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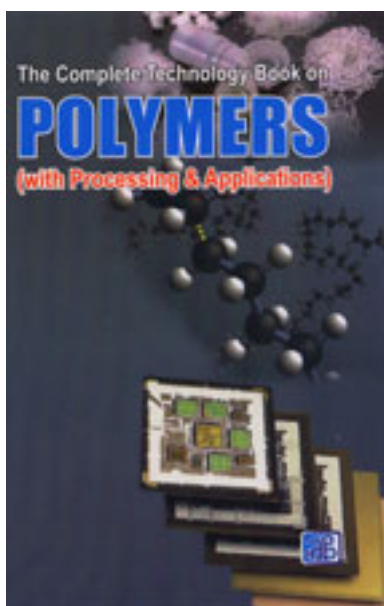
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The Complete Technology Book on Polymers (with
Processing & Applications)



Code:	ENI181
Format:	Paperback
Indian Price:	1100
US Price:	30
Pages:	560
ISBN:	8178330105
Publisher:	Pacific Business Press Inc. Asia

Polymers are the most rapidly growing sector of the materials industry. No wonder polymers are found in everything from compact discs to high tech aerospace applications. The Indian plastic and polymer industry has taken great strides. In the last few decades, the industry has grown to the status of a leading sector in the country with a sizable base. The material is gaining notable importance in different spheres of activity and the per capita consumption is increasing at a fast pace. Continuous advancements and developments in polymer technology, processing machineries, expertise and cost effective manufacturing is fast replacing the typical materials in different segments with plastics. Monomers and polymers are of little or no practical use until the raw product from the manufacturing process been transformed by more or less standardized fabrication and processing techniques into useful forms. There are different methods of processing of polymers for solid; molding, extrusion, calendaring, sheet forming, laminating and impregnating and for liquids and melts; coating, expanding or foaming, casting, spinning, laminating and impregnating. Plastics are divided into thermosetting and thermoplastic materials. Compression and transfer molding are the two main methods used to produce molded parts from thermosetting plastics; however, injection molding is under development and may become important in future. Plastic foams are from a wide variety of polymers have a wide range of applications and are made by a variety of methods depending upon the polymer and the application. Elastomers are indispensable to our modern civilization, without them two of largest industries; transportation and electrical, would never have attained their present state of development. The reason why plastics are popular is that they may offer such advantages as transparency, self lubrication, light weight, flexibility, economy in fabricating and decorating. Properties of plastics can be modified through the use of fillers, reinforcing agents and chemical additives. Polymer Energy system is an award winning, innovative, proprietary process to convert waste plastics into renewable energy. On the basis of value added, Indian share of plastic products industry is about 0.5% of national GDP.

Some of the fundamentals of the book are modified natural products, synthetic condensation products, melamine formaldehyde resins, aniline formaldehyde resins, miscellaneous amino plastics, sulfonamide formaldehyde resins, polyesters, saturated polyesters, linear polycarbonates, unsaturated polyesters, polymerized oils, synthetic addition products, aliphatic hydrocarbons and derivatives polyethylene, powder technology for coating of plastics, acrylic and polyurethane dispersions in industrial coatings for plastics, water borne coatings for plastics

adhesion of water borne coatings on plastics, fabricating and processing, cold bending, hot bending, stretch forming, plug and ring forming, slip forming, drawing

die pressing, roto forming, veneering, post forming, fluid pressure forming, vacuum forming methods, pressure forming methods, laminating and impregnating etc.

Three factors are essential for any successful processing of polymers, namely materials, machinery and process control. Polymers have importance in manufacturing of various domestic and industrial products. This book is an invaluable resource to new entrepreneurs, technocrats, researchers, professionals etc.

