

The slide features a central graphic with the word "biopolymers" in a large, green, lowercase font. The "bio" part is stylized with a leaf and a circular arrow. A large green arrow curves around the text. In the top right corner, there is a blue box with the King Saud University logo and text: "جامعة الملك سعود King Saud University Department of Chemistry College of Science". In the top center, a grey box contains "Biopolymers Chem 563". In the bottom right, a grey box contains "Dr. Mohamed El-Newehy" and the URL "http://fac.ksu.edu.sa/melnewehy". At the very bottom, there is a line of Arabic text: "المعهد السعودي للعلوم والدراسات التطبيقية" and "د. محمد النويهي".

جامعة الملك سعود
King Saud University
Department of Chemistry
College of Science

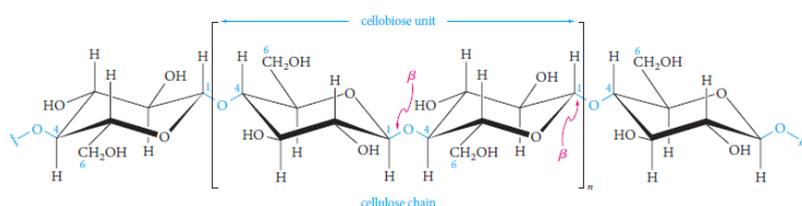
Biopolymers
Chem 563

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المعهد السعودي للعلوم والدراسات التطبيقية
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CELLULOSE

- **Cellulose** is an *unbranched* polymer of glucose joined by 1,4- β -glycosidic bonds.
- X-ray examination of **cellulose** shows that it consists of linear chains of cellobiose units in which the ring oxygens alternate in “forward” and “backward” positions.
- These linear molecules, containing an average of 5000 glucose units, aggregate to give fibrils bound together by hydrogen bonds between hydroxyls on adjacent chains.
- **Cellulose fibers** having considerable physical strength are built up from these fibrils, wound spirally in opposite directions around a central axis.

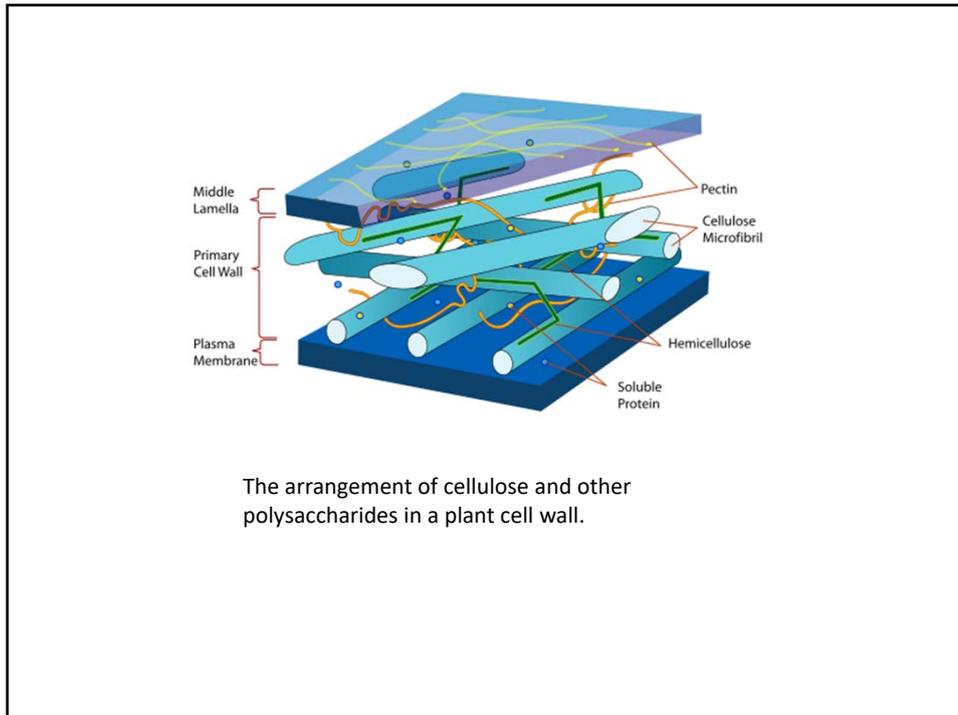


Partial structure of a cellulose molecule showing the β linkages of each glucose unit.

