° C) water is lost, first from that absorbed by the cellulose and then by b - elimination from the cellulose hydroxyls. At still higher temperatures (>250° C), several competing pyrolytic reactions begin to take over. These reactions can be grouped into three basic classifications: the first group occurs at lower temperatures and is similar to the aging reactions. Products are water, CO, CO_2 and a carbonaceous char. At higher temperatures, another reaction begins to take over which results in depolymerization of the cellulose chain and formation of anhydroglucose derivatives, volatile organic materials and tars. At still higher temperatures, more-or-less random

bond cleavage of cellulose and intermediate decomposition products results in formation of a variety of low molecular weight compounds [70].

2.8.5 Radiative degradation

Radiatiative degradation can affect nature polymers (cellulose, hemicellulose, and lignin.) in two ways, chain scisson and crosslinking. Photochemical radiation, such as light at 2800 angstroms, has the ability to break C-C bonds and both scission and crosslinking. Stronger radiation, such as high-energy electrons, X-rays, and gamma rays can initiate the formation of radicals which can unsaturate the chemical bonding and lead to both chain scission and crosslinking. The predominance of a hugely crosslinkined mass or a jumble of low-molecular-weight fragments depends mostly upon the rate of crosslinking, a function of the polymer [71].

There are two types of radiative degradation, photolysis, and radiolysis. Photolysis occurs under the influence of photochemical radiation, light in the wavelength of 100 to 10,000 angstroms which imparts energy in the range of 100 to 1000 kcal/mole. Degradation of the polymer chain by this method is due to the absorption of energy in discrete energy units by specific functional groups that are on the chain.

Radiolysis occurs under the influence of ionizing radiation, which is X-rays, electron beams, and gamma rays. Radicals form by a random ray striking a particular atom and initiating an energy transfer. The presence of a radical initiates unsaturation in chemical bonding, chain scission, and crosslinking, as well as volatile fragements that initiate the formation of more radicals, perpetrating the reactions.

2.8.6 Biological degradation

Driven by the awareness the care should be taken not to exhaust the world's natural resources and deteriorate the environment by using non-degradable and non-recyclable materials, the development of biodegradable polymers has been focused. In general, the fully recyclable materials are completely biodegradable within a considerably short period of time. There is an enormous

potential for application of natural biopolymers as the packaging materials of the future generation [72].

Biopolymer films are generally designed using biological materials such as polysaccharides, proteins, lipids, and their derivatives. Films primarily composed of polysaccharides (cellulose and derivatives, starch and derivatives, gum, etc.) or proteins (gelatin, gluten, zien, etc.) have suitable overall mechanical and optical properties. In contrast, films composed of lipids (waxes, lipids or derivatives, etc.) or polyesters (poly-D-β-hydroxybutyrate, polylactic acid, etc.) have good water vapor properties, but are usually opaque and relatively flexible. Lipid films could also quite fragile and unstable.

The bio-degradation of polymers on a natural level is familiar to everyone in the form of incomplete degradations such as fossil fuels, and complete degradations such as those of carbohydrates (starch, cellulose, hemicellulose, and lignin).

Natural products that are particularly susceptible to biological attack include:

- Starch - degraded easily by bacteria and fungi.

- Cellulose - attack by biological agents, through enzymatic hydrolysis.

- Enzymatic Degradation

Enzymes are mostly involved in the chemical mode of polymer degradation, pertaining to the decomposition of polymers that are a part of organized living species. Organized species have evolved to the point where they have enzymes that can break down certain polymers (such as proteins) in their digestive systems, which have become highly specific to their biological process. This beta 1, 4 glucosidic linkages is broken by beta-glucosidase: [73].

$$
\text{Cellulose} \xrightarrow{\text{b-1, 4 glucanase}} \text{Cellobiose} \xrightarrow{\text{b-glucosidase}} \text{Glucose}
$$

Enzymatic degradation occurs by a catalytic process. Molecular conformation is very important to the specificity of the enzyme, and the enzyme can be rendered inactive (denatured) very quickly by varying the pH, temperature, or solvent. Some enzymes require other enzymes (co-enzymes) to be present in order to be effective, in some cases forming association complexes in which the coenzyme acts as a donor or acceptor for a specific group.

In synthetic polymers, chain ends tend to be deep in the polymer matrix and since enzymes tend to attack only at the chain ends, the process is quite slow.