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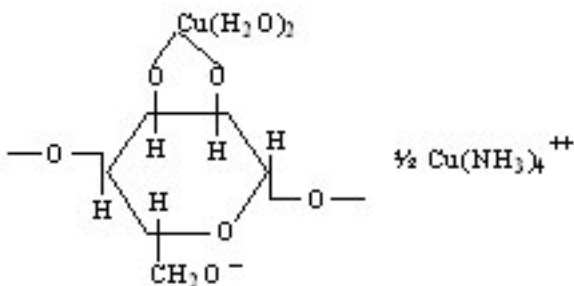
Sample Chapter:

Modified Natural Products

CUPRAMMONIUM RAYON

In 1857, the German chemist and botanist, Schweitzer, discovered that cotton and paper were soluble in an ammoniacal copper hydroxide solution $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$. Then, later in the nineteenth century, the American inventor, Weston, produced filaments from such a solution for electric lamp filaments. In 1890, the French chemist, Despaissis, was granted the first patent for making a cuprammonium artificial silk. The first commercial development took place in Germany under Pauly's patent but was later abandoned. Much later, in 1918-19, a German firm, Bemberg A.G., started production, using a different process, and several plants in Europe produced this type of rayon. It was not until 1924-25 that an American plant, established by Bemberg, began production in this country.

The principal raw materials used in the cuprammonium process are purified cotton linters or wood pulp, the latter being more generally used today. In one process, aqueous copper carbonate is mixed with the cellulosic material in a shredder to form copper cellulose. After expression of liquid, the residual cake is mixed with aqueous ammonia and caustic soda to form a viscous solution. The solution, containing about 8 per cent cellulose, is stored, filtered, and vacuum deaerated. Glucose is usually added to stabilize the solution and improve spinning properties. The cellulose now probably exists in the form represented by where the original ammonia-copper complex is destroyed and two molecules of water are complexed with the copper.



The spinning solution is forced through relatively large holes in nickel spinnerets; subsequent stretching of the filaments reduces their diameter. A thread from a 0.0002 inch orifice may be stretched to as small as one denier in this process. As the filaments emerge from the spinnerets, they pass through coagulating baths, which may be acid or alkaline. Sulfuric acid baths are now less common than alkaline baths. The yarn is then washed, dried, and wound on bobbins. As many as 400 threads are spun simultaneously. After treatment with dilute sulfuric acid to remove residual copper, the yarn is bleached, washed again, and dried. It is essential that the copper salts and the ammonia used be recovered, else the cost of the process would be prohibitive. In this sense, the production of cuprammonium rayon parallels that of soda ash by the ammonia process, wherein the intermediates are of greater value than the final products, and the process is competitive only because of an efficient recovery process. The ammonia is recovered from the dissolving tank and from alkaline coagulating tanks by passage through an ammonia scrubber. Copper from coagulating baths and from the acid and water purification systems is recovered by precipitation.

Approximately 0.57 pound of ammonia, 0.40 pound of caustic, 0.75 pound of copper salt, and 0.92 pound of cotton linters are needed to make one pound of cuprammonium rayon.

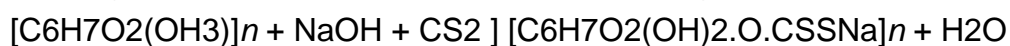
Cuprammonium rayon (often referred to as Bemberg rayon because the Bemberg Corporation is probably the sole producer) resembles real silk in fineness of filaments, luster, and softness. However, since it is regenerated cellulose, it also has most of the properties of cotton and viscose rayon. Probably its chief virtue is its capability of being drawn to very fine filaments, as low as 0.4 denier. The fineness of filament gives cuprammonium rayon great pliability and good draping qualities; hence it is used in apparel manufacture, especially for women's wear. It has been widely used as a substitute for silk.

Due to the inherently high cost of manufacture, even with a good recovery process, the production of cuprammonium rayon is very small. In the United States today, probably no more than 3 per cent of the rayon is manufactured by this process, the remainder being made by the viscose process.