- **Cellulose** was originally “discovered” by Payen in 1838. For thousands of years, impure cellulose formed the basis of much of our fuel and construction systems in the form of wood, lumber (cut wood), and dried plant material.
- **Cellulose** served as the vehicle for the retention and conveying of knowledge and information in the form of paper, and clothing in the form of cotton, ramie, and flax.
- Much of the earliest research was aimed at developing stronger materials with greater resistance to the natural elements (including cleaning) and to improve dyeability so that the color of choice by common people for their clothing material could be other than a drab white.
- In fact, the dyeing of textile materials (mainly cotton) was a major driving force in the expansion of the chemical industry in the latter part of the nineteenth century.

- **Cellulose** is a polydisperse polymer with a degree of polymerization (DP) that ranges from 3500 to 36,000.
- Flax has a DP of 36,000 or an average molecular weight of 5,900,000.
- Regenerated cellulose, such as rayon and cellophane, is produced by precipitating solutions of native cellulose in a nonsolvent.
- **Cellulose**, which comprises more than one-third of all vegetable matter, is the world's most abundant organic compound.
- Approximately 50 billion tons of this renewable resource are produced annually by land plants, which absorb 4×10^{20} cal of solar energy.

- Wood, cotton, hemp, linen, straw, and corncobs are mainly cellulose.
- Cellulose is not found in a pure form but rather is associated with other materials such as lignin and the so-called hemicelluloses.
- Cotton contains the purest form of cellulose.
- Wood, in its dry state, contains 40–55% cellulose, 15–35% lignin, and 25–40% hemicellulose.
- Plant pulp is the major source of commercial cellulose through the sulfite and the alkaline processes.
- The extraction of cellulose from plants is called pulping.
- Pulping is generally achieved using thermomechanical, chemical, or mechanical approaches.
- Pulp is dissolved when removal of the hemicelluloses and lignin are required.
- After pulping, the pulp is bleached to achieve the desired whiteness.



- The major source for non-textile fibers is wood pulp.
- The major source for textile cellulose is cotton, which is pure enough to be directly used without purification.
- **Cellulose** is used in the textile industry in cloths, cartons, carpets, blankets, and sheets.
- Paper is made from cellulose.
- Cellulosic fibers are also used as filter materials in artificial kidneys and reverse osmosis though today most kidney dialysis units use cuprammonium tubular films derived from cellulose rather than cellulose itself.

- While the celluloses are often largely linear polymers, they are not soluble in water because of the presence of strong intermolecular hydrogen bonds and sometimes the presence of a small amount of crosslinking.
- Highly ordered crystalline cellulose has a density as high as 1.63 g cm^{-3} , while amorphous cellulose has a density as low as 1.47 g cm^{-3} .
- High molecular weight native cellulose, which is insoluble in 17.5% aqueous sodium hydroxide solution, is called *α -cellulose*.
- The fraction that is soluble in 17.5% sodium hydroxide solution but insoluble in 8% solution is called *β -cellulose*, and that which is soluble in 8% sodium hydroxide solution is called *γ -cellulose*.

- Strong caustic solutions penetrate the crystal lattice of α -cellulose and produce an alkoxide called *alkali or soda cellulose*.
- *Mercerized cotton* is produced by aqueous extraction of the sodium hydroxide.
- *Cellulose ethers* and *cellulose xanthate* are produced by reactions of alkyl halides or carbon disulfide, respectively, with the alkali cellulose.

- Most *linear celluloses* may be dissolved in solvents capable of breaking the strong hydrogen bonds.
- These solvents include aqueous solutions of inorganic acids, calcium thiocyanate, zinc chloride, lithium chloride, dimethyl dibenzyl ammonium hydroxide, iron sodium tartrate, and cadmium or copper ammonia hydroxide (Schweitzer's reagent).
- *Cellulose* is also soluble in hydrazine, dimethyl sulfoxide in the presence of formaldehyde, and dimethyl formamide in the presence of lithium chloride.
- The *average molecular weight of cellulose* may be determined by measuring the viscosity of these solutions.
- The product precipitated by the addition of a nonsolvent to these solutions is highly amorphous regenerated cellulose.

