



Review

Chitosan functionalized poly(vinyl alcohol) for prospects biomedical and industrial applications: A review



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ABSTRACT

Chitin and chitosan are amino polysaccharides having multidimensional properties, such as biocompatibility, biodegradability, antibacterial properties and non-toxicity, muco-adhesivity, adsorption properties, etc., and thus they can be widely used in variety of areas. Although human history mainly relies on the biopolymers, however synthetic materials like polyvinyl alcohol (PVA) have good mechanical, chemical and physical properties. Functionalization of PVA with chitin and chitosan is considered very appropriate for the development of well-designed biomaterials such as biodegradable films, for membrane separation, for tissue engineering, for food packaging, for wound healing and dressing, hydro gels formation, gels formation, etc. Considering versatile properties of the chitin and chitosan, and wide industrial and biomedical applications of PVA, this review sheds a light on chitin and chitosan based PVA materials with their potential applications especially focusing the bio-medical field. All the technical scientific issues have been addressed highlighting the recent advancement.

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Abbreviation: AFS, applied field strength; CS, Chitosan; CH, Chitin; DSC, Differential Scanning Calorimetry; DMEM, Dulbecco's modified Eagle's medium; FBS, fetal bovine serum; FE-SEM, Field Emission Scanning Electron Microscopy; FTIR, Fourier Transform Infrared Spectroscopy; GTR, guided tissue regeneration membrane; HPN, hybrid polymer network; HRP, horseradish peroxidase; PET, poly(ethylene terephthalate); PVA, poly vinyl alcohol; PVC, poly vinyl chloride; NMR, Nuclear Magnetic Resonance Spectroscopy; QCh, quaternized chitosan; $(n_e)_{soln}$, solution entanglement number; TEOS, tetraethylorthosilicate; TS, tensile strength; Tm, transition melting; Tg, Glass Transition Temperature; UV-Vis, ultra violet-visible; WAC, Water absorption capacity; XRD, X-ray diffraction.

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1. Introduction

On the basis of origin three main classes of polymers, synthetic, natural and semi synthetic are known [1]. Mostly polysaccharides occurring in nature are acidic like cellulose, dextrin, pectin, alginic acid, agar, agarose and carragenas while chitin and chitosan are basic polysaccharides. Many investigations have been made since 1990 on chitin and chitosan as these two polymers exhibit large number of excellent biological properties in human body [2,3] and immunology [4,5]. Chitin which is a natural polysaccharide was first identified in 1884. It is hard, inelastic and nitrogenous polysaccharide. Different living organisms are used for the manufacturing of this biopolymer [6,7]. It is second most abundant naturally occurring homopolymer after cellulose [8–10]. On the basis of product origin, chitin is insoluble in water, dilute acids and alcohol. Although chitin is not found in cellulose producing organisms yet it is considered as derivative of cellulose and its annual amount is estimated as much as cellulose. The progress in chemistry of chitin is significant as it has become interested as a functional biomaterial with high potential. On transformation of chitin into chitosan there will be more applications of chitin [11–13]. Chitosan is polysaccharide formed as a result of deacetylation of chitin [14,15] is also known as soluble chitin. Chitosan is soluble in some aqueous acidic solution and also in some selective *N*-alkylidination [16–18]. Chitosan is less present in living organisms and observed only in some microorganisms [19]. Other names used for term chitosan include poliglusam, deacetylchitin and poly-*D*-glucosamine. Due to inter and intra-molecular hydrogen bonding, chitosan has rigid crystalline structure. Both chitin and chitosan are renewable polymers. The reaction of chitosan as compared to cellulose is more versatile due to presence of NH_2 groups in chitosan.

1.1. Sources of chitin and chitosan

The most abundant source of chitin is marine invertebrate, insect, fungi etc. [20]. Chitin is basically naturally occurring carbohydrate polymer, found in crustacean skeleton, e.g., crab, shrimp and lobster [21–23] and also in the exoskeleton of marine zooplankton species including coral and jellyfishes [24]. Insects have chitin in their wings like butterflies and lady bugs and also in cell wall of mushroom, fungi and yeast [25–30]. It is found frequently in plants as cell wall material and also in animal cuticle. Although some fungi contain chitosan [31], it is however obtained by deacetylation process of chitin [32]. The isolation of chitin from different sources may be affected by percentage amount of chitin [33,34]. In the world wide, the Nigeria has highly available sources of chitin [35,36].

1.2. Extraction and purification of chitin and chitosan:

According to Gopalakannan et al. [37] two crustacean species shrimp and squilla shell are widely employed for the extraction of chitin by chemical method. The chitin is converted into soluble useful chitin known as chitosan [38]. It would be profitable to recover the by-products of seafood processing, from technological point of view as they are rich in compounds of high value like chitin

products. The literature has reported that both chitin and chitosan are extracted from *Parapenaeus longirostris* and *Squilla mantis* as by-products. As a result various products of chitin and chitosan having high antibacterial activities could be generated. For optimum recovery both acid and alkali treatments are required. Dried shell wastes are washed by using tap water and deproteinized using NaOH for the removal of residual protein from the shell. Then demineralization is done using HCl. The sample is collected, washed and dried. After that deacetylation by NaOH solution is carried out for obtaining chitosan at about 90–90 °C for 2 h. Chitosan could be soluble in solution of acetic acid but chitin not. The final yield product are of white color and water insoluble (Fig. 1a).

The obtained chitosan was purified to make it suitable for different uses. Three steps were involved in purification process, (1) removal of insoluble with filtration, (2) re-precipitation of chitosan with NaOH solution, (3) demetallization of chitosan [39].

1.3. Characterization of chitin and chitosan

Both chitin and chitosan can be characterized by biological activity as both exhibit antifungal and antimicrobial properties. This characterization has resulted in their applications in the commercial disinfectants [40–44]. Antifungal activity of chitosan is higher but against fungi it is less effective. Chitin is found in two states α -chitin where chains are anti-parallel and β -chitin with parallel chains [45]. Different methods like x-ray diffraction [46–49], IR spectroscopy [50–56] and NMR [57–60] were used for the study of their crystalline structures. When the degree of deacetylation (DA) is lower than 0.5 the chitosan becomes soluble in aqueous acidic medium. The first step involved in chitosan characterization is to determine the molecular weight, degree of deacetylation and the distribution of acetyl group along the chain [61,62]. Against a number of gram positive and gram negative bacteria, chitosan exhibits antimicrobial activity [63,64].

1.4. Chemistry and properties of chitin and chitosan

Structure of chitin is shown in Fig. 1(b) is composed of *N*-acetyl glucosamine repeating units [65] that are joined together by a β -(1–4)-linkage. These repeating units combine to form long chains of chitin. Another structure shown in Fig. 1(b) is of cellulose. Cellulose is naturally occurring polysaccharide. Cellulose molecules consist of at least 500 molecules of glucose. These glucose chains joined together in parallel manner to form micro fibrils of cellulose in which hydrogen bonds exist.

Chitosan is obtained as a result of alkaline deacetylation of homopolymer chitin (1 → 4) linked 2-amino-2-deoxy- β -*D*-glucan. Hence chitosan is a copolymer composed of *N*-acetyl glucosamine and is shown in Fig. 1(b) [66–68]. In sugar backbone there is β -1,4-linked glucosamine along with high degree of *N*-acetylation. This structure is almost similar to cellulose, only difference is in replacement of acetyl amino group to hydroxyl group on C-2 position. We can thus say chitosan is poly *N*-acetyl-2-amino-2-deoxy-*D*-glucopyranose. These units are linked together by (1 → 4)- β -glycosidic bonds [69,70].

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