VISCOSE RAYON

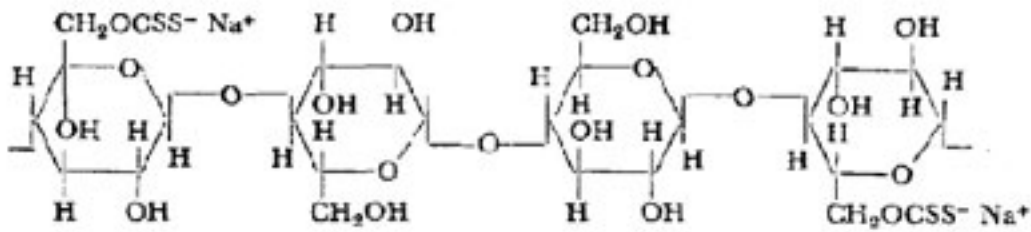
Although the viscose process for making rayon was the last of the three commercial processes to be developed, it has, since about 1910-11, been by far the most important. The process is rather lengthy (taking several days to a week) and requires careful control throughout; yet all the raw materials are fairly cheap, with the result that viscose rayon can generally be made to sell below the price of all other rayons. This is the chief reason for its greater success.

The development of viscose rayon is due mainly to the work of two English chemists, Cross and Bevan, who obtained a patent in 1895 on rayon manufacture. They discovered that when cellulose is treated with caustic soda and then with carbon disulfide, it is converted into a new compound. This new compound, when dissolved in caustic soda, produces a viscous solution which Cross and Bevan termed "viscose." As with cuprammonium rayon, cotton linters or wood pulp are used, the latter being preferred due to its lower cost. [A viscose plant has been built in the Philippines recently to convert sugar-cane waste (bagasse) into rayon]. Cellulose pulp from cotton linters, northern spruce, western hemlock, or southern pine is steeped or mercerized in an 18 per cent caustic soda solution to form sodium cellulose. After expression of liquid in hydraulic presses, the sodium cellulose is shredded into crumbs. The crumbs are aged for two to three days in steel or iron cans so that partial oxidation and depolymerization occur. They are then blended with carbon disulfide vapor in large, rotating churns under carefully specified and controlled conditions. A gelatinous mass of sodium cellulose xanthate is formed [the sodium salt of the cellulose acid ester of xanthogenic (dithiocarbonic) acid, HO.CSSH], together with some adsorbed caustic soda:

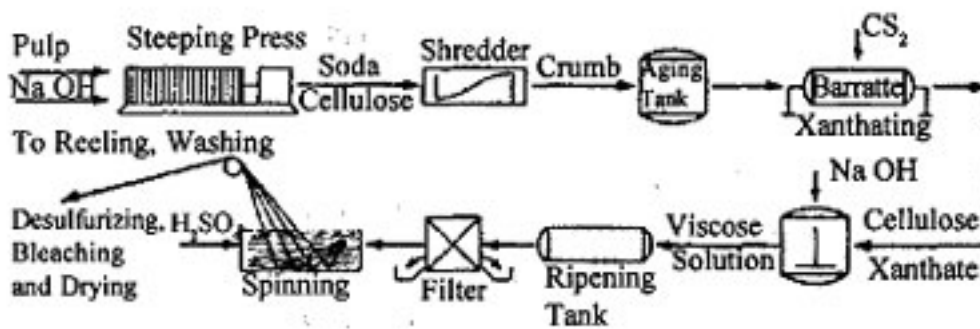


Although almost complete xanthation can be obtained, normally only about one to two hydroxyl groups per cellobiose residue are xanthated, as this is sufficient to allow solution or dispersion of the product in more caustic solution.

A portion of a cellulose xanthate chain may be represented as follows:



The solubility of this polymer in aqueous media is due to its lack of symmetry, which decreases hydrogen bonding, and to the ionic character of the xanthate group. Thus, a dilute caustic solution is added to the xanthate in a mixer, and the mass is stirred until a homogeneous, viscous mass of viscose is obtained. At this time, the luster of the rayon is controlled. If nothing is added, a high luster rayon is obtained; to obtain a dull or semidull yarn, a pigment, usually titanium dioxide or a mineral oil, is added which causes the yarn to reflect diffusely. Since these additives are incorporated into the yarn, they cannot be later washed out.



