## 2.2.1. Cellulose Acetate

2.2.1.1. Chemistry of Cellulose Esterification

The esterification reaction of the primary and secondary hydroxyl groups of cellulose does not basically differ from that of other alcohols. The peculiarities lie in the macromolecular structure of the cellulose molecule. The splitting of the molecule chain competes with the catalyzed esterification, but can be fairly well controlled under appropriate conditions. The speed and completeness of the reaction is dependent on the quality of the cellulose, whereas the different reactivities of the primary and secondary hydroxyl groups [83], [86] have little influence on industrial processes.

Acids, acid chlorides, and acid anhydrides are possible *esterification reagents* for the three hydroxyl groups in each glucose unit.
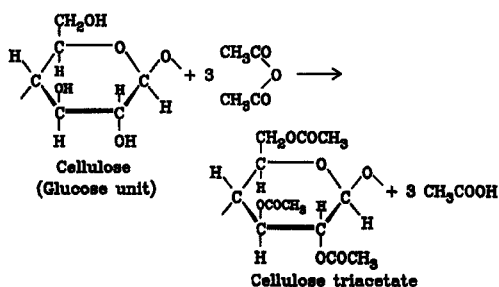
Esterification with free acids, with the exception of formic acid [87], whose esters are not stable, requires such high temperatures and catalyst concentrations that only low molecular mass products are obtained. Acid chlorides in pyridine, however, were suggested for use in the production of esters from higher fatty acids (lauric acid, stearic acid, and palmitic acid), without ever having attained any industrial significance. Attempt was made to manufacture cellulose acetate industrially with acetyl chloride and catalysts, but the process proved to be useless.

All industrial processes in current use, therefore, are based on acetic acid anhydride as a reactant, whereby theoretically 3 mol of anhydride per unit of glucose are used and 3 mol of acetic acid are formed.

Attempts to use ketene, which could be directly accumulated without incurring acetic acid, which must again be processed, did not lead to any results [88].

Numerous *catalysts* were suggested to accelerate the reaction. Only sulfuric acid and perchloric acid are of any practical importance. Zinc chloride, which is required in large

amounts of 0.5 – 1 part per part of cellulose, is no longer used today because of the high reprocessing costs. Other mineral acids, however, are not sufficiently acidic in the water-free acetic acid – acetic acid anhydride system. The catalytic effect of sulfuric acid is primarily in the rapid and quantitative formation of acidic cellulose – sulfuric acid esters (sulfoesters) [89], which are substituted by acetyl groups as the reaction progresses and the temperature rises.

Due to the topochemical character of the reaction, soluble cellulose esters with low acetic acid content can be obtained only from the triester stage by way of hydrolysis. Incompletely esterized and insoluble derivatives are found in addition to the triester before completion of the reaction.

Cellulose esters with low acetic acid content are produced by subsequent *hydrolysis* in a homogeneous system by adding water or dilute acetic acid to destroy the excess anhydride and possibly by adding sulfuric acid for acceleration and then again split off under controlled conditions (temperature, water content, and time) a certain number of acetyl groups without further breakdown of the cellulose chain.

2.2.1.2. Raw Materials

Cellulose. The production of high-quality cellulose esters requires that special attention be paid to the selection of the starting materials. The cellulose bases generally consist of highly purified cotton linters with an α-cellulose content of over 99 % and celluloses from wood pulp which contain between 90 and 97 % α-cellulose.

After the long layered spinnable cotton has been freed of the cotton seed by ginning, the remaining shorter fibers on the seed pod are usually removed with two cuts before the seeds go to the oil presses for further processing. The first cut gives about 4 % longer linters relative to the entire cotton flower, which are preferentially processed to medicinal cotton, felt, paper, etc. The second cut gives about 8 % shorter layered linters, which are best suited for further chemical processing.

The raw linters undergo mechanical cleaning by means of screening, pressure boiling in a 3 – 5 % sodium hydroxide solution, and finally acid – alkaline bleaching. Special care should be taken during drying, since local overdrying of cellulose, the water content of which should lie between 3 and 8 %, impairs the reactivity considerably. Table 9 shows analytical values of good linters [90].

