Review on the Applications of Modified Chitosan as an Alternative Novel Materials for Chemical Technology

SANI NAZIFI DALHATU[1], SULEIMAN YUSUF SULE[2], AMINU DABO SHUAIBU[3], RIDWANU MURTALA[4]

[1, 2, 3, 4]*Department of Chemistry Aliko Dangote University of Science and Technology Wudil*

Abstract- ***The paper reviewed the applications of modified chitosan as alternative materials in chemical technology. It starts with an introduction to chitosan and the importance of modifications then discusses the different types of modified chitosan materials. The main body focuses on the diverse applications of these modified chitosan materials, such as water treatment, catalysis, drug delivery, and other emerging uses. The conclusion summarizes the key points and highlights future research directions.***

Indexed Terms- ***Chitin, Chitosan, Chitosan Derivatives, Chemical Technology, Novel materials***

I. INTRODUCTION

Polymer modification itself is another research area in which different properties can be added to the polymer to enhance its performance and expand its application. Many researchers reported the use of Chitosan for various applications such as corrosion inhibition[1], drug delivery [2], water purification [3], and many more. Chitosan modification is now a subject of interest for polymer chemist as it is easy, cheap, and safe. Polymer modification can be carried out in many ways such as composite formation, crosslinking, functionalization, and blending. The paper reviewed the applications of chitosan and its modified form in various chemical technologies.

1.1 Source of chitosan

Chitin is a natural linear cationic polysaccharide consisting of β-(1,4) linked N-acetyl-D-glucosamine [4]. A heteropolysaccharide comprising β-1,4-linked D-glucosamine and N-acetyl-D-glucosamine makes up chitosan, which is produced by deacetylating chitin using a strong NaOH solution (Figure 1). The amount of acetamide groups present, represented by the degree of acetamidation (DA), distinguishes chitin from chitosan. If the percentage is greater than 50%, chitin is identified, and if it is less than 50%, chitosan [5]. The percentage of deacetylation, which represents the proportion of acetyl groups extracted from chitin during the chitosan manufacturing process, is frequently favored when discussing chitosan. [6], [7]. Some describe the two (chitin or chitosan) base on their solubility in acetic acid solution [8]. The polymer in question is mainly found in insects, fungus, diatoms, and marine life. α, β, and γ (parallel, antiparallels, or a combination of both) constitute the three different polymorphic forms of chitin that assemble in these species [9]. It was discovered that where they originate determines the form of the chains, with α-chitin being the most prevalent form. Contrary to chitin, chitosan is rarely found in nature.

Strong chemical treatments, such as deproteinization with hot alkali (NaOH 1 N, at 60-100 °C for several hours) and demineralization with acid (HCl 0.3-2 N, at about 100 °C for one or two days) to remove calcium carbonate and discoloration, are necessary for the extraction of chitin (Figure 1) from fishery wastes (carapace of crustaceans and shellfish). In order to prevent a drastic drop in the polymer's molecular weight, the deacetylation step is rarely finished. In general, using high temperatures increases reaction rates and yields [10]. The concentration of strong bases, temperature, and the time frame of the deacetylation process represent a few of the variables that often affect the degree of deacetylation. Ultrasound and microwave technologies were also suggested as ways to improve the extraction and deacetylation processes[11]. Additionally, biological treatments provide an

alternative to such harsh chemical reactions: proteins can be removed using lactic acid bacteria and bacterial protease, and enzymes are also an option for deacetylation[12].

To further purify the product, it is use to dried and then redissolved in an organic acid solution. The resulting chitosan takes the shape of an amorphous solid. Its molecular weight can exceed 3 × 106 Da, however it is usually composed of 100–1000 kDa molecules with tiny numbers of smaller molecules (10–50 kDa). Its DD is typically larger than 70% (between 70% and 80% in average). The mean molecular weight and polydispersity of chitosan preparations differ significantly amongst them [13]

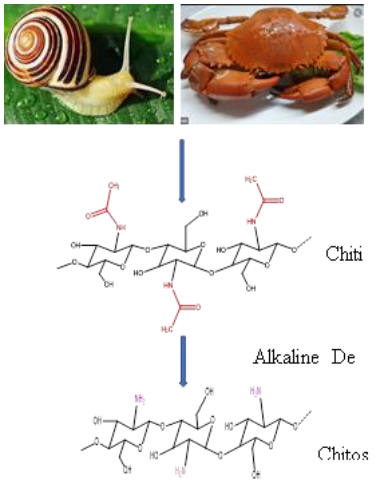

Figure 1: Extraction of Chitosan from Chitin

1.2 Chitosan derivatives

Many researchers suggested that the properties of particular polymer could be improved by modifying its molecular structure. This modification can be achieved through various methods which include a composite with nanomaterial [14], introducing various functional groups on chitosan structure [5] and modification of chitosan backbone by grafting with other polymers [7], [15].

