Cellulose Derivatives

V.K. Broker.

Introduction :

From the beginning of the civilisation "CELLULOSE" is known and abundantly available to mankind in innumerable forms and with a characteristic versatility unmatched by any naturally occuring polymer. In Carbohydrate Chemistry, cellulose is classified as a naturally occuring fibrous polymer, containing anhydro glucose units of formula $C_6H_{10}O_5$. Some of its typical properties like insolubility in practically all solvents, thermal unstability etc. had been the puzzling hurdles to the carbohydrate scientists for quite some period. However, with increasing understanding of the chemistry and technology celulose has now been successfully converted into derivatives having additional favourable properties.

Classification

In this article cellulose derivatives have been categorised into (1) Esters and (2) Ethers.

(1) Esters :

(A) Inorganic :

Two of the most common inorgancis ester of Cellulose are Nitrate and sulfate.

(a) Nitrate :

Cellulose nitrate is an inorganic ester of Cellulose in which some of the hydroxyl groups have been replaced by the radical ONO_2.

It may be prepared by treating Cellulose with anhydrous nitric acid, in the liquid or vapor form. It is a white, fibrous, highly flammable solid. The most important properties of Cellulose nitrate that attract its uses in lacquer coatings, inks and adhesives are its solubility, solution viscosity, compatibility with modifiers such as plasticizers, resins and pigments, stablity, durability and exceedingly good physical properties.

(b) Sulfate :

Cellulose sulfate may be prepared by the reaction of Cellulose with 70–75% sulfuric acid or with Chlorosulfonic acid in the presence of pyridine. This readily water soluble and heat stable derivative was introduced commercially for general thickening and emulsion stabilizing applications. This product is similar to CMC in many of its solution properties.

(B) Organic :

Some of the common organic esters are as follows : Cellulose acetate, Cellulose acetate propionate and Cellulose acetate Butyrate.

(a) Acetate :

Cellulose acetate may be prepared by the reaction of Cellulose with acetic acid, acetic anhydride and sulfuric acid. Cellulose Acetate is a white, odorless, tasteless, non-toxic solid. Cellulose acetate is useful because of its good solubility in acetone, its thermoplasticity and the excellent colour, clarity, stability and durability of its films. It is used for textile fibres, plastic, film, sheeting and lacquers. In recent years it is used in very large quantities in cigarette filters and as injection molding plastics.

(b) Acetate butyrate & Acetate propionate.

Cellulose acetate butyrate and propionate are the two mixed esters of cellulose. They are manufactured by the same general process as that of Cellulose acetate. For example, Cellulose acetate butyrate may be prepared by the reaction of Cellulose with acetic acid, butyric acid, butyric anhydride and sulfuric acid. Cellulose acetate propionate and cellulose acetate butyrate can be used in plastics, film, thin sheeting and lacquers. These esters are compatible with a variety of plasticizers and resins.

(2) Ethers :

Cellulose ethers are high-molecular weight compounds wherein the hydrogen of the hydroxyl groups of cellulose has been partially replaced by alkyl or substituted alkyl groups in order to modify the character of the native cellulose. Ethers of cellulose are organosoluble and thermoplastic, water-soluble or

V.K. Broker.
Cellulose Products of India Limited
Kathwada–Ahmedabad.

aqueous alkali soluble depending upon the type and the degree of structural change effected. The active hydroxyls of cellulose are etherified by organic halides, alkane oxides, or olefins activated by polar substituent groups in the presence of alkali. Cellulose is treated with sodium hydroxide and the resultant alkali cellulose reacts with the etherifying reagent. During etherification of cellulose, the gradual increase in degree of substitution is accompanied by a transition from insoluble cellulose through solubility in the following series of solvent types : aqueous alkali, water, water-alcohol mixtures, hydrocarbon-alcohol mixtures, or equivalent solvents and finally aromatic hydrocarbons. Thus, cellulose ethers may range from insoluble surface modifiers of textiles through alkali-soluble products that may be coagulated to films and fibres through water soluble products that are thickners and protective colloids and organo soluble ethers that may be used in lacquers and other protective coatings. Organo soluble cellulose ethers may be molded into various shaped plastic materials by extrusion, injection molding or similar procedure.

Commercially important cellulose ethers are Sodium Carboxy Methyl Cellulose, Methyl Cellulose, Ethyl hydroxy ethyl cellulose, Hydroxy ethyl cellulose and Hydroxy alkyl methyl cellulose.

(a) Sodium Carboxymethyl Cellulose (CMC).

Sodium Carboxymethyl Cellulose was developed in Germany shortly after 1st world war and was introduced as a substitute for gelatin. Commercially, the term carboxymethyl cellulose is applied to a water soluble cellulose ether which is actually the sodium salt of carboxymethyl cellulose. It is also frequently called eellulose gum, CMC OR Sodium cellulose glycolate. It is a valuable cellulose derivative with the following properties which make it useful in a variety of applications.