For a long time, cellulose from wood pulp could only be used for the manufacture of lower-quality cellulose esters because of the 90 – 95 % α-cellulose content. Celluloses with an α-cellulose content of 96 % have been available for about 20 years. Due to special processing techniques, they give cellulose esters comparable to those produced from linters as far as tensile strength, color, clarity of the solutions, and light stability as well as thermal stability are concerned.

Table 11. Physical characteristics of cellulose acetate [90], [92], [98]

Characteristic	Triacetate	Secondary acetate
Density, g/cm^3	1.27–1.29	1.28–1.32
Thermal stability, °C	>240	ca. 230
Tensile strength of fibers, kg/mm^2	14–25	16–18
Tensile strength of foils		
longitudinal, kg/mm^2	12–14	8.5–10
transverse, kg/mm^2	10–12	8.5–10
Refractive index of fibers toward the fiber axis		
longitudinal	1.469	1.478
transverse	1.472	1.473
Double refraction	–0.003	+0.005
Dielectric constant ε		
50–60 Hz	3.0–4.5	4.5–6.5
10^6 Hz		4.0–5.5
Dielectric loss factor tan δ		
50–60 Hz	0.01–0.02	0.007
10^6 Hz		0.026
Specific resistance, $\Omega \cdot cm$	10^{13}–10^{15}	10^{11}–10^{13}
Specific heat, $J\,g^{-1}K^{-1}$		1.46–1.88
Thermal conduction, $J\,m^{-1}h^{-1}K^{-1}$		0.63–1.25

2.2.1.5. Properties of Cellulose Acetate

Cellulose acetate and the other fatty acid esters are white, amorphous products that are commercially available as a powder or flakes. They are nontoxic, odorless, tasteless, and less flammable than nitrocellulose. They are resistant to weak acids and are largely stable to mineral and fatty oils as well as petroleum.
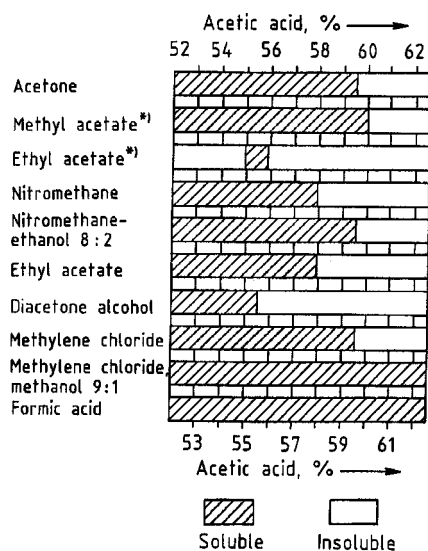
Some physical characteristics are given in Table 11.

Properties and applications of cellulose acetates are primarily determined by the following:

1) viscosity of their solution
2) degree of esterification or the amount of bound acetic acid

Viscosity as an indicator for the degree of polymerization influences to a great extent the mechanical properties of the resulting fibers, films, or plastic masses, as well as their workability.

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Table 12. Solubility of cellulose acetate at various degrees of esterification [91]

Degree of esterification	Bound acetic acid	Chloroform	Acetone	2-Methoxyethanol	Water
2.8–3.0	60–62.5%	soluble			
2.2–2.7	51–59%		soluble		
1.2–1.8	31–45%			soluble	
0.6–0.9	18–26%				soluble
<0.6	<18%				

Acetic acid, % ⟶

52 54 56 58 60 62

Acetone
Methyl acetate[*]
Ethyl acetate[*]
Nitromethane
Nitromethane-ethanol 8:2
Ethyl acetate
Diacetone alcohol
Methylene chloride
Methylene chloride-methanol 9:1
Formic acid

53 55 57 59 61
Acetic acid, % ⟶

Soluble   Insoluble

Figure 11. Solubility of cellulose acetate in various solvents (abridged according to [99])
* Technical grade

The *degree of esterification* primarily determines the solubility and compatibility with softeners, resin, varnish, etc., and ultimately also influences the mechanical properties.