- Microbial Degradation

Microorganisms, such as fungi and bacteria, degrade cellulose, hemicellulose, and lignin by ingesting the carbon molecules that are the backbone of the cellulose, hemicellulose, and lignin. Given either an aerobic (fungi) or an anaerobic (both fungi and bacteria) environment, microbial degradation is theoretically possible. However, optimal growth conditions (water, light) are rarely found and the microorganisms usually do not penetrate deeper than the surface of a part.

2.9 Microwave Induced Esterification of Cellulose

Since this work has been focused on the microwave induced esterification of paper mulberry for degradable film preparation. Therefore, some related researches are briefly reviewed as follows.

In 2002, C. Satge, B. Verneuil, R. Branland, P. Krausz, and C. Petit [1] examined rapid homogeneous esterification of cellulose induced by microwave irradiation. The aim of this work is the esterification of cellulose with lond chain acyl chloride in homogeneous media induced by microwave irradiation. The system used was cellulose/lauroyl chloride/DMAc/LiCl and DMAP as a catalyst. The used of microwave resulted in a dramatic drop in reaction time: 1 min irradiation was sufficient. They studied the degree of substitution (DS), weight increase and molar yields in function of lauryl chloride and DMAP amount. They also determined mechanical and thermal properties of the sample with DS = 2.4. The results of this experiment found maximum of the microwave irradiation power of 300 W for 60 s.

Increasing reaction time beyond 1 min resulted in a temperature increase and cellulose degradation as attested by a drop in WI (%weight increase). DMAP did not have any influence on the DS, but the yield was dependent on DMAP especially for the lowest lauroyl chloride concentrations. Either DS or yield was influence by lauroyl chloride, when lauroyl chloride (equiv.) was increased, then DS will increase until to constant. In term of WI, when lauroyl chloride (equiv.) was increased, then WI will increase until to constant. The plastic tested had a DS of 2.4. The elastic modulus is much lower than those of packaging product. The thermal decomposition temperature was 185°C. The loss of weight was 65%. The weight loss revealed a modest biodegradation of plastic films for a DS > 1. A loss of 15% in weight for DS = 0.7.

G. Antava and P. Vasvasova [8] investigated the obtaining of cellulose stearate under microwave heating. This study presents the possibility for obtaining cellulose stearate by direct esterification and tranesterification under microwave heating. Research is made upon the influence of the diffenrent parameters such proportion of the initial substances, quantity of catalyst and duration of reactions upon the degree of esterification. The most suitable conditions for carrying out direct esterification of cotton and alkaline cellulose with stearic acid under microwave heating are: mol proportion-cellulose: stearic acid-1: 3, catalyst 0.044 mol p-toluene sulphonic acid per mol cellulose, power of the microwave heating 600 W and duration of the process 7 min.. The resulting product is cellulose stearate with 0.26 degree of substitution and 31.6 % of combined stearic acid when they use cotton and 0.23 degree of substitution and 29.5 of combined stearic acid when they use alkaline cellulose, while under the conventional heating conditions direct esterification is not observed. At tranesterification carried out under the same condition for the period of 10 min. A product with 0.41 degree of substitution of hydroxyl groups and 42.9 % of combined stearic acid is obtained while under the conventional heating conditions in the presence of the solvent dimethylsulphoxide and duration of the process 360 mins the cellulose stearate has degree of substitution 0.35.

In 2000, Erik Esveld, Farid Chemat, and Jacco van Haveren [9] studied using a pilot scale continuous microwave dry-media reactor the production of waxy esters. The solvent free esterification reaction between stearic acid and stearyl alcohol

has been examined with montmorillonite clay as catalyst. To aim for industrial application the system has been studied on reaction rate, product purity, catalyst behavior and water removal as function of the process conditions. To avoid an etherification side reaction and to aim for the highest reaction rate, the temperature should be strictly maintained at 170 °C. This is providing on larger scale by the application of microwave heating. Although the examined acid clay was found to lose its catalytic activity at very low water activities, a yield of 95% pure stearyl stearate can be obtained by simply filtering of the clay without solvent extraction or distillation. The waxy esterification reaction was investigated with the pilot plant continuous microwave dry-media reactor (CMDA). The reaction time needed for 95% yield was reduced by a factor 20-30 in comparision with industrial conventional reactors. This was due to the more homogenous heat tranfer of microwave, which allows reaching a higher bulk temperature.

In 1999, Gourson C. el al. [7] investigated preparation of biodegradable plastic in microwave oven and sovent-free conditions. With the aim of the obtention of biodegradable material, they describe a new method for the esterification of microcrystalline cellulose. This methodology uses microwave irradiation under solvent-free conditions in the presence of basic catalysts such as DMAP, Al_2O_3, and K_2CO_3. In a general procedure, a mixture of cellulose, fatty acid chloride and catalyst was irradiated in an open beaker flask in a domestic microwave oven 750 W. They found that the reaction time had dropped from 5 h to 9 min. The plastic obtained were analysed by infra-red spectroscopy and NMR. In conclusion, they have prepared a plastic in economic and mild conditions. They have shown, for the first time, that microwave irradiation could be used for the modification of naturally occurring polymers under mild conditions and without solvent.

Fritz and Shenk [74] have shown that acid catalysis occurred to a significant extent even in the presence of pyridine, which was present in a large excess over the sulfuric acid. Furthermore, pyridine was not an ideal catalyst. Therefore, they suggest that sulfuric acid could catalyst the tranformation of pyridine in a very reactive cation, as already described for the acid-catalyzed acetylation of cellulose when sulfuric or perchloric acid was used. Pyridine might form a pyridinium salt with hydrochloric acid released by lauroyl chloride during esterification. This

mechanism is further supported by the fact that alkaline activation, which also leads to a decrease in the degree of polymerization, gives a low amount of esterified product (0.04 g/g after alkaline activation, instead of 1.93 g/g after acid activation).

In 1994, Pinglang Wang and Bernard Y. Tao [75] investigated synthesis and characterization of long-chain fatty acid cellulose ester (FACE). Long-chain fatty acid cellulose esters (FACE) were synthesized by acid chloride-pyridine reaction with different degrees of substitution (DS). The hydrolyzed soybean oil was used as unsaturated fatty acid, its unsaturation degree, and composition were analyzed by ^{1}H and ^{13}C-NMR methods. The chemical structures of FACE were confirmed by solid-state ^{13}C-NMR, and substitution reaction of fatty acid chloride on cellulose was analyzed by IR spectroscopy. FACE (s) are insoluble in common organic solvents, such as benzene, toluene, THF, etc., at refluxing temperature. As the DS increased, the tensile strength of extruded FACE films decreased, but elongation increased.

In 1995, S. Thiebaud and M. E. Borredon [76] studied solvent-free wood esterification with fatty acid chloride. A method for wood esterification using fatty acid chlorides in the absence of organic solvents is proposed. The experimental conditions being optimal (nitrogen flow rate, temperature and reaction time, quantity of fatty acid chloride), there was an increase in weight of 87% and a 60% ester content for the sample esterified with octanoyl chloride. Results, they found nitrogen flow rate increase and % weight increase increase until to constant of 2.0 g of wood with 0.3 mole of $C_8H_{15}OCl$ at 120°C for 4 h. Effect of reaction time; when reaction time increase and % WI increase until to constant of 2.0 g of wood with 0.3 mole of $C_8H_{15}OCl$ at 120°C, nitrogen flow rate 170 ml/min. Effect of temperature; when temperature increase being 130°C and % WI increase after that temperature drop and % WI decrease. The infra-red analysis before and after esterification; the intensity of the absorption band of the O-H bond vibrations decrease, whereas those of C-H and C-O bonds increase. This synthesis method was applied was applied to other acid chloride. Significantly less weight increase was obtained with an increase in the number of carbon atoms in the corresponding acyl group. The change in apparent melting temperature when increase in the number of carbon atoms result in a decrease

in the apparent melting temperature of the esterified specimen and was improved in thermoplastic properties.

In 1996, James E. Sealey, Gamini Samaranayake, Jason G. Todd, and Wolfgang G. Glasser [77] investigated novel cellulose derivatives preparation and thermal analysis of waxy esters of cellulose. Cellulose esters with linear aliphatic acyl substituents ranging in size from C_{12} (lauric acid) to C_{20} (eicosanoic acid) were prepared in homogeneous solution (DMAc/LiCl) using a novel synthetic method based on the use of a mixed p-toluenesulfonic/carboxylic acid anhydride. The resulting waxy cellulose esters had a high degree of substitution (DS), between 2.8 and 2.9, and showed little degradation. Thermal analysis of these cellulose derivatives by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) revealed a series of transitions that represented motion by both ester substituents and cellulosic main chain. Broad crystallization and melting transitions attributed to side-chain crystallinity were observed in the range between –19 and +55 °C; these side-chain T_m and T_c transition temperatures increased by 10 °C per carbon atom of the ester substituent. The T_g of these derivatives increased linearly with increasing substituent size from 94°C for C_{12} (cellulose laurate) to 134°C for C_{20} (cellulose ecicosanoate). 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 T_m values of 96°C and 107°C, respectively.

In 1998, S. Thiebaud and M. E. Borredon [78] studied the analysis of the liquid fraction after esterification of sawdust with octanoyl chloride-production of esterified hemicellulose. Solvent-free esterification of wood with octanoyl chloride produced an esterified material with a weight increase of 87% and an ester content of 60%. However, a fraction of sawdust (22% of the esterified wod) was solubilized during this esterification. Chemical analyses showed that it contained essentially esterified and hydrolyzed hemicelluloses with small amount of esterified cellulose. The reactivities of oakwood sawdust and wheatbran hemicellulose were compared under different reaction conditions. Pure hemicelluloses were more reactive and more readily hydrolyzed (without using solvent) than sawdust, to give esterified oligomers and polymers with a high degree of substitution, and which were solubilized (48% of

the esterified hemicellulose) in the reaction medium. The use of pyridine as a toxic solvent limited the acid hydrolysis of the polysaccharides chains and therefore their solobilization.

In 1999, G. Chauvelon, L. Saulnier, A. Buleon, and co-workers [3] studied acidic activation of cellulose and its esterification by long-chain fatty acid. Celluose-enriched residues from wheat bran can be transformed in bioplastics after esterification of the cellulose by lauroyl chloride. Before the esterification reaction, an activation step with a swelling of the sample in dilute acid and subsequent drying was required. This activation had a marked influence on the amount of esterified product and its degree of subtitution. Using pure cellulose as well as cellulose-enriched agricultural residues, they have shown that the cellulose was totally recovered after this pretreatment and that partial hydrolysis of cellulose chains occurred during the drying step, which probably improved the accessibility to chemical reagents. Results; The amount of esterified product was higher in Rind than in Ralk (0.75 and 0.66 g/g, respectively), despite a lower cellulose content and a lower amount of sulfate linked to cellulose. After a pretreatment with sulfuric acid, Ralk had long cellulose chains. The yield of recovered glucose was lower for CA (68%) than for CF (92%), but the amount of esterified products for CA was higher than for CF , which was explained by the higher DS obtained for CA (1.7) than for CF (1.2). The crystallinity of cellulose had also an important influence on the esterification by lauroyl chloride since the yield of recovered cellulose was higher for CF (92%), which is amorphous, than for CA (68%).In contrast, the DS was lower for CF than for CA. The degradation of cellulose occurred during esterification when sulfuric acid used for the acid activation was too concentrated; this degradation was probably due to the hydrolysis of cellulose. The optimal concentration of sulfuric acid has been shown, for crystalline cellulose to be 0.75 mol/L.

In 2000, J.M.Fang, R.C. Sun, J. Tomkinson, and P. Fowler [79] investigated acetylation of wheat straw hemicellulose B in a new non-aqueous swelling system. The acetylation of wheat straw hemicellulose B was carried out in a homogenous N, N-dimethylformamide and lithium chloride system with acetic anhydride using 4-dimethylaminopyridine as a catalyst. The degree of substitution of

hemicellulose B acetates ranged between 0.59 and 1.25 as a function of experiment conditions. Under an optimum condition (85 °C, 60 h), approximately 75% of the free hydroxyl groups in native hemicellulose B were acetylated. The molecular weight measurement (31,890-34,090 g/mol^{-1}) showed a controllable degradation of hemicellulose B chains during the reaction at temperature 60-85°C and duration of 2-60 h. It was found that the thermal stability of the products was increased by chemical modification.

In 2001, Yifang Ou, Qiulian Huang, and Jianan Chen [2] studied degradation of new cellulose-based complex material. The degradation of a kind of cellulose- based complex material was investigated by the soil bury and exposure methods. The result showed that the average molecule weight of the sample decreased 66.7% and the copper number increased from 1.32 to 7.58 after 9 weeks as measured by the soil bury method. Meanwhile the average molecular weight decreased 38.7% and the copper number increased from 1.32 to 5.00 after 14 weeks of exposure under the sun.