During the subsequent ripening period, which takes from four to five days and is done in tanks in an insulated room at 15° to 20° C, the molecular structure is retained, but the viscosity slowly decreases, then rises again, partly due to regeneration of some cellulose by slow hydrolysis of xanthate and partly by the salting-out of inorganic by-products. The regenerated cellulose is maintained in emulsion form by the undecomposed xanthate, which acts as a protective colloid. During this process, the color of the mass turns from white to an orange-yellow.

After proper ripening, the solution is filtered, vacuum deaerated, refiltered, and spun, as with cuprammonium rayon. The spinneret may be a platinum alloy containing from 10 to 120 holes for ordinary rayon and more than 3,000 for tire cord and tow. The holes are generally from 0.002 to 0.004 inch in diameter. The final size of the filaments depends more on the rate of supply of the solution to the spinneret and the amount of stretching during coagulation than upon the size of the spinneret holes. All of the monofilaments from a single spinneret are combined into a single thread of rayon yarn.

The spinning bath, made of sheet lead, contains a solution of sulfuric acid and additives maintained at 40°

to 55°C. A representative composition is as follows:

	<i>Per Cent</i>
Sulfuric acid	9-12
Sodium sulfate	17-20
Glucose	2-5
Zinc sulfate	1
Water	67-71

Sometimes a small quantity of magnesium sulfate is also added.

Although the composition of the bath has been determined empirically, the probable functions of the ingredients are as follows: The sodium sulfate precipitates the sodium cellulose xanthate from the viscose solution in the form of filaments and the sulfuric acid converts them into cellulose. The glucose helps to prevent crystallization of the salt formed during precipitation and also gives pliability and softness to the yarn. The zinc sulfate gives added strength to the yarn (see below) and is also responsible for its serrated cross-section, for if it is omitted, the filaments are round or oval and do not accept dyes as well. Sodium sulfate or sodium acid sulfate is always formed in sulfuric acid baths, due to the sodium hydroxide in the viscose. Its concentration is maintained within the limits given above.

The yarn after spinning is impure and relatively weak. Purification consists of washing, desulfurizing (sometimes called sulfiding), bleaching, and washing. The first wash is with water, the second is with sodium sulfide solution, the third with slightly alkaline sodium hypochlorite (followed by neutralization with dilute hydrochloric acid), and the final wash is with water again. Continuous spinning has been achieved by elimination, where possible, of the desulfurizing and bleaching steps.

The regenerated cellulose in the final product is identical to the cellulose from which it came except that the long cellulose molecules have been partly hydrolyzed and degraded into shorter, although still very long, molecules. It should be borne in mind that fibers can be made only from long molecules, and that, during and subsequent to the manufacture of a fiber, hydrolytic conditions should be avoided. Some degradation is inevitable, but means to minimize this considerably have been found. In viscose rayon, the cellulose molecules are about one third as long as those in the original cellulose; i.e., the initial degree of polymerization of about 1,100 has been reduced to one of about 350.

The tensile strength of ordinary viscose fiber varies between 25,000 and 50,000 psi; however, the tensile strength drops about 50 per cent upon soaking in water.

High-strength or high-tenacity viscose achieves its greater strength (twice that of ordinary viscose) from orientation of the molecular crystallites by cold stretching during regeneration. Complete regeneration of the coagulated filament is delayed until the filament can be stretched from 50 to 250 per cent, the lower range being used to produce medium-tenacity yarn. The zinc ions added to the bath react with the cellulose xanthate to yield a zinc cellulose xanthate which acts as an outer skin in the form of an elastic gel. This gel decreases the rate of regeneration by the sulfuric acid and facilitates stretching. The presence of zinc ion also appears to improve fatigue resistance of the yarn. For high-tenacity rayon, the concentration of zinc sulfate in the regeneration bath may run as high as 10 per cent, and it is likely that the concentration of sulfuric acid is higher also—from 45 to 75 per cent.

Viscose fibers find more than half their market in tires and other industrial uses; most of the remainder goes into apparel and household fabrics. About nine out of every ten tires made in the United States contain

rayon cord; half of this tire cord is used in truck tires. High-strength viscose rayon, such as Cordura, is used in the manufacture of tire cord for heavy-duty purposes. The total amount of yarn presently produced is close to a billion pounds per year. Thus, it is not surprising that the viscose industry is the largest producer of man-made fiber and is the chief consumer of carbon disulfide and a major consumer of sulfuric acid and caustic soda. Viscose is lower in price than all other staple fibers, natural or synthetic.