- We also call the linkage, by agreement with the anomeric nature of the particular carbons involved in linking together the glucosyl units, a *beta*; or β *linkage*. Thus, this linkage is a β 1 \Rightarrow 4 linkage.
- The other similar 1 \Rightarrow 4 linkage found in starch is called an *alpha* or α linkage.
- The geometric consequence of this difference is great.
- The linear arrangement of cellulose with the β linkage gives an arrangement where the OH groups reside somewhat uniformly on the outside of the chain allowing close contact and ready hydrogen bond formation between chains.

- This arrangement results in a tough, insoluble, rigid, and fibrous material that is well suited as cell wall material for plants.
- By comparison, the α linkage of starch (namely amylose) results in a helical structure where the hydrogen bonding is both interior and exterior to the chain allowing better wettability.
- This difference in bonding also results in one material being a “meal” for humans (the α linkage) whereas the other is a meal for termites.
- The reason for this is the difference in the composition of enzymes present in different species—humans with the enzyme capability to lyse or break α linkages and cows and termites and other species with symbiotic bacteria in their digestive systems that furnish the enzymes capable to digest or break the β glucoside linkages.

- The various crystalline modifications have different physical properties and chemical reactivities.
- These variations are a consequence of the properties varying according to *plant source, location in the plant, plant age, season, seasonal conditions, treatment, etc.*
- Thus, in general, bulk properties of polysaccharides are generally measured with average values and tendencies given.
- These variations are sufficient for most applications but possibly not for specific biological applications where the polysaccharide is employed as a drug, within a drug delivery system, or as a biomaterial within the body.

Some average physical properties for cellulose

Table 10.4 Average Specific Bulk Physical Properties for Cellulose

Density (specific gravity)	1.5–1.6
Average percentage crystallinity	
Native	70
Regenerated	40
Refractive index	1.5–1.6
Specific heat, J/g-degree	1.2
Ignition point, °C	>290
Heat of combustion, kJ/g	17
Resistance, Ω -cm	20,000
Insulating value, kV/cm	500

Paper

- It is believed that paper was invented by Ts'ai in China around the second century A.D.
- The original paper was a mixture of bark and hemp.
- Paper was first produced from rags in the United State by William Rittenhouse in Germantown, PA, in 1690. Paper was named after the papyrus plant, *Cyperus papyrus*.
- Paper comes in many forms with many uses; The book you are reading is made from paper, we have paper plates, paper napkins, newspapers and magazines, cardboard boxes, in fact the amount of paper items is probably over twice that of all the synthetic polymers combined by weight.
- About 30% of paper is writing and printing paper. The rest is mainly used for tissues, toweling, and packaging.
- If you rip a piece of ordinary paper (not your book page please), you will see that it consists of small fibers.
- Most of these cellulosic fibers are randomly oriented, but a small percentage are oriented in one direction because the paper is made from a cellulose-derived watery slurry with the water largely removed through use of heated rollers.
- Modern paper is made from wood pulp, largely cellulose, which is obtained by the removal of lignin from debarked wood chips by use of chemical treatments with sodium hydroxide, sodium sulfite, or sodium sulfate.
- Newsprint and paperboard, which is thicker than paper, often contains a greater amount of residual lignin.

- Wood is almost entirely composed of cellulose and lignin.
- In the simplest papermaking scheme, the wood is chopped (actually torn) into smaller fibrous particles as it is pressed against a rapidly moving pulp stone.
- A stream of water washes the fibers away dissolving much of the water-soluble lignin.
- The insoluble cellulosic fibers are concentrated into a paste called pulp.
- The pulp is layered into thin sheets and rollers are used to both squeeze out much of the water and to assist in achieving paper of uniform thickness.
- This paper is not very white. It is also not very strong because the remaining lignin is somewhat acidic (lignin contains acidic phenolic groups that hydrolyze to give a weakly acidic aqueous solution) that causes the hydrolytic breakdown of the cellulose. Most newsprint is of this type or it is regenerated, reused paper.

- Pulping processes are designed to remove the nonsaccharide lignin portion of wood, which constitutes about 25% of the dry weight.
- The remaining is mostly cellulose with about 25% hemicellulose (noncellulose cell wall polysaccharides that are easily extracted by dilute aqueous base solutions).
- **Pulping procedures can be generally classified as semichemical, chemical, and semimechanical.**
 - In *semimechanical pulping*, the wood is treated with water or sulfate, bisulfite, or bicarbonate solution that softens the lignin. The pulp is then ground or shredded to remove much of the lignin giving a purified or enriched cellulose content.
 - The *semichemical process* is similar but digestion times are longer and digesting solutions more concentrated giving a product with less lignin, but the overall yield of cellulose-intense material is lowered by 70–80%. Further, some degradation of the cellulose occurs.
 - Most paper is produced by the *chemical process* where chemicals are employed to solubilize and remove most of the lignin. While overall yields are lower than the other two main processes, the product gives good quality writing and printing paper. Three main chemical processes are used. In the soda process, extracting solutions containing about 25% sodium hydroxide and 2.4% sodium carbonate are used. In the sulfite process the extracting solution contains a mixture of calcium dihydrogen sulfite and sulfur dioxide. The sulfate process utilizes sodium hydroxide, sodium monosulfide, and sodium carbonate in the extracting solution.

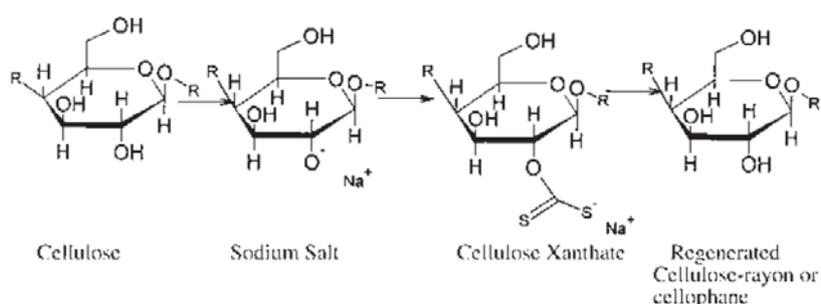
- After the chemical treatment, the pulped wood is removed, washed, and screened.
- Unbleached, brown-colored paper is made directly from this material.
- Most whiten or bleached paper is made from treatment of the pulp with chlorine, chlorine dioxide, hypochlorite, and/or alkaline extraction.
- In general, sulfate pulped paper is darker and requires more bleaching and alkaline extraction to give a “white” pulp.
- If pure cellulose was solely used to make paper, the fiber mat would be somewhat water-soluble with only particle surface polar groups and internal hydrogen bonding acting to hold the fibers together.
- White pigments such as clay and titanium dioxide are added to help “cement” the fibers together and to fill voids producing a firm, white writing surface. This often occurs as part of an overall coating process.

- Most paper is coated to provide added strength and smoothness.
- The coating is basically an inexpensive paint that contains a pigment and a small amount of polymeric binder. Unlike most painted surfaces, most paper products are manufactured with a short lifetime in mind with moderate performance requirements.
- Typical pigments are inexpensive low-refractive index materials such as platelike clay and ground natural calcium carbonate. Titanium dioxide is used only when high opacity is required. The binder may be a starch or latex or a combination of these. The latexes are usually copolymers of styrene, butadiene, acrylic, and vinyl acetate.
- Other additives and coloring agents may also be added for special performance papers. Resins in the form of surface coating agents and other special surface treatments (such as coating with polypropylene and polyethylene) are used for paper products intended for special uses such as milk cartons, ice cream cartons, light building materials, and drinking cups.
- The cellulose supplies the majority of the weight (typically about 90%) and strength with the special additives and coatings providing special properties needed for the intended use.
- Recycling of paper continues to be advantageous.
- Today, up to about one half of our paper products are recycled, and this fraction is increasing as we do a better job of collecting and recycling paper products.

Cellulose-Regenerating Processes

- **Cellulose** is sometimes used in its original form as fibers for textile and paper.
- **Cellulose** is modified through dissolving and reprecipitation or through chemical reaction.
- The **xanthate viscose process** which is used for the production of rayon and cellophane is the most widely used regeneration process.

The cellulose obtained by the removal of lignin from wood pulp is converted to alkali cellulose. The addition of carbon disulfide to the latter produces cellulose xanthate which is eventually changed back again and regenerated to cellulose.



