

CROSSLINKING AGENTS USED FOR CELLULOSIC FIBER

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Abstract: Cellulose is the most abundant, renewable and biodegradable polymer in nature and along with its derivatives has been widely used in textiles (cotton, linen, viscose, and acetate), plastics (cellophane and celluloid), paper, food (thickener agent, enhancer of organoleptic properties, texture modifier, etc). This review article describes the crosslinking agents and the resulting physical and mechanical properties of cellulose derivatives. Different crosslinking agents such as dialdehydes, acetals, phosphorous derivatives, silica derivative, epichlorohydrin and polycarboxylic acids are selected for the discussion because they present a toxicity and better biodegradability are able to react efficiently.

Keywords: crosslinking agents, toxicity, biodegradability etc.

1. Introduction

The polymer material based on petroleum has significantly increased. These materials can lead to environmental problems because they are non-recyclable and non-biodegradable. Cellulose fibers are the most abundant polymer in nature and it is largely available, renewable, biodegradable, biocompatible and its derivative has been widely used in textile (cotton, linen, viscose, and acetate). Cellulose is made up of poly (β ,1,4-D-anhydro glucopyranose) units. The reactivity of hydroxyl of hydroxyl groups at positions 2,3 and 6 of the glucosyl unit offer a variety of possibilities for making useful derivatives from this raw material. The derivative results in a wide range of chemical entities with a high variety of water solubility, porosity, mechanical strength and stability. This proceeds mainly through esterification and etherification reaction involving the hydroxyl groups.

Crosslinkers have the aptitude to enter in the crystalline region of cellulose fibers and connect cellulose inter chains. They also make a network in relation with the curing and drying condition which is a key element in textile development. They are able to link with a number of dynamic groups in the polymer such as hydroxyl group in cellulose. The obtained change in the amorphous and crystalline of cellulose fibers is a result of intermolecular and intermolecular hydrogen link. The goal of this paper is to review and describe the different crosslinking agents and reaction for cellulose. Traditionally, the functionalization reaction of cellulose are carried out using harmful solvents such as dimethyl sulphoxide (DMSO), formaldehyde, dimethyl formade(DMF), tetrahydrofurane, ethylamine etc. They are proved to be toxic and carcinogenic to humans.

For this reason, it is important to develop a series of alternative, less toxic and safer crosslinking agents. They include dialdehydes, epichlorohydrin, adipic anhydride and citric acid, which replace the traditional toxic and non-biodegradable crosslinking materials and at the same time render the expected functional properties.