(i) Easy solubility in hot and cold water.

(ii) Adhesive and binding nature.

(iii) Efficient thickening action in water solution.

(iv) Resistance to grease, oil and organic solvents and film forming properties

CMC has a wide range of physical and chemical properties which makes it useful in various industries like textile, paper, drilling fluids, foundry, ceramics, cosmetics, pencils, food, pharmaceuticals etc.

Manufacture :

Sodium Carboxymethyl cellulose can be prepared from pure wood pulp or cotton linters pulp by reacting them with sodium hydroxide to form alkali cellulose and then treating the alkali cellulose with monochloro acetic acid or its sodium salt either in traditional shredder process, dry mixing process, suspension process or circulation process to produce CMC. The principle by-products of the reaction are sodium chloride and sodium glycolate. On drying the reaction mass, a technical grade of CMC is produced containing about 55 to 70% active material which contributes to all the properties of CMC. For food and pharmaceutical grades of CMC the reaction mass can be purified by the use of alcohol-water mixtures to extract the salt without dissolving the ether. The typical reaction may be represented in the following way.

$$\text{R cell OH} + \text{NaoH} + \text{ClcH}_2\text{ CooNa} = \text{RCell ocH}_2\text{ CooNa} + \text{Nacl} + \text{H}_2\text{O}$$

Each of the anhydro-glucose units possess three reactive hydroxyl groups with which etherifying agent can reaet. A theoretical complete reaction would mean the introduction of three carboxymethyl groups per anhydroglucose unit giving a degree of substitution (D.S.) 3.0. But this has never been attained. Commereial CMC, generally has an average D.S. of less than 1.5. The most common substituion range is between 0.4 and 0.8.

The properties of CMC can be controlled by varying the uniformity of substituion, the degree of substitution (D.S.) and the degree of polymerization (D.P.). Solubility in water, particularly the characteristics of solution, depends not only on D.S. but also on the uniformity of distribution of substituting carbo xy methyl group along the polymer chain. The more uniform the distribution of the substituted group the more smooth and the less thiotropic the solution will be. By controlling its D.S. its solubility in caustic water or Organic solvent is varied. Difference in D.P. has a profound effect on the viscosity and the film strength property. In practical applications, viscosity is of the paramount importance. CMC is commercially available in viscosities above 3000 cps in 1% solution to 25 cps in 2% solution and even lower viscosity products are available in market.

Applications :

The basic properties that enhance its commercial value are due to its thickening, solid suspending in aqueous media, emulsion stabilizing, mositure absorbing and film forming properties. These properties have been utilized in divergent applications.

Textile Industry

Sodium Carboxymethyl cellulose has received considerable attention in the textile industry. Because of its superior properties, it has replaced many conventional sizing, finishing and printing materials. Besides, it solves the pollution problems. It is stable at the pH of the common printing dyes is readily washed out of the textile with water.

Other textile applications include its use as a scaffolding fibre, as a binder for non woven fabrics and when insolubilized as a permanent finish.

Detergent Industry

CMC is believed to function as a soil suspending anti–re-deposition agent. CMC keeps the soil in a suspended stage which has been removed from the cloth by the detergent so that there will be no further redeposition of the soil on the cloth. This soil anti-redeposition property is caused by electrostatic repulsion between the negatively charged dirt particles and the negativity induced by CMC. This property has been used to up-grade synthetic detergents and builders.

Paper Industry

The grease resistance and the film forming characterristics of CMC have made it a useful additive for paper and paper board products. It can be used along or in conjuction with starch on the size press to give increased dry strength properties and improved surface characteristics. It is used as beats additive and helps in size and colour retention in pulp or paper.

Paper, such as box–board is highly porous. When paper board is coated with CMC a glossy finish is obtained in addition to grease proofing and lesser ink absorption properties. In coating operations, the presence of CMC controls the viscosity and flow properties of the coat-ink colour. suspends and deflocculates the pigment. It also binds the coating to the paper more efficiently, thus providing a more suitable printing surface with less dusting.

Drilling Fluids :

In the oil industry, drilling muds are used to lubricate and cool the bit and to carry cuttings away from the bore hole. These fluids are primarily aqueous dispersions of clay, bentonite, and weighting agents, such as barytes. Water loss inhibitors are used in these systems to facilitate viscosity control and to minimise water loss into porous strata. The excellent deflocculating characteristics and thickening action of CMC make it an efficient water loss agent.

Ceramics :

CMC is used by the ceramic industry because of its ability to suspend solid and act as a green strength binder prior to firing. Its most important applications are in glazing of sanitary ware and structural tile, in refractories as a jigger body additive and as a plasticizer for electrical porcelain.

Foundry :

CMC can be used in foundry as a core binder. Its advantages over other binders are based on a combination of the following properties : low drying temp., green hot strength, low decomposition temp., and low gas evolution.

Pharmaceuticals and Cosmetics :

CMC is used as a suspending agent in lotions and as a thickner for jellies. salves, ointments. It is used in medicinal tablets because of its binding and swelling properties. It is also used in hand creams, shampoos, bubble baths and tooth pastes.

Foods :

Being physiologically inert, CMC finds its abundent uses in many of the food stuffs like jellies, puddings, Icecream, syrups, cakes and many other backed foods. Many of the unique properties that make CMC useful in food preparations are texturizing agent, protective colloid, preservative, dehydrating agent and water binding etc.

Miscellaneous :

CMC has a variety of other uses. It can be used in autopolish, in suspension polymerization, to make water soluble, films, in leak detectors for gaseous systems, in molding extrusion of lead pencil and coal briqueetes and many others.

(b) Ethyl Cellulose :

Ethyl cellulose, is manufactured by the reaction of ethyl chloride with alkali cellulose, followed by the isolation, washing and drying of the product. Ethyl cellulose which is a thermoplastic, is insoluble in water but soluble in organic solvent.

Ethyl cellulose is tough, stable to heat flexible even at very low temperature. Soluble in a wide range of organic solvents, widely compatible with waxes, resins and plasticizers, nontoxic and relatively low infiammability. It can be formulated into plastics, melts, lacquers, sheeting, varnishes, inks and adhesives. In the plastics field, its uses are similar to those of Cellulose acetate butyrate and nylon. Ethyl cellulose is used as a film former in pharmaceutical applications to decrease moisture sensitivity and to prevent discoloration. Also it is used as a binder and filler in dry vitamin preparation and as a protective coating for vitamins.

(c) **Ethyl Hydroxyethyl cellulose :**

This mixed ether is prepared by treating alkali cellulose with a mixture of ethyleneoxide (Hydroxy ethylating) and ethyl chloride (ethylating).

Ethylhydroxyethyl cellulose are used as thickners in emulsion paints, as wall paper paste, as thickners in paint removers and as foundry core binders,

(d) **Hydroxyethyl cellulose :**

Hydroxyethyl cellulose is a water soluble ether that results from the reaction of ethyleneoxide with cellulose. Water soluble HEC differs from some others nonionic water-soluble cellulose derivatives in that it is equally soluble in both hot and cold water and is not as readily precipitated from its aquous solutions by salts. HEC is not significantly thermoplastics.

The uses of HEC are based upon its nonionic character, its lack of a gel point and its tolerance of cations. It is used as thickner in latex paints in several other compositions such as adhesives. It is used as protective celloid in emulsion polymerization of vinyl acetate vinyl chloride its copolymers. It is added to portland cement composition to prevent water loss. It is also used as a binder in nonwoven fabrics. It is used in paper sizing, as a warp size for textiles and as a finishing size.

Methyl cellulose

Methylcellulose is cold-water soluble ether that is the reaction product of alkali cellulose and methyl chloride. It is a white, odorless, tasteless, nontoxic solid. Its uses are based upon its cold-water solubility, its compatibility in solution with heavy metal, salts, its insensitivity to pH, its surface activity, and its gelation from solution upon heating or upon salt addition.

Methyl cellulose is used in ceramics to impart cohesiveness to the mortar and as a binder and suspending agent in ceramic glazes. It is used as a paper coating to impart wax and oil resistance. Methyl cellulose is used in the leather industry to adhere hides to pasting platens during the drying operation. It is also used as a protective colloid and stabilizer in multicolour lacquers. Because it is used extensively in the pharmaceutical, cosmetic and food industries.

Hydroxyalkyl Methyl cellulose :

Now-a-days two types of hydroxy alkyl methyl celluloses are prepared in the world (i) Hydroxy ethyl methyl cellulose (ii) Hydroxy propyl methyl cellulose. The first one is prepared by treating alkali cellulose first with ethylene oxide and then methyl chloride, while another ether can be prepared by treating alkali cellulose with propylene oxide and then methyl chloride.

Hydroxy alkyl methyl cellulose is used in a variety of applieations as thickners and protective colloids.

Indian Scene

There are very few selected number of cellulose derivatives being manufactured in India at present.

"CELLULOSE PRODUCTS Of INDIA LTD.,"

&

"GUJCHEM DISTILLERS INDIA LIMITED are the pioneer in respect to commercial production of CMC in India. Their present productions are 4000 and 2000 M. Tonnes/year respectively.

Acknowledgement :

The author is highly thankful to Dr. C.D. Dhariyal, our Chief Technical Executive for his encouragement and many helpful suggestions during the preparation of this Article.

Bibliography :

1. Herman F. Mark, Encyclopedia of Polymer Science & Technology Vol. 3, 1965 (Inter Science Publishers).
2. Kirk–Othmer, Encyclopedia of Chemical Technology, Vol. 4, 1964 (Inter Science Publishers).
3. Ott & Spurlin, Cellulose & Cellulose Derivatives Vol. I, II, III (Inter Science Publishers, 1955).
4. Roy L. Whistler, Industrial Gums (Academic Press, 1973).