- The **orange-colored xanthate solution, or viscose**, is allowed to age and is then extruded as a filament through holes in a spinneret. The filament is converted to cellulose when it is immersed in a solution of sodium bisulfite, zinc sulfate, and dilute sulfuric acid.
- Cellophane is produced by passing the viscose solution through a slit die into an acid bath.

The overall viscose process can be described as follows:

Native cellulose ⇒ steeping/pressing ⇒ shredding ⇒ aging ⇒ xanthation ⇒ dissolving in sodium hydroxide ⇒ filtration ⇒ ripening/deaeration ⇒ regeneration in acid bath ⇒ stretching ⇒ cutting ⇒ finishing ⇒ drying

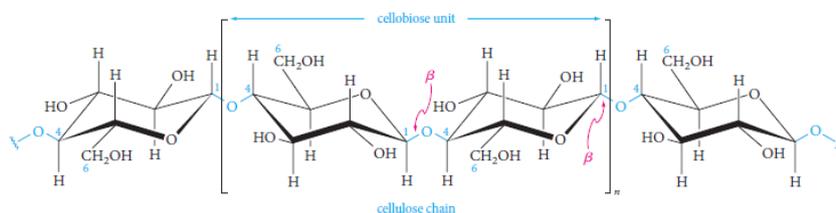
- Partially degraded cellulose is called **hydrocellulose** or **oxycellulose**, depending on the agent used for degradation.
- The term **holocellulose** is used to describe the residue after lignin has been removed from wood pulp.
- Cellulose soluble in 17.5% aqueous sodium hydroxide is called **hemicellulose**.

Important textile fibers, including cellulosic fibers.

Fiber name	Definition	Properties	Typical uses	Patent names (assignees)
Rayon	Regenerated cellulose with substitutes no more than 15% of the hydroxyl groups' hydrogens	Highly absorbent; soft; comfortable; easy to dye; good drapability	Dresses, suits, slacks, blouses, coats, tire cord, ties, curtains, blankets	Avril (FMC Corp.), Cuprel (Beaunit), Zantrel (American Enka)
Acetate	Not less than 92% of the hydroxyl groups are acetylated, includes some triacetates	Fast-drying; supple; wide range of dyability; shrink-resistant	Dresses, shirts, slacks, draperies, upholstery, cigarette filters	Estron (Eastman), Celanese acetate (Celanese)
Triacetate	Derived from cellulose by combining cellulose with acetic acid and/or acetic anhydride	Resistant to shrinking, wrinkling, and fading; easily washed	Skirts, dresses, sportswear (pleat retention important)	Amel (Celanese)

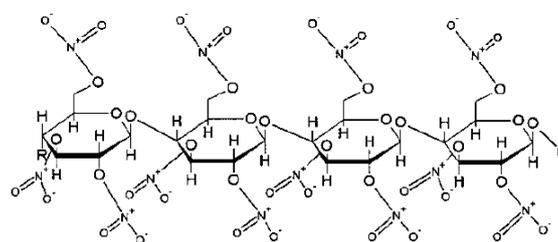
ESTERS AND ETHERS OF CELLULOSE

- It must be remembered that the three hydroxyl groups on the individual cellulose rings are not equivalent.
- The two ring hydroxyls are acidic with pKa values similar to hydroquinone while the third non-ring hydroxyl is similar to an aliphatic hydroxyl in acidity.
- The average number of hydroxyl groups that are reacted are often given as the degree of substitution, or DS.



Inorganic Esters

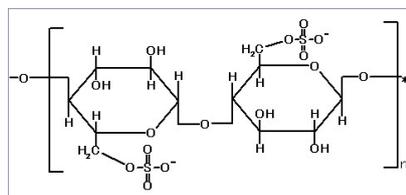
- The most widely used so-called “inorganic ester” of cellulose is **cellulose nitrate (CN)**, also called **nitrocellulose and guncotton**.
- **Cellulose nitrate** was first made around in 1833, when cellulose-containing linen, paper, or sawdust was reacted with concentrated nitric acid.
- It was the first recognized “synthetic” cellulose product.
- Initially, **CN** was used as a military explosive, and improve.
- **Celluloid** was produced in 1870 from a mixture of CN and camphor.



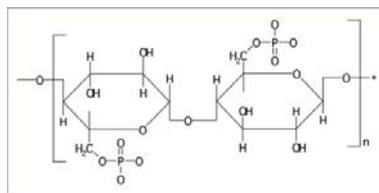
Cellulose Nitrate

Inorganic Esters

- **Cellulose sulfate esters** are also available from the reaction of cellulose with concentrated sulfuric acid.
- **Cellulose phosphate esters** are produced from reaction with phosphoric acid and urea.



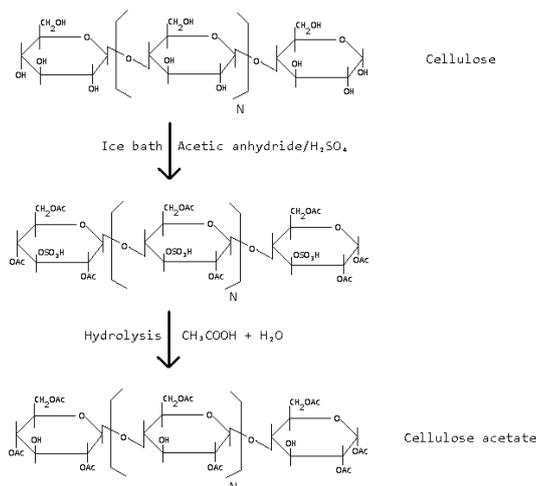
Cellulose sulfate



Cellulose phosphate

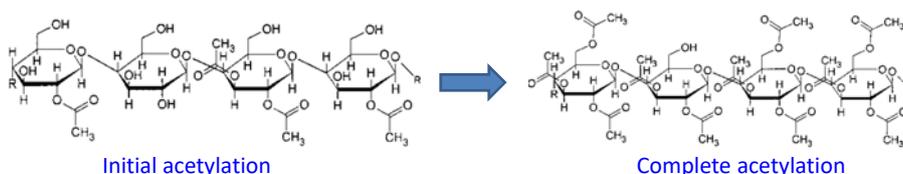
Organic Esters

- The most important cellulose ester is **cellulose acetate** because of its use in fibers and plastics.
- It was first made in 1865 by heating cotton with acetic anhydride.



Organic Esters

- During World War I, a cellulose acetate coating replaced the highly flammable CN coating on airplane wings and fuselage fabrics.
- **Properties of cellulose acetate versus the amount of substitution.**
 - The melting point generally decreases with decreasing acetylation.
 - Lower acetylations give products with greater solubility in polar liquids and corresponding decreased moisture resistance.
- **Cellulose acetate** is made using heterogeneous solutions containing cellulose, sulfuric acid as the catalyst, and acetic anhydride in acetic acid.
- The ring hydroxyl groups are acetylated initially prior to the C-6 exocyclic hydroxyl.



Organic Esters

- Resistance to slightly acidic and basic conditions is important for textiles that are to be laundered.
 - In general, triacetate materials are more resistant than acetate textiles to basic conditions.
 - Both are resistant to mild acid solutions but degrade when exposed to strong mineral acids.
- In general, they offer a comparable stability to light as that offered by cotton and rayon.
- While cellulose acetates are the most important cellulose esters, they suffer by their relatively poor moisture sensitivity, limited compatibility with other synthetic resins, and a relatively high processing temperature.

Organic Esters

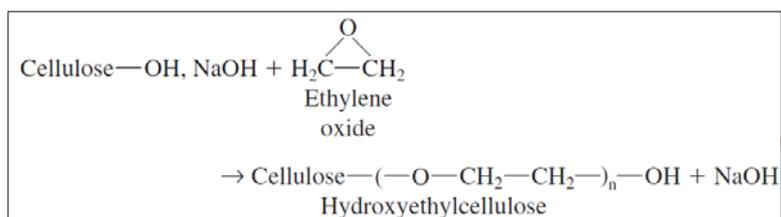
- In triacetate products, only small amounts (on the order of 1%) of the hydroxyls remain free and of these generally about 80% are the C-6 hydroxyl.
- The most common commercial products are the triacetate (DS approaching 3) and the secondary acetate (DS about 2.45).
- *Cellulose acetate* is available as plastics, in films, sheets, fibers, and in lacquers.
- Acetate fiber is the generic name of a fiber that is partially acetylated cellulose.
- The fiber is also known as cellulose acetate and triacetate fiber.
- It is nontoxic and generally nonallergic, so is ideal from this aspect as clothing material.
- *Other organic esters* are commercially available, namely, *cellulose butyrate* and *cellulose propionate*, by far the most widely used is cellulose acetate.