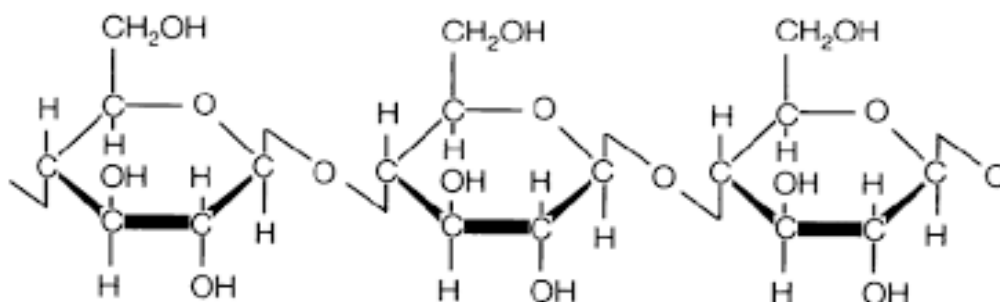


Fig 1: Schematic of a cellulose chain

2. DIALDEHYDES AS CROSSLINKING AGENTS

Traditionally, formaldehyde and dimethylol methyl carbamate (DMMC) dissolved in either phosphoric or sulfuric acid have been used as a model crosslinking agent for cellulose, rendering a product with excellent applications in the textile industry since the resulting fibers possess higher wrinkle recovery than the parent material⁸. Formaldehyde is absorbed in the cellulose fibers without the presence of catalyst because of the ease of formation of the hemiformal product. Recent efforts to develop formaldehyde-free agents have led to the use of less toxic dialdehydes such as glutaraldehyde and glyoxal, which can be used in materials which are not intended for human implants. In general, dialdehydes impart resilience, thermal stability and improve the mechanical properties of cellulose fibers. A major consequence of this crosslinking reaction is a reduction of the water absorption capacity of the crosslinked product compared to the parent cellulose. Briefly, cellulose is soaked in the dialdehyde solution at pHs between 3 and 5 in the presence of a catalyst, followed by curing, washing and drying. The curing step guarantees the absorption of the dialdehyde onto the structure of cellulose improving the crosslinking efficiency. However, if the curing step is not employed, the crosslinking efficiency is too low or negligible. It is well known that the dialdehyde reacts with the hydroxyl groups of cellulose to form an acetal under a catalyst of Lewis acid. The acetal formed is stable under neutral and alkaline conditions. the drawback of this reaction is the stability of these cellulose derivatives because the reaction of dialdehydes with the hydroxyl groups of cellulose forms acetals which in turn, have different degrees of hydrolysis rate. The reaction efficiency increases steadily as the concentration of dialdehyde increases and is favored by high curing temperatures, probably due to the more available aldehyde groups for crosslinking.

2.1 Glyoxal

Glyoxal does not offer a toxicity issue since it is endogenously produced during the normal cellular metabolism by a multitude of enzyme-independent pathways, and it is metabolized by the glyoxalases enzymatic group. The high concentrations of glyoxal, favors the acetylation of cellulose, which is reflected in a lower fiber strength and water sorption. A typical reaction condition comprises a soaking time from 5 to 15 min, a glyoxal concentration between 6 to 12%, a curing temperature between 50 and 140 °C, a curing time from 5 to 60 minutes and the presence of 1% boric acid (catalyst). Since the acetal formation is reversible, the presence of an acid catalyst is a prerequisite for the reaction. Glyoxal treatment without catalyst imparts temporary strength, because hemiacetal bonds can be replaced by hydrogen bonding when the cellulose derivative is soaked in water.

2.1 Glutaraldehyde

This material has been found appropriate to crosslink starch, dextran, chitosan, polyvinyl alcohol and cellulose¹⁷. Glutaraldehyde is present as a hydrate in water solution, improving the ability to crosslink cellulose. Acetals of glutaraldehyde and cellulose could have a high resistance to hydrolysis because of its cyclic structure. Glutaraldehyde could easily condensate or polymerize in aqueous solutions forming polyglutaraldehydes which can be acetylated and form products with high thermal stability. In the most common approach, cellulose is immersed in the glutaraldehyde solution between 3 and 16 hours and the curing time is varied between 2 and 6 minutes, at a temperature range from 80 to 150°C. The glutaraldehyde concentration is also important for the efficiency of crosslinking. Thus, only concentrations higher than 8% show the aldehyde peak in the FT-IR spectrum. The main concern is the final washing step to eliminate by-products and traces of glutaraldehyde in the cellulose particles. Glutaraldehyde has some reactivity towards cellulose, even if no catalyst is present. At the same reaction conditions, glutaraldehyde is much more efficient for acetylation than glyoxal rendering higher strength in the cellulose particles.

3. ACETALS

Acetals provide an interesting crosslinking approach, since the reactions do not go through the hemiacetal intermediate. Acetals, which react with cellulose, come from the dialdehyde that can form a five (tetrahydrofuran) or six membered (tetrahydropyran) rings, such as succinaldehyde and glutaraldehyde. The reactivity of acetals increases with the increased branching of the alkoxy group, but the increase is often hindered by the effect of solvents. However, the loss of cellulose fibers with crosslinking agents is greater for acetals than when conventional crosslinkers such as formaldehyde are used because even the most reactive acetals are less reactive than the more rigorous reactions with conventional agents. One of the most promising crosslinking acetals is the 2,5-dimethoxytetrahydrofuran. It is used with MgCl₂·6H₂O (2 - 5%) in 0.5% citric acid at pH of 5 and at a curing temperature from 100 to 160°C. Interestingly, highly reactive acetals come from reactive aldehydes that are themselves reactive with cellulose. Thus, the highest fiber durable press and cellulose elasticity is achieved with 1,1,4,4-tetramethoxybutane (derived from succinaldehyde) and 1,1,5,5-tetramethoxypentane (derived from glutaraldehyde). The reactive acetals require low curing temperatures to avoid cellulose degradation. In general, these acetals have a low

efficiency as crosslinkers compared to the conventional toxic crosslinking agents, such as dimethyloldihydroxyethyleneurea (DMDHEU) which is the typical crosslinker for cellulose employed commercially to improve the elasticity in cotton fibers. Thus, the crosslinked materials produced with 1,1,5,5-tetrametoxypentane are more sensitive to hydrolysis than the commercial crosslinked product with DMDHEU.

3. Polycarboxylic acids

Polycarboxylic acids esterify cellulose through the formation of a five member cyclic anhydride (reactive intermediate) by dehydration of the carboxylic groups bound to the adjacent carbons in the backbone of the molecule²¹. For this reason, polycarboxylic acids having their carboxyl groups linked to adjacent carbons of their molecular backbone are capable of forming a five member cyclic anhydride, being more effective for esterifying cellulose than those polycarboxylic acids having their carboxyl groups linked to their alternate carbons^{22, 23}. Zhou and collaborators (1995) reported that an effective crosslinking agent should possess three or more carboxyl groups bounded to the adjacent carbons of their molecular backbones and that the reaction mechanism involves the formation of a cyclic anhydride intermediate to form an ester²⁴. According to Yang and Wang (1997), the ester formation increases as the temperature increases from 110 to 200°C. The anhydride formation first increases and then starts to level off at 160°C once the product is formed. In the absence of catalyst, the ester formation is negligible. In addition, Yang and collaborators (2003) reported that the steric hindrance of the polycarboxylic acid on the other hand, reduces accessibility of cellulosic hydroxyl groups, reducing the amount of crosslinked product, but at the same time increasing the untreated anhydride intermediate on the cellulose particles.

4. Phosphoric acid (PA)

The reaction of PA and cellulose leads to swelling and crosslinking, producing a material with flame retardant properties as reported by Blanchard et al. (2000) (Figure 11). The typical process involves soaking the fibers in a 4% w/v PA followed by curing at 80°C for 10 min and a final drying step at 21°C for 24 h. The PA treated samples present a higher activation energy for decomposition and lower heat of combustion than the untreated cellulose³¹. This implies that a lower amount of heat is liberated during the actual combustion process due to the catalytic dehydration effect of PA. The flame retardant properties of fibers can be improved by using polycarboxylic acids and sodium hypophosphite as efficient catalysts. In this case, the mechanism involves the formation of a five member cyclic anhydride when the temperature reaches the vicinity of their melting point and the formation of anhydride which is accelerated when the temperature increases above their melting point.

5. EPICHLOROHYDRIN (EPC)

EPC reacts with cellulose through a formation of two ether bonds between two cellulose chains, usually between the hydroxyl groups at C3 and C6, as suggested by Ishimura and collaborators. The best crosslinking performance is achieved between 1 to 2 hours at 50°C at a CEL:NaOH:EPC molar ratio of 1:1.5:0.5-1. In general, the crosslinked product is more stable than the parent cellulose, which is reflected by the lower mass loss shown by the TGA³⁶. It is suggested that these crosslinked materials are able to absorb drugs in which the rate of absorption is pH-dependant.

6. SILICA DERIVATIVES

Recent attempts have been made to create organico-inorganic hybrid materials (OIHs) where cellulose and silica represent the organic and the inorganic components, respectively. The inorganic particles govern the properties of density, free volume and thermal stability, whereas hardness, brittleness and transparency depend on the organic host polymer. The properties of OIHs depend on the synthesis conditions, especially the mineral acid catalyst, which might damage the fragile polymer matrix during the aging and drying steps. Nonetheless, if the catalyst concentration is increased, the amount of amorphous material also increases. Thus, a high concentration of the catalyst might favor hydrolysis rather than condensation. An excess of water promotes the condensation reactions to form a gel. In the resulting material, silicon dioxide particles cover interruptedly the cellulose particles. The hydrophobic character of SiO₂ decreases the water retention capacity of cellulose, but at the same time improves the thermal stability. The cellulose-silicon dioxide modified nanoparticles using the environmentally friendly NMMO (N-methyl morpholine-N-oxide) as solvent, rendering a transparent material of high thermal stability. Interestingly, this material is more amorphous and has lower tensile strength, but higher elongation (more plasticization) than the original cellulose, due to the added amorphous silicon dioxide.

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