Staple rayon or "fluff" is made in the same way as filament rayon except that a larger nozzle with from 2,500 to 4,000 openings is used for the spinneret. This produces a ropelike product which is cut into short lengths and then fluffed by blowing air through it. The staple is packed in bales like raw cotton and is used on standard cotton-weaving machines. About one fifth of the viscose rayon made is produced as tow or staple fiber.

In Europe, several regenerated cellulosic fibers are made which are like cuprammonium or viscose fibers but differ in after-treatment or source. Tenasco and Durafil are British products which have higher tenacities than normal rayon. Their manufacture is similar to that of American high-tenacity rayon; i.e., more zinc sulfate or more concentrated sulfuric acid is used in the regenerating bath. Fortisan, both a British and an American fiber, is made by stretching cellulose acetate in steam under pressure and then saponifying the stretched yarn to yield regenerated cellulose. It is the most highly oriented and strongest of any of the modified natural and synthetic fibers yet made, having a tensile strength of almost 140,000 psi. Since all three fibers have lower extensibilities, moisture regain, and affinity for dyes than normal rayon, they are used only when their greater strength is necessary, as in tire cords, except in the United States, where Fortisan is used in draperies and linings, presumably not only because of its strength but also because of its resistance to sunlight. In Germany, a wool-like staple fiber, known as Lanusa, is made by a combination of the viscose and cuprammonium processes, which gives it a round cross-section and a wool-like appearance and feel.

REGENERATED CELLULOSE FILM

Regenerated cellulose film, or cellophane, is the most widely used thin, transparent packaging material. It was first made in France as early as 1908. Small quantities were imported into the United States until 1924, when American production began.

The method of manufacture of regenerated cellulose film is almost identical to that of viscose rayon. The principal difference is the method of extrusion. Instead of forcing viscose through spinnerets, it is extruded from a casting machine into the acid coagulating bath.

The film produced is too brittle for commercial use without the addition of plasticizer. Suitable plasticizers or softeners improve flexibility and decrease the tendency for the film to rattle. Water is probably the most efficient plasticizer; to incorporate it into the film, the sheet is passed through a glycerol bath, after removal of sulfur and bleaching. The glycerol itself has some plasticizing effect but, being hygroscopic, also holds some water in the sheet. Approximately 7 per cent glycerol is absorbed by the film. Similar hygroscopic plasticizing agents, including ethylene glycol, glucose, and other polyhydric alcohols, are also used. The film is finally dried by passage over heated rolls.

Regenerated cellulose film is very sensitive to changes, in relative humidity and shows appreciable dimensional variation with such changes. Further, water vapor is readily transmitted by the film, and the plasticizers used are readily leached out. As a result, when the film was first used for food wrapping, it was found that baked goods, in particular, dried out too quickly. A moistureproofed sheet was developed in 1927 which opened up thousands of new uses for the product.

The usual method of moistureproofing consists in coating the sheet with a very thin layer of lacquer, which includes cellulose nitrate as the film-forming ingredient, a plasticizer for the nitrate, a resin, and a wax. The wax, usually paraffin, is responsible for most of the moisture-vapor-transmission resistance of the coating. Approximately four fifths of regenerated cellulose film is moistureproofed.

A major reason for using unsupported films is their transparency. Cellulose films are widely used to protect and improve the sales appeal of merchandise. Cellophane transmits most of the ultraviolet light as well visible light. A newer, similar packaging material (Sylphwrap) is claimed to exclude ultraviolet light; hence, this film should offer great protection against rancidity. In order to seal cellulose film to itself for packaging uses, a large amount is coated with heat-sealing lacquers which usually are also formulated to be water-vapor resistant.

Regenerated cellulose film is also produced as seamless tubing (Visking) for sausage casing. Although edible, it is not assimilated by the body.

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