The wide span of solubility properties of hydrolyzed cellulose acetate is shown in Table 12.

The compatibility of the plasticizer and the solubility in polar solvents increase with decreasing acetic acid content while the solubility in nonpolar solvents decreases. Moreover, a correlation between the incompatibility with nonsolvents such as water, alcohol, benzene, or toluene and a decreasing degree of esterification exists. Furthermore, a number of solvent combinations are known which are able to dissolve the cellulose acetate although each of the components is a nonsolvent.

Figure 11 shows a selection of solvents for the industrially interesting range of esterification (52–62% bound acetic acid). Detailed information on solubility and softener selection can be found in the literature and the manufacturers' information brochures.

2.2.3. Cellulose Acetate Fibers

Cellulose acetate is the most important cellulose ester. It is primarily used for textile yarn and cigarette filter tow. The cellulose acetate is usually dissolved in a suitable organic solvent and spun by dry spinning. Secondary (2.5) acetate with an acetic acid content of 54–56% is normally used, whereas only a small amount of cellulose triacetate is normally produced.

2.2.3.1. Properties

The viscosity and the filterability of the spinning solution (spinning dope) are particularly important in the production of cellulose acetate fibers. The spinning dope has a high viscosity, which depends on the degree of polymerization. The strength and stretch properties of the fibers also depend on the concentration and the degree of polymerization as well as on the distribution of the acetate groups along the cellulose chain.

Because the fibers are produced by extruding the spinning dope through minute spinnerette holes, insoluble particles must first be removed from the spinning dope by filtration. These particles are primarily composed of very small, incompletely acetylated cellulose fibers or gels, which can obstruct the spinnerett holes.

Secondary acetate and triacetate fibers have similar physical properties (Table 15). Their densities are lower than that of viscose rayon fibers and equal to that of wool. For textile yarns, the fibers should be as free of color as possible.

The chemical reactions of cellulose acetate are similar to those of organic esters. Cellulose acetate is hydrolyzed by strong acids and alkali; it is sensitive to strong oxidizing agents but not affected by hypochlorite or peroxide solutions.

Acetate fibers cannot be dyed under the same conditions as viscose rayon fibers because their swelling properties are different. Acetate fibers can only be dyed with water-disperse dyes at the boiling point of the medium usually in the presence of carriers. The carriers promote fiber swelling and enhance dye uptake by the fibers. The dyeing process coupled with the textile spinning operation assures color fastness.

Table 15. Physical properties of acetate fibers and tow [107]

	Secondary acetate	Triacetate
Strength, cN/dtex	1.0–1.5	1.0–1.5
Stretch, %	25–30	25–30
Density, g/cm^3	1.33	1.30
Moisture uptake, % (65% relative humidity, 20 °C)	6–6.5	4–4.5
Water retention capability, %	25–28	16–17
Melting point, °C	225–250	decomposition at 310–315
DP	300	300

Table 16. Typical properties of acetate wood pulps

Characteristic*	Sulfite softwood pulp (conifer)	Sulfate hard-wood pulp (deciduous)
R_{10}, %	95	96
R_{18}, %	97	98
Ash, %	0.08	0.08
Silica, %	0.001	0.003
Calcium, %	0.006	0.008
Pentosans, %	1.2	1.2
Moisture content, %	6.5	6.5
Apparent density, g/cm^3	0.45	0.5
DP	2300	1700

* R_{10} and R_{18} are residues in 10 or 18% sodium hydroxide at 20 °C [108]

Triacetate fibers have better wash-and-wear properties than secondary acetate because of better dimensional stability and higher crease resistance.

2.2.3.2. Raw Materials

Wood pulp produced from various softwood (conifer) or hardwood (deciduous) species is the cellulose source for the production of cellulose acetate fibers. The wood pulps are produced by the sulfite pulping process with hot alkali extraction or by the prehyrolized sulfate (Kraft) process with cold caustic extraction. The lignins and hemicelluloses are removed from the wood to give wood pulps with an α-cellulose content of over 96% (Table 16). High-purity cotton linters are no longer used in the production of cellulose acetate fibers for economic reasons.