Organic Esters

- Cellulose acetate is used in the manufacture of display packaging and as extruded film for decorative signs, and to coat a variety of fibers.
- Injected molded products include toothbrush handles, combs, and brushes.
- It is also used in lacquers and protective coatings for metal, glass, and paper.
- Cellulose acetate films are used in reverse osmosis to purify blood, fruit juices, and brackish water.
- Some eyeglass frames are made of cellulose acetate.
- Biodegradable film, sponges, and microencapsulation of drugs for control release also utilize cellulose acetate.
- Cellulose triacetate is used for photographic film bases.
- Numerous continuous filament yarns, tows, staples, and fibers are made from cellulose acetate.

Organic Ethers

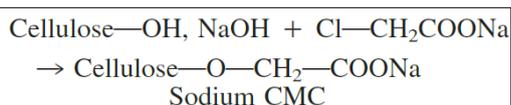
- Reaction with an epoxide such as ethylene oxide under alkaline conditions gives **hydroxyethylcellulose (HEC)**



- Industrially, **HECs** with DS values below 2 are used.
- Low DS materials (to about 0.5) are soluble only in basic solutions while those with DS values of about 1.5 are water-soluble.
- **HEC** is used as a protective colloid in latex coatings and pharmaceutical emulsions; as a film former for fabric finishes, fibrous glass, and in aerosol starches; thickener for adhesives, latex coatings, toothpaste, shampoos and hair dressings, cosmetic creams and lotions, inks and joint cements; lubricant for wallpaper adhesives and in pharmaceutical gels; and as a water binding for cements, plastics, texture coatings, ceramic glazes, and in printing inks.

Organic Ethers

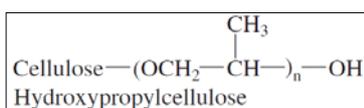
- **Sodium carboxymethylcellulose (CMC)** is formed by the reaction of sodium chloroacetate with basic cellulose solutions.
- It is soluble in both hot and cold water.
- **CMCs** are used as thickening, binding, stabilizing, and film-forming agents.



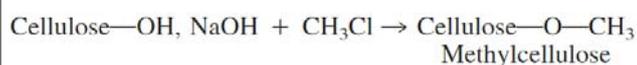
- **Carboxymethylhydroxyethylcellulose (CMHEC)** is synthesized from the reaction of hydroxyethylcellulose with sodium chloroacetate.
- The product is a mixed ether.
- Solutions can be gelled by addition of solutions of aluminum and iron salts.

Organic Ethers

- **Hydroxypropylcellulose (HPC)** is a thermoplastic nonionic cellulose ether that is soluble in both water and a number of organic liquids.
- It is synthesized through reaction of the basic cellulose slurried with propylene oxide.



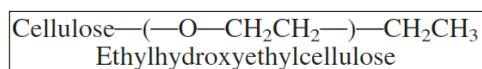
- **Methylcellulose (MC)** is formed from basic cellulose and its reaction with chloromethane.



- **Methylcellulose** is used as an adhesive; in ceramics to provide water retention and lubricity; in cosmetics to control rheological properties and in the stabilization of foams; in foods as a binder, emulsifier, stabilizer, thickener, and suspending agent; in paints, paper products, and plywood as a rheology control for the adhesive; in inks and in textiles as a binder and for coatings.

Organic Ethers

- *Ethylhydroxyethylcellulose (EHEC)* is a nonionic mixed ether available in a wide variety of substitutions with corresponding variations in aqueous and organic liquid solubilities.
- It is compatible with many oils, resins, and plasticizers along with other polymers such as nitrocellulose.
- Water-soluble EHECs with DS values about 0.9 .
- *EHEC* is synthesized through a two-step process beginning with the formation of the HEC-like product through reaction between the basic cellulose and ethylene oxide.
- The second step involves further reaction with ethyl chloride.



- Uses for the *water-soluble EHEC* include in water-borne paints, pastes, polymer dispersions, ceramics, and cosmetics and pharmaceuticals.
- Cellulose undergoes reaction with activated ethylenic compounds such as acrylonitrile giving *cyanoethylcellulose* via a Michael addition.

