

Chemical Modification of Cellulose and its possible applications: A review

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Abstract:

Nature is the best the resource to use to achieve the goal of sustainable development for a safer world. In the current scenario the society is used to polymers to large extent in day to day life. To protect environment, it is essential to use environment benign polymers. Out of all available natural polymers cellulose have highest abundance in nature but due to some unfavourable properties such as low solubility, poor swellability, lack of thermoplasticity, high hydrophilicity and lack of antimicrobial properties cellulose needs modification. In this review article various chemical modifications of cellulose such as esterification, etherification, grafting, crosslinking are highlighted. There is considerable amount of property change of cellulose after different modifications. The applications of modified cellulose on various sectors such as drug carrier, lithium ion batteries, dye adsorption, metal ion absorption, removal of sulfates using modified cellulose have been discussed.

I. Introduction

In this 21st Century the demand of use of biodegradable polymer increasing day by day. As in daily life of society is surrounded with use of polymeric materials hence it is essential to use biodegradable polymers for sustainable development. Polysaccharides are the most abundant natural polymers on earth having notable structural variety and implausible biological functions and these are cheap in cost. It is the major constituent of all plants and many other organisms on earth. Due to intermolecular hydrogen bonding and glycosidic linkage cellulose have a large structure, the anhydro glucose units (AGUs) in cellulose joined to each other by covalent bond which form a large macromolecular chain. β -D-anhydro glucopyranose is the monomeric unit which forms the large macromolecular structure of cellulose [1]. Due to presence of hydroxyl group in cellulose there is extensive hydrogen bonding between the chains and within the chain. Cellulose is highly abundant, relatively low cost its properties can be modified penetratingly modified through substitution reaction of its hydroxyl group. Cellulose majorly used in textiles, plastics, paper, food and as a pharmaceutical additive. The reactivity of the hydroxyl groups at positions 2, 3 and 6 of the glucosyl units offers a vast possibility for its modification. The primary -OH group attached to C-6 is highly reactive compare to other -OH groups, the C-2 OH is the less reactive and the C-3 OH is the weakest for bending due to the formation of hydrogen bond with the neighbouring oxygen molecule [2]. Hence cellulose can be modified to increase its different physical properties such as water solubility, porosity, mechanical strength, swelling ability and stability. Due to some limitations of cellulose like lack of solubility, poor thermoplasticity, high hydrophobic nature and poor antimicrobial property [3]. To overcome such drawbacks, the controlled physical and chemical modification of the cellulose structure is necessary. Cellulose can be functionalized using different chemical methods such as esterification, etherification, crosslinking, grafting and cationization etc.

Different Chemical Modification methods of Cellulose

1. Acylation

Acylation is a method in which cellulose is modified by means of different acylating agents. Cellulose can be modified with p-nitro benzoyl chloride in a homogenous mixture of N-butylpyridinium chloride and dimethylsulfoxide (BPyCl/DMSO) in mild basic medium. In this chemical modification N,N-dimethylacetamide/lithium chloride (DMAc/LiCl), a mixture of dimethylsulfoxide (DMSO) and tetrabutylammonium fluoride trihydrate (TBAF .3H₂O) used as solvent. Ionic liquids such as 1-N-butyl-3-methylimidazolium chloride ([Bmim]Cl), and 1-allyl-3-methylimidazolium chloride ([Amim]Cl) can be used for acylation of cellulose. The esterification reaction was carried out in ionic liquid 1-butylpyridinium chloride (BPyCl) with cosolvent dimethylsulfoxide (DMSO) mixture in presence of bases such as triethylamine, pyridine, and 4-dimethylaminopyridine (DMAP). The reaction was carried out for 3 h to lower the degradation of cellulose due to

HCl. The HCl was captured in order to prevent the degradation of cellulose. Mostly nitro benzoylation reaction prefers C6-OH but esterification reaction at C2-OH and C3-OH also possible. On modification of cellulose with *p*-nitrobenzoylchloride there is decrease in crystallinity which accelerates cellulose decomposition [4].

2. Grafting

Cellulose grafting usually done by applying copolymerisation technique which based on mainly three approaches i.e. grafting to the cellulose, grafting from cellulose and grafting through the cellulose. In grafting to approach the backbone of the cellulose attached to end functional group of the polymer where as in grafting from cellulose modification the polymer chain makes growth from cellulose backbone. Monomers usually co-polymerised using grafting through method [6]. Cellulose modified by grafting technique have different physicochemical properties and functionality than pristine cellulose [5]. The grafting of cellulose carried away by various physical and chemical methods such as radical polymerisation, gamma radiation grafting, UV induced grafting, plasma grafting, cationic and anionic grafting etc.

Radical polymerisation:

Radical polymerisation is applicable in various monomers like methacrylate, acrylamides, styrene, butadiene, vinyl acetate and different water soluble monomers like acrylic acid, hydroxy acrylates etc. This type of polymerisation can be used for various functional groups such as OH, NR₂, COOH, CONR₂ etc. This process can be carried out under mild condition under wide range of temperature.

Radical polymerisation proceeds via three steps i.e. Chain initiation, chain propagation and chain termination. Some initiators are used for initiation process, propagation process carried out due to subsequent addition of monomers where as termination process carried out by chaintransfer, disproportionation and combination [6].

Gamma-Radiation grafting

γ -radiation grafting carried out by pre-irradiation and mutual irradiation method. In pre- irradiation method, introduction of monomer and swelling agents was done by irradiation. In irradiation method grafting was done by trapping radicals at the interphase between crystalline and amorphous regions. The grafting by using UV radiation causes less degradation of polymers especially for allylic and vinyl monomers [6].

Ultraviolet-radiation induced grafting.

In ultraviolet grafting cellulose is grafted with glycidyl methacrylate, 2-hydroxyethyl methacrylate etc, in the presence of photo initiators like uranyl nitrate in UV light. Different additives like ceric ammonium nitrate, poly methyl methacrylate were also grafted to cellulose using UV radiation [6].

Plasma grafting.

Plasma treatment has also been used for grafting of cellulose. The successful plasma graft copolymerisation of acrylamide and 2-hydroxyethyl methacrylate (HEMA) onto cellulose fibre has been reported [7,8,9, 10].

(a) Cationic graft polymerisation

Cationic grafting was done by grafting of isobutylene and a methyl styrene on to a cellulosic substrate. The graft polymerisation initiated reactive sites with isobutylene and a methyl styrene. The resulting grafted cellulose exhibited water resistance properties [10].

(b) Anionic graft polymerisation.

Anionic polymerisation of cellulose was done by grafting with acrylonitrile, methacrylonitrile and methyl methacrylate. The alkali metal alkoxides of the cellulose backbone were used as the initiator. This process is carried out at low temperature along with solvents like liquid NH₃ are used [10].

3. Cross Linking:

Crosslinking of cellulose can be done using various crosslinking agents such as dialdehydes, acetals, polycarboxylic acid, phosphorus derivatives, silica derivatives, epichlorohydrin and Polyepichlorohydrin. Crosslinking of cellulose can be done by using aldehydes like formaldehyde and dimethylol methyl carbamate (DMMC). Due to crosslinking there is increase in hydrophobicity of cellulose which decreases the water. The crosslinking with cellulose occurs in the amorphous region. Glutaraldehyde also used as a crosslinking agent for cellulose in the presence of Al₂(SO₄)₃ as catalyst. Glyoxal can also be used as crosslinking agent for cellulose and it also increases the strength of the cellulose. Polycarboxylic acid like polymaleic acid (PMA), itanoic acid (IA), polyitanoic acid (IA) used for crosslinking of cellulose. Due to crosslinking there is increase in flame resistance and elasticity in cellulose fibre. Phosphoric acids also used for crosslinking of cellulose and due to crosslinking there is increase in swelling as well as flame retardant properties of the modified cellulose. Cellulose phosphate also used for treatment of calcium related disease.

Epichlorohydrin is an excellent crosslinking agent and it is also used for crosslinking of various biopolymers. Epichlorohydrin enhances the swelling ability, porosity of the native cellulose. Cellulose crosslinked with silica have enhanced hydrophobic property due to which water retention of modified cellulose is less compare to native cellulose. SiO₂ enhances the thermal stability of modified cellulose [11, 12,13, 14].

4. Cationization

Cationization modification of cellulose improves different physical properties such as dyestuff, surfactant adsorption, increases cotton zeta potential etc. Due to this change in physical properties of modified cellulose increases the cotton absorption property. Cationization can be done by using reagents such as 3-epoxypropyltrimethylammonium chloride (EPTAC), 3- chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) and hydroxide ions. When anhydro glucose units (AGU) of cellulose undergoes esterification with chloroacetic acid then solubility of modified cellulose is enhanced. Due to increase in solubility of modified cellulose it can be used in food, cosmetics, thickener and emulsion stabilizer etc. Fabricated cationic starches used to prepare mats, carpets etc. which can be reused as they are intrinsically fabricated [15,16].

5. Etherification

Etherification of cellulose can be done by using ethers and esters, which results in formation of cellulose acetate (CA) and methylcellulose (MC). Etherification of cellulose has been done by using protecting group like trityl chloride using DMAc/LiCl as solvent. Hydroxyethyl and hydroxypropyl derivatives of trityl cellulose were heterogeneously synthesized in a mixture of isopropanol and water. Tritylation can also be performed by using ionic liquids such as -butyl- 3-methylimidazolium chloride ([Bmim]Cl) and 1-allyl-3-methylimidazolium chloride ([Amim]Cl) [17].

6. Esterification

Esterification of cellulose can be done by using various acylating agents such as pivaloyl chloride, adamantoyl chloride and 2,4,6-trimethyl benzoyl chloride using solvents like DMAc/LiCl, DMSO/TBAF, [Amim]Cl at the lowest reaction temperature. Sulfonic acid such as methyl sulfonate and benzene sulfonate derivatives used for crosslinking of cellulose. p- toluenesulfonyl chloride (p-TsCl) also used as esterifying agent for esters of cellulose [17].

Applications of modified cellulose

(a) Drug Carrier

Modified cellulose can be used as conceivable drug carrier. Grafted polymer contains different functional groups, cross linkers in the cellulose graft copolymer matrix. Cellulose graft polymers have hydrophobicity which helps interaction with drug and it involves different weaker forces such as van der Waals forces, electrostatic force etc. Chemical interactions involve chemisorption and reversible chemical reactions between the functional groups of the drugs and carrier molecules. Cellulose hydrogels are prepared by using Sodium CMC and epichlorohydrin as crosslinking agent and have great efficiency to act as super adsorbent. Hydrophilic carriers show a faster rate of drug release as compared to a hydrophobic carrier. So modified cellulose can be used as potent drug carrier in future [8].

(b) Lithium ion batteries

Grafted cellulose materials can be potentially used in various fields like binders for high capacity anodic electrodes like Si in which discharge potential is low and charge capacity is high. Grafted celluloses can be used as separators between anode and cathode of Li ion batteries[8].

(c) Dye adsorption

Dye accumulation in the water bodies is the major concern for water bodies as well as aqua life. To overcome this problem use of natural polymer in the modified form as a better adsorbent. As natural polymers are nontoxic, biodegradable and recyclable so use of natural polymer will be beneficial for environment. Modified cellulose have higher adsorption capacity than raw cellulose due to presence of different functional groups such as -NH₂, -OH group in the modified form. Grafted cellulose has porosity property which enhances their adsorption property. Oxidising cellulose have aldehydic functional group which acts as active sites for chemisorption of dyes. When anionic functional groups such as carboxylate (-COO⁻) and sulfonates (-SO₃⁻) are attached to cellulose then adsorption of cationic dyes. Modified cellulose adsorbs cationic dyes at high pH where as anionic dyes are adsorbed at low pH [8, 18].

(d) Metal ion sorption

Metal ion adsorption a major role can be played by modified celluloses. Different industries such as electrochemical, leather, chemical, paint and dyeing industries releases heavy metals such as Co^{2+} , Co^{3+} , Zn^{2+} , Mn^{2+} , As^{3+} , Mo^{2+} , V^{3+} , Cr^{6+} , Al^{3+} , Sb^{3+} etc. to water bodies which affects the aqua life. Modified grafted cellulose has different force of attraction which plays an important role regarding adsorption of metal ions. Physical attractive forces like hydrogen bonding, Vander Waals force, steric interaction and dipole induced dipole interaction plays vital role for adsorption of metal ions. Anionic pollutants like CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, MnO_4^- , PO_4^{3-} , $\text{S}_2\text{O}_3^{2-}$, AsO_4^{2-} , and AsO_2^- are adsorbed by protonated amine groups. Grafted cellulose fabrics exhibited 99% antimicrobial activity against *Escherichia coli* and *Staphylococcus aureus* bacteria [8, 19, 20].

(e) Removal of sulfates

Water pollution one of the reason for various disease in living organisms. Sulphur pollution affects water bodies in a greater extent as sulphate ions are corrosive in nature it also causes the material degradation. Chemically modified cationized cellulose nanofibers (c-CNF) acts as a good adsorbent for sulphates. The use cationized cellulose nanofibers considered as an inexpensive method for sulphur removal from water bodies. As enough number of active sites are available in c-CNF hence the adsorption of sulphur becomes easier. At lower pH value adsorption of sulphate ions becomes easier as they form corresponding bisulphate ions (HSO_4^-) [21].

II. Conclusion:

From the above review it can be clearly concluded that modified cellulose overcomes the drawbacks of pristine cellulose to a greater extent by different chemical modifications. The chemically modified cellulose can have various potential applications in different fields related to everyday life. The modified cellulose have potential to replace traditionally used synthetic polymers which are detrimental to environment. The esterified, etherified, crosslinked, cationized, grafted cellulose have wide applications starting from drug delivery to different cation and anion adsorption. The future of polymer is with biodegradable polymers such as cellulose, starch, lignin etc. out which cellulose will be the key as it is most abundant among all biodegradable polymers. More and more research must be carried out to used modified cellulose a potential material to replace synthetic materials.

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