Due to the desirable properties such as biodegradable, non-toxic, abundant in nature and being able to form membrane, fiber, gel and microspheres, Chitosan is utilized in a wide range of applications including water purification [15], drug delivery [16], medicine and cosmetics [17] and food preservatives (Jianglian, 2013). In particular, chitosan is considered as a good corrosion inhibitor for metal but its poor solubility in some acidic media limits the application of chitosan as corrosion inhibitor[19].

For certain applications, the chitosan backbone can be altered to increase desirable characteristics and stability. The active sites for chitosan alteration are its-NH_2 and -OH groups. The most popular methods for modifying chitosan are curing, mixing, cross-linking, graft co-polymerization, and composites with other materials. Blending is the process of simply combining two or more polymers [20]. Graft co-polymerization entails the covalent linking of polymers, whereas curing uses thermal, electrochemical, or UV processing techniques to create three-dimensional linkages inside the polymer mass, turning the polymers into a solidified mass [21]. Blending, which is physically mixing two or more polymers, produces physical alteration. It is among the simplest and most traditional methods of changing polymers. Depending on the ratios of the polymers being combined, the blend's quality and performance can change. The most cost-effective method for customizing the characteristics of polymers for a given use is blending [22]. Changes to a compound's functional groups are accomplished through chemical modification, which can be performed in a number of ways, such as chemical, photochemical, radiation, pharmaceutics plasma-induced, and enzymatic grafting techniques[23]. A variety of derivatives, including quaternized, thiolated, carboxymethylated, and amphiphilic derivatives, are produced when chitosan is chemically modified.

1.3 Methods for chitosan modification

The major advantage of chitosan is the existence of modifiable positions in its chemical structure [24]. By connecting the macromolecular chains by grafting or cross-linking events, chitosan can be modified to produce variants with better qualities. Grafting reactions occur when additional functional groups are added to chitosan, increasing the number of adsorption sites and, in turn, the adsorption capacity. However, the adsorption capability is somewhat reduced by the cross-linking events because some

chitosan functional groups [10], [25] (hydroxyl or amino groups) are unable to interact with the metals because they are attached to the cross-linker. As a result, chitosan's primary, secondary, and amino groups can be grafted with a range of polymer materials. In addition to maintaining chitosan's natural biocompatibility and degradability, the graft copolymer increases its solubility and confers additional unique qualities. [26]. Because of this, there are many dependable traditional procedures for creating graft copolymers, including chemical, photochemical, biochemical (enzymatic), and physical (plasma-induced) methods. Table 1 summarized a few current reports on chitosan modification, techniques, and applications.

Table 1: Recent development on method and application of modified chitosan reported

Modified chitosan	Methods	Application	Characterization methods	Sources
cross-linked carboxyl-grafted chitosan derivatives	Free radical grafting	Utilized as adsorbents to remove medicinal compounds including diclofenac from aqueous solutions.	SEM, FTIR, XRD	[27]
Sulfone-modified chitosan		as an effective adsorbent for the removal of hazardous Hg(II) metal ions		[28]
Hydrogel (CTS-g-GMA)-PEGDA	Photo polymerization method	to increase its capacity to absorb water and employ it as a medication delivery method	FTIR, TGA and DTA	[29]
Chitosan -graft- Phema	gamma radiation method	to improve its water absorption ability and use it as a drug delivery system	ATR-FTIR, XRD, TGA	[30]
pyridine-based triple quaternized chitosan derivatives	Thermal mathods, quaternazation reaction	Used as anti-fungal activity	H1 NMR, FTIR, Elemental analysis	[31]
Carboxy methyl chitosan derivatives		As corrosion inhibitor for mild steel in HCl	FTIR, Surface tension activity	[32]
Chitosan- graft-polystyrene	Radical Polymerization		FTIR, TGA, and elemental analysis	[33]
Chitosan-graft- acrylic acid	Free radical technique	Release of diclofenac	FTIR, TGA, XRD, and SEM	[34]
Poly(poly(ethylene glycol) methyl ether methacrylate) grafted chitosan		for dye removal from water	FTIR, TGA, H1 NMR, and GPC	[3]

citric acid-graft- chitosan	Thermal grafting	to promote the biomineralization	XPS, FTIR	[23]

1.4 Characterization methods

Some of the most common analytical techniques used to characterize polymeric materials according to the previous report are; Fourier transmission infrared (FTIR), NMR, X-ray diffractometer (XRD), differential scanning Calorimeter (DSC), thermogravimetric analysis (TGA), elemental analysis, and mw analysis. Characterization is use to understand the important changes or transition from one compound to another. Some of the most common method of polymer characterization was presented Table 2.

Table 2: Methods for polymer Characterizations

Analytical techniques	Function	References
FTIR	Specific functional groups present in the polymer	[35]–[37]
XRD	Polymorphism of polymers	[27]
DSC	Melting point, Glass transition temperature and purity	[38]
TGA	Decomposition temperature	[30], [39]
XPS	explore the chemical composition on the surface of a sample	[40]
NMR	to understand the chemical environment of each H and Carbon in the compound and hence to predict the exact structure of the compound	[41]
Elemental analysis	Elemental composition such as C, H, N content	[42]
MW analysis	Gain in molecular weight after grafting characterized	[42]

1.5 Chitosan modification with other polymers having versatile properties to enhance its properties and its application in various field

Polymer modification is a vast research area in which different properties can be added to the polymer to enhance its performance and expand its application. This can be achieved in many ways such as grafting, polymer composites, doping, crosslinking and functionalization. Polymer grafting was reported to be one of the easiest and cheap methods [10].

The desirable nature of chitosan opens the chance for its modification results for its applications in many areas. According to the previously publish research, chitosan and its derivatives have been modified and applied in different field as reported below. [43] Synthesized Chitosan-graft-poly (2-hydroxyethyl methacrylate-co-itaconic acid) for different feed ratios of 2-hydroxyethyl methacrylate and itaconic acid and characterized by FTIR, thermogravimetry, and swelling in simulated biological fluids (SBF) and evaluated as a drug carrier with model drug, tramadol hydrochloride (TRM). Grafting decreased the thermal stability of chitosan. [44] Produced Self-assembled amphiphilic micelles using chitosan and polycaprolactone (PCL) and utilized as carriers of

paclitaxel (PTX) to improve its intestinal pharmacokinetic profile. The grafted polymer was quite good for the task with high performance.

In a report publish by [45] chitosan-graft-poly (acrylic acid) was synthesized and used it as superabsorbent materials with antimicrobial activities use as water absorbent. The adsorbent were characterized by FT-IR and SEM. Antimicrobial activity of the hydrogel against equilibrium degree of swelling (EDS). An amount of 0.75 g of chitosan in the hydrogel was found to be effective against Escherichia coli. [33] Grafted styrene onto chitosan by conventional free radical polymerization technique, using potassium persulphate (KPS) as the initiator. They reported the highest percentage grafting as 180% at 1:4 at chitosan: styrene weight ratio, 0.4 g KPS and 70^0C reaction temperature. Another report by [46] produced nano particle of Carboxymethyl chitosan by graft copolymerization with different monomers to enhance its applications. The co-polymer was used for anti-bacterial activities against Gram-positive and Gram-negative bacteria. Their report shows outstanding performance for that applications.

Another group [47] Prepared a composite absorbent using diatomite, chitosan, and polyvinyl alcohol, and glutaraldehyde as a cross-linking agent. The composites were utilized for adsorption of mercury from waste water. This composite was characterized using FT-IR spectra, SEM, XRD, BET and, UV–Visible spectra. The results show a good performance with maximum adsorption capacity of 195.7mgg^{-1} at one hour of contact time and room temperature. In a study reported by [48], Chitosan TPP beads and Chitosan TPP beads was produced and characterized by FTIR and SEM analysis. The sample was used as an adsorbent for the removal of iron from waste water The composite give a promising results with the adsorption capacity up to 232mg/g.

The adsorption capacities of a chitosan-PPEGMA 50/50 physical mixture and pure PPEGMA were also investigated by [49]. Two Chitosan derivatives were synthesized using Triethylenetetramine and poly(ethylene imine) as aminated reagent by emulsion cross-linking method. These derivatives have been utilized as an adsorbent for anionic dye reactive yellow. The microspheres were fully characterized by FTIR, SEM, XRD, EDS and TGA. The results show a very good adsorption capacity of the reactive yellow in aqueous solutions up to 88.56% [49].

CONCLUSION

Modified chitosan materials have shown significant potential as alternative and novel materials for various chemical technology applications. Chemical modifications such as grafting, crosslinking, quaternization, carboxylation, and phosphorylation have been employed to improve the solubility, stability, reactivity, adsorption, catalytic, and antimicrobial properties of chitosan. Thus there are so many other derivatives that are yet to explore with many can be used for other applications. The modified chitosan materials have shown a promising applications in water treatment and purification (heavy metal removal, dye adsorption, disinfection), catalysis and adsorption (heterogeneous catalysts, adsorbents for organic pollutants, supports for immobilized enzymes), drug delivery and biomedical applications (controlled drug release, tissue engineering, wound healing) and, Emerging areas like sensors, packaging, food preservation, