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Advances in Chitosan Grafted Copolymer and Their Applications

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Abstract: The effect of grafting on the chemical and physical properties of chitosan has been reviewed in the light their different applications i.e. biomedical, biosensor, water purification and packaging. The grafting methods and condition are discussed along with their comparative advantages and disadvantages. Further, the suitability of chitosan grafted copolymer in sensing, drug delivery, dyes removal and packaging has been described with suitable examples and illustrations.

Keywords: Chitosan, Grafting, Properties and applications.

I. Introduction

Grafting is a versatile polymer modification technique to design and develop the several chitosan (CHIT) based polymeric assembly and nanostructure like micelle, hydrogel, dendrimers, nano particle and nano roods with several advanced features like responsiveness, strength, surface area, florescence and antimicrobial properties [1, 2]. These composite properties CHIT has been made it suitable for several application in biomedical, sensing, packaging and water purification with effective parameters [3]. Although, the grafting is an very popular practice by chemists to modify the different polymer afterlinking the chain of two monomers with objective to manipulate the chemical compositions. However, the current innovation towards chemical engineering with size, shape and dimension confinements after using different templates advance grafting for making several advanced materials with functionality and other features for use in different applications [4]. These advantageous features in grafted chitosan hybrid structure have been reported as a potential material to advances several industrial and biomedical devices with improved parameters. The importance of materials has been also supported by increase trend in publications by chemist, physicist, and engineers, but a comprehensive review on this topic essentially requirement for a new researcher. In the objective present review article discuss the current progress and potential in chitosan grafted hybrid structure along with significant potential applications. The illustration and schemes are also incorporated the make the materials interesting and effective on the basis of reported literature.

II. Overview to Chitosan

CHIT is deacetylated derivative of chitin, present in cell wall of fungi and exoskeleton arthropods, crustacean and molluscs. The degree of deacetylation yields different grade of CHIT with different properties. The basic strategy to convert chitin to chitosan is shown in Fig. 1.

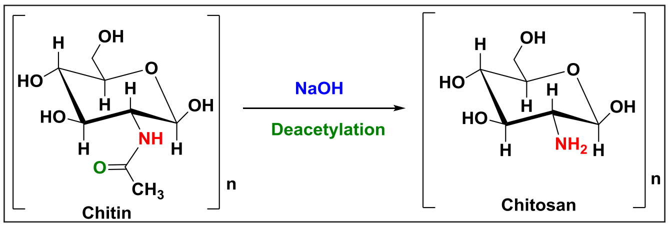

Fig. 1: Transformation of Chitin to Chitosan

The degree of deacetylation controls the several properties of CHIT like film forming ability, surface tension, viscosity tensile strength and barrier properties. Zhao *et al.* has reported that 95.2% degree of deacetylation in CHIT exhibit superior barrier properties than 85% along with anti-bacterial properties against E-coli for packaging application of fruits and vegetables [5]. Another variation in CHIT is structure, size and dimensions for manipulation of chemical and physical properties. In example the reduction in size of CHIT after milling in a ball mill yield CHIT is size of 250-600 nm having charged crystallinity and rheological properties for different application. Thus, manipulation in size has yielded several nano structured CHIT like particle, rod, fibre and tubes for several advanced properties and applications [6, 7]. Although, several properties are manipulated by above mentioned processes but chemical behaviours is still need to be modify and in this context grafting and composite formation are utmost suitable stages. In these chemical modification processes the grafting is the most appropriate to modify CHIT at molecular level with several advantageous features like flexibility, reactivity, conductivity and strength [8].

III. Grafting

In general grafting is a method to develop copolymer consists of main chain of a single monomer, while branched chain are from other polymer segments. The arrangement of both chain main and grafted chains have evolves several unique features in grafted copolymers in the term of shape, solubility, stability and strength. A simple illustration of a graft polymer is shown in Fig. 2, consists of main chain from monomer M_1 and grafted chain from M_2.

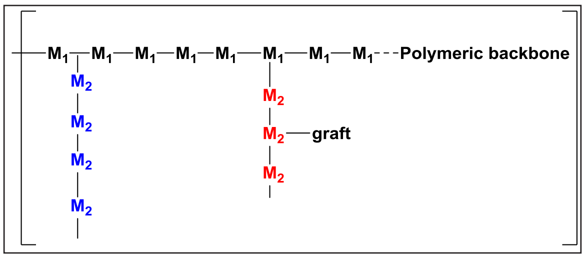

Fig. 2: Illustrative Structure of Representative Grafted Copolymer

This addition of different monomer in CHIT advances its several properties in example CHIT is electrically insulating polymer but its grafting with chain of polyaniline make it conducting along with responsiveness nature to be used in chemical sensing of hydronium ions present in solution or developed in-situ with time [9]. The basic mechanism of grafting is in-situ polymerisation, which is basically the polymerisation of monomer like aniline in the presence of CHIT using suitable solvent and polymerising agent like ammonium persulphate and coper sulphate. In mechanism initially, the aniline starts polymerisation due to the polymerising agent. However, after increasing its length the viscosity decreases and further addition of polymerising agent oxidises CHIT into its macro ion. Further, the both macro ions combines and produces chitosan grafted polyaniline (CHIT-g-PANI) with optimised properties [10]. The scheme of grafting is presented in Fig. 3 along with conditions.

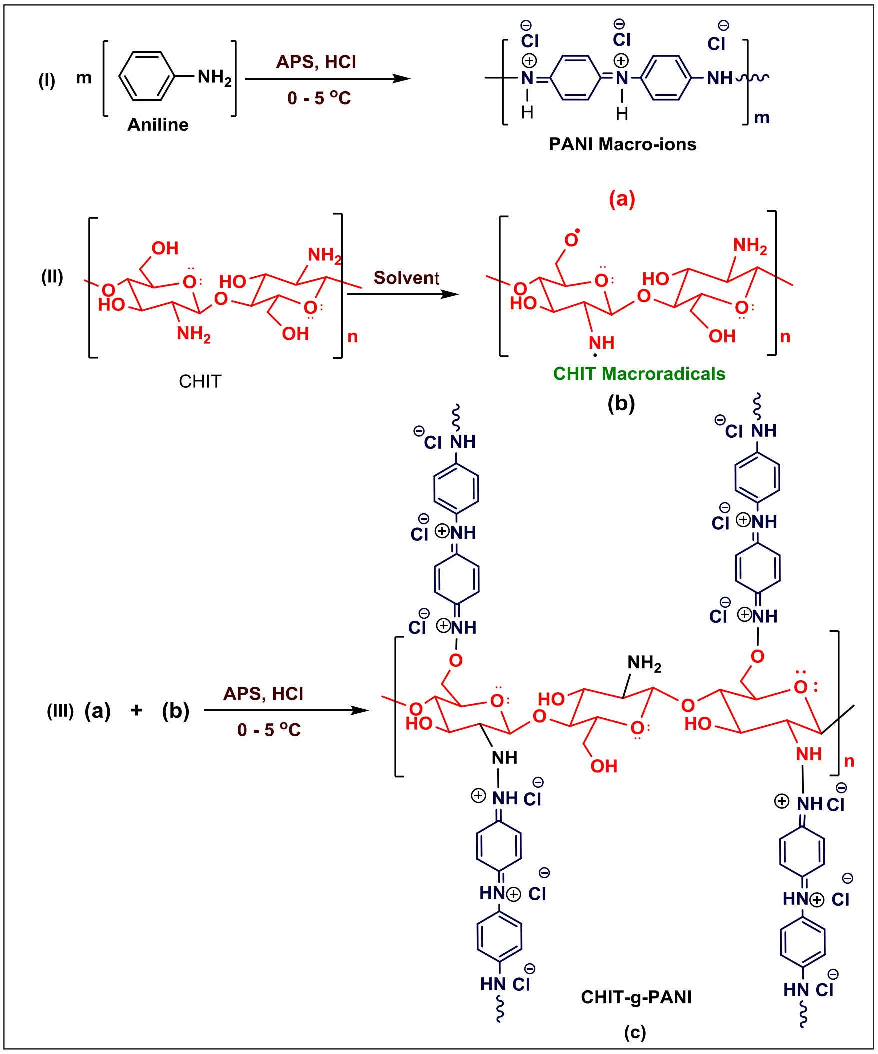

Fig. 3: Grafting Mechanism between CHIT and Polyaniline

Further in polymerisation free radical, ionic and redox mechanism are used with their inherited limitation and advantages along with steps of activations [11].

IV. Applications

The multi components synergised and chemically engineered grafted chitosan exhibits several advantageous surface and bulk properties for use in wide range applications. The illustrations of properties influenced application of g-CHIT are depicted under following sections:

A. Biomedical

Inherited biocompatibility and multifunctionality in CHIT are significant reason for use in different biomedical applications like tissue engineering, organ transplant, drug delivery and biosensing. Further, the properties are further improved by grafting in term of physical properties like electrical conductivity and mechanical strength. In an example the grafting of CHIT with polypyrrole yields micellar structure with electrical conductance and adherability for enzymes like urease [12]. Thus developed nano micelles have been used for effective sensing of urea with excellent parameters. The sensing scheme and synthetic steps are shown in Fig. 4.

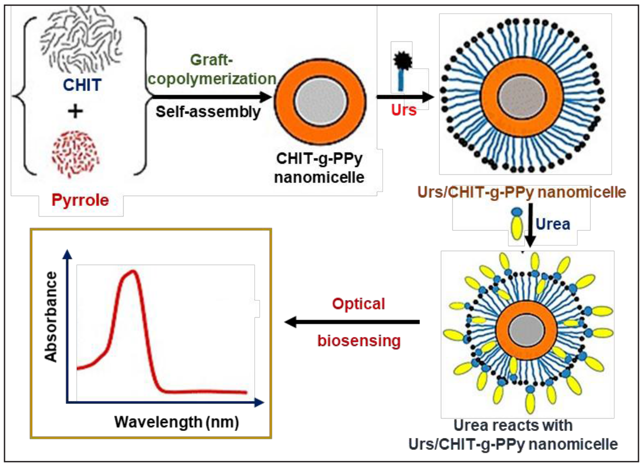

Fig. 4: Opto-Chemical Urea Sensing over CHIT Grafted Polypyrrole Micelle

The structural rearrangement during grafting also develops charge, functionality and responsiveness in hybrid polymer matrix to use as scaffold for tissue engineering and injectable vehicle for drug delivery. Nisar *et al.* prepared the glutamic acid grafted CHIT hydrogel after irradiation of γ-rays under optimised condition and doses. The obtained hydrogel exhibits porous and responsive hydrogel for use as effective delivery of anti-cancer drug i.e. Doxorubicin with potential to use for localised therapy [13]. Some other significant application of g-CHIT in biomedical are listed in Table I.

Table I: Applications of g-CHIT into Bio-Medicals

Sr. No.	*Composition*	*Properties*	*Application*	*Ref.*
1	Protocatechuic acid grafted carboxymethyl chitosan	pH sensitive and antioxidants	Protective towards oxidative damage	[14]
2	Polypyrrole, chitosanand collagen	Improved cell adhesion and electrical conductance	Scaffold for cardiovascular tissues	[15]
3	Polycaprolactone and Chitosan	Increases the cell growth and proliferation without any toxicity	Liver cell	[16]
4	Carboxymethyl β-cyclodextrin grafted carboxymethyl chitosan	pH sensitive	Release of insulin	[17]
5	Cyclodextrin-grafted chitosan	Antibacterial activity towards different strains	Controlled release of silver sulfadiazine	[18]
6	Chitosan-*graft*-Poly (l-lactide)	Enhanced mechanical stability and bioactivity	Bone tissue engineering	[19]
7	ZnO encapsulated polyaniline grafted chitosan	Improved electrical conductivity, chemical stability and self activating in nature	Urea sensing	[20]
8	Chitosan grafted amino acids	Cell adhesion and re epithelization	Wound dressing	[21]
9	Chitosan-grafted graphene oxide/magnetic nanoparticle	pH sensitive and drug release	Theranostic applications	[22]

B. Water Purification

The g-CHIT has been also used as adsorbents and photocatalysts for purification of water from different pollutants like heavy metals, dyes and organic molecules. The basic properties of adsorbent are high surface area, porosity and tuneable adsorption energy. The grafting with other polymers in the presence of metallic components also develop catalytic properties to remove organic dyes after catalytic degradation [23]. In example, Darzi *et al.* has prepared PAMAM grafted CHIT hybrid-based adsorbents with high surface area for batch purification. The prepared adsorbent are used for adsorptive removal of Congo Red and Amido Black 10B with removal capacity of 489.8 mg/g at optimum conditions [24]. Similarly, a ternary grafted chitosan composite consist of titanium dioxide, CHIT and hydroxyapatite has been prepared by coprecipitation technique. The composite exhibits improved surface area, catalytic activity, stability and porosity for improved degradation efficiency of organic dyes i.e. Methylene Blue and Rhodamine. The improvement in catalytic activity is due to reduction in band gap from 3.23 eV of TiO_2 to 2.01 eV in grafted composite due effect of grafting [25]. The degradation mechanism and the effect of composite in dyes removal are shown in Fig. 5.

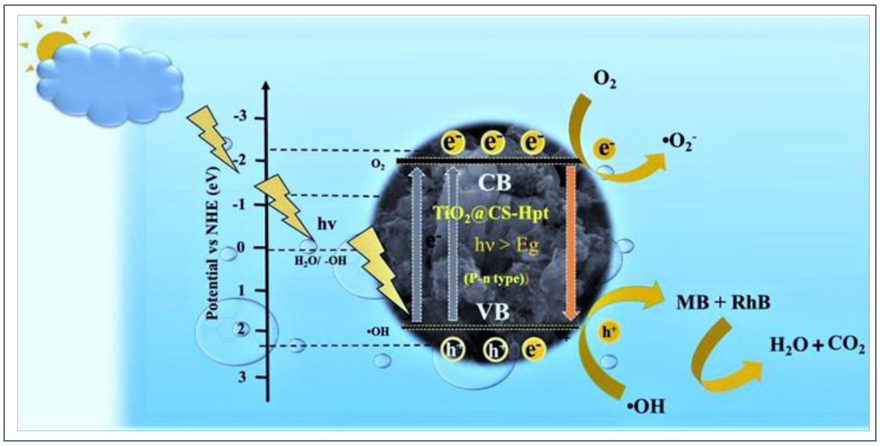

Fig. 5: Photocatalytic Mechanism for Degradation of MB over Grafted CHIT, TiO_2 and Hydroxyapatite Composites

Some other good examples of water purification using g-CHIT are shown in Table II along with basic properties and composite.

Table II: Adsorbent Water Purification over Grafted Chitosan

Sr. No.	*Adsorbent*	*Properties*	*Pollutants*	*Ref.*
1	CHIT grated EDTA	Coordinating electrostatic interaction	Co and Sr	[26]
2	Dopamine, CHIT and lactic acid	High surface area and adsorption capacity	Copper	[27]
3	CHIT grafted carboxylic acid	Electrostatic interaction and hydrogen bonding	Sulfanilamide	[28]
4	Thiourea and CHIT	Renewable sorption properties with high adsorption capacity	Metal ions i.e. Cd, Cu, Co and Ni	[29]
5	Iron oxide, CHIT and PANI	Catalytic ability	Paracetamol	[30]
6	Gallic Acid-Grafted Chitosan and Polysulfide	Optimised size exclusion	Congo red	[24]
7	Poly (1-vinylimidazole) and chitosan	pH effective sorbent	Cadmium	[31]
8	Chitosan and PEI	High adsorption based magnetic separation	Cadmium	[32]
9	Chitosan and glyoxal	Magnetically active adsorbent	Organic dye	[33]

C. Packaging

The negative environmental effect of non-biodegradable packaging materials have compelled scientist and technologist to design biodegradable packaging materials. In this reference the optimised properties of g-CHIT have widely explored in both active and passive packaging materials as well as edible coating. The basic steps to develop packaging material after manipulating the mechanical strength, gas barrier and functionality. The use of different plasticise lie glycerol, xylitol, and sorbitol were used to develop plasticity in chitosan for processing of g-CHIT into film, coating and sheets [34]. The used constituents during grafting of CHIT has their own impact on the packaging film. In an example the grafting of gallic acid to CHIT develop intrinsic antioxidant property along with optimum H_2O and CO_2 transmission ratesfor packaging. Thus developed gallic acid grafted chitosan found suitable for packaging of mushroom as active packaging for extended shelf life with suitable strength [35]. Zhang *et al.* has developed cellulose fibre grafted CHIT containing curcumin by an innovative method. The film exhibits excellent antibacterial properties along with UV shielding and synergised mechanical strength and water barrier for active packaging. The basic scheme for preparation of composite and properties are shown in Fig. 6 [36].

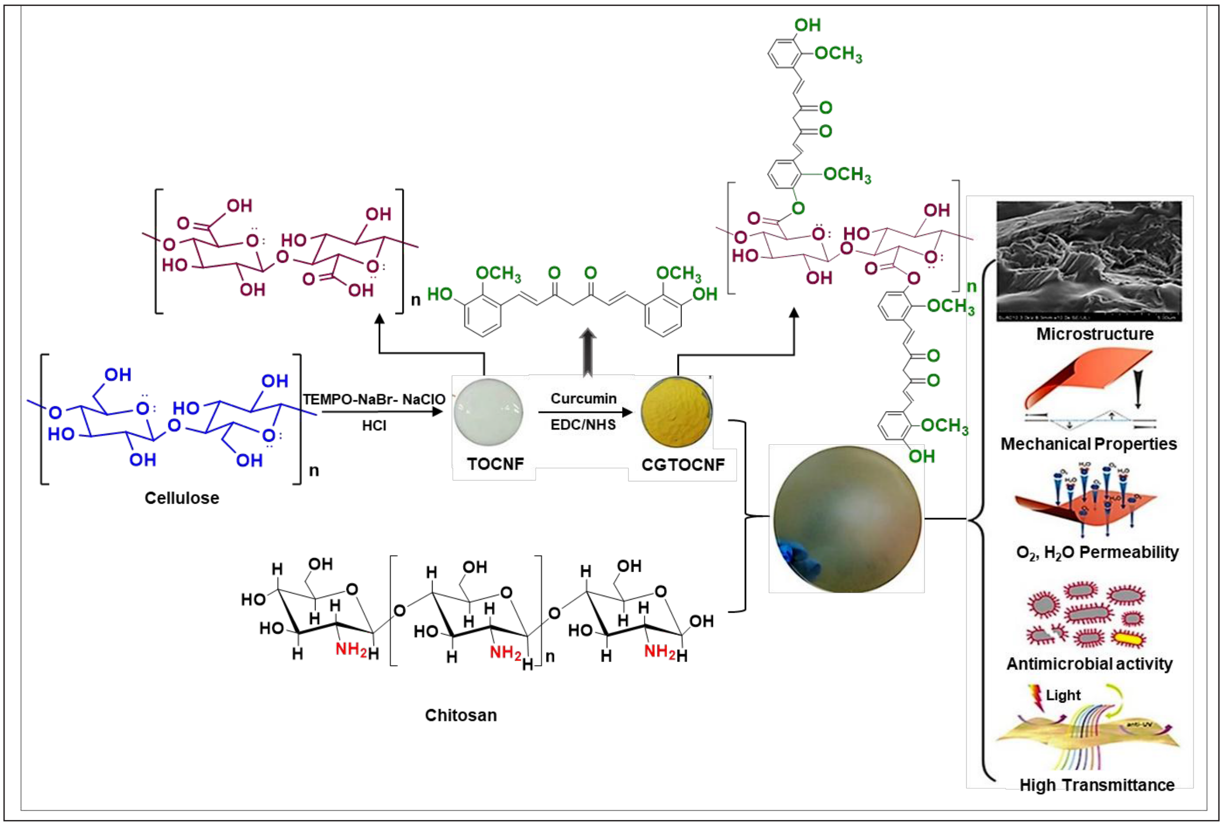

Fig. 6: The Scheme of Development of Cellulose Grafted Chit along with Properties [36]

Some other advanced application of g-CHIT in packaging of different perishable and non-perishable items are listed in the Table III, along with brief properties.

Table III: Application of g-CHIT into Packaging

Sr. No.	*Composition*	*Properties*	*Applications*	*Ref.*
1	Gallate grafted CHIT	High tensile strength and elongation at break	Packaging with extended shelf life	[37]
2	CHIT and polyethylene glycol methyl ether methacrylate	Antioxidant and antimicrobial properties	Active food packaging	[38]
3	Catechol, CHIT and gelatine	Antibacterial activities against *S. aureus* and *E. coli*	Food packaging	[39]
4	CHIT and poly (dimethylsiloxane)	Water and oil resistant	Kraft paper	[40]
5	CHIT and gelatine	Best thermal and water stability	Active food packaging	[41]
6	Cellulose and CHIT	Plastic behaviour	Food packaging	[42]
7	Cellulose grafted with chitosan	Antimicrobial	Sanitary products	[43]
8	Gelatin and chitosan	Improved tensile strength	Food packaging	[44]
9	Styrylquinoxalin-*grafted*-chitosan	Good mechanical and antibacterial properties	Food packaging	[45]

V. Conclusion

The importance g-CHIT based hybrid materials are described in term of their use in biomedical, water purification and packaging applications. The chemical scheme involved in grafting are described along with their minute condition and developed properties with suitable illustrations.

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