For the production of high-quality cellulose acetate fibers the wood pulp must have good swelling properties for uniform accessibility of the cellulose to the catalyst and the acetylation agent and a uniform reactivity. In addition, it must produce a spinning solution without fibers and gels which can easily be filtered.

2.2.3.3. Production

The general points discussed in Section 2.2.3.1 for the production of cellulose acetate also apply here. The sulfuric acid catalyst initially forms the cellulose sulfate ester. The sulfate groups are then replaced by acetyl groups as the acetylation proceeds. The sulfate ester contents is further reduced in the hydrolysis stage. However, any sulfate ester groups remaining at the end of the hydrolysis stage must be neutralized with an appropriate stabilizer, e.g., magnesium salts [109], [110]. Any "free" sulfate ester groups will affect the stability of the acetate because under the influence of heat and humidity they splitt off as sulfuric acid and degrade the fiber [111].

For secondary acetate spinning, acetone is used as the solvent. For triacetate, the solvent is 90 % dichloromethane and 10 % methanol or acetic acid (wet-spinning process). The viscosity of the spinning solution with a cellulose acetate concentration of 20 – 30 % is between 300 and 500 Pa s at 45 – 55 °C. The spinning dope is filtered in one or more steps and is then deaerated in large vessels.

Dry spinning is used almost exclusively; wet spinning is occasionally used for triacetate only. The spinneretts for textile filament have between 20 and 100 holes and those for tow up to 1000. The fibers are formed by evaporating the solvent with a countercurrent of air at 80 – 100 °C in a 4- to 6-m spinning column. The fibers are then stretched while still plastic to increase their strength. Melt spinning of cellulose acetate or triacetate has no commercial importance due to the limited heat stability at the melting point.

A core-skin structure is formed in triacetate fibers. The acetyl groups are distributed very regularly in cellulose triacetate compared to secondary acetate; therefore, crystallization occurs when triacetate fibers are heated at 180 – 200 °C (heat setting) [107], [111], [112]. This heat treatment, which enhances the wash-and-wear properties of triacetate textiles, requires several minutes at 180 °C or several seconds at 220 °C. Heating for shorter periods is not effective and longer heating periods lead to deterioration of the mechanical properties of the textile. Heat-setting reduces water retention to 10 % and water absorption to 2.5 %.

2.2.3.4. Uses

By blending and twisting of cellulose acetate or triacetate fibers with nylon or polyester a combination of properties is achieved that make them suitable for different end uses in linings. In this way the weaker physical properties of acetate fibers can be compensated for while maintaining the positive characteristics, for instance, the high moisture absorption and the silk-like softness.

Due to the unique hydrophobic – hydrophilic properties, semipermeable membranes made from cellulose acetate fibers have a remarkable potential in desalination (reverse osmosis) of water.

Table 17. Worldwide production of textile fibers (1000 t) [114]

Fiber	1993	1995
Man-made fibers *	19781	21741
Synthetics	16652	18471
Cellulosics	3129	3270
Cotton	18494	18602
Wool	1687	1767
Silk	68	92

* Excl. polyolefin fibers, textile glass fibers, and acetate cigarette filter tow.

Cellulose acetate hollow fibers are also suitable for gas separation and hemodialysis [113].

For cellulose acetate is non-toxic, biodegradable and the raw material is a renewable natural polymer, it is expected to find application for other uses in the future.

2.2.3.5. Economic Aspects

Secondary acetate and triacetate fibers for textiles and filter cigarette tow accout for 80% of all cellulose ester production. The balance is used for plastics and film. Secondary acetate and triacetate textile fibers have a small share (about 1%) of all textile fiber production.

In the late 1990s synthetic fiber production continued to expand (Table 17), whereas the acetate production was stable at about 850 000 t/a. The acetate fiber production decreased slightly compensated by a slight increase in filter tow production. The five largest manufactures of filter tow are Hoechst-Celanese and Eastman Chemicals in the United States, Rhodia Acetow in Germany, Daicel in Japan, and Courtaulds in the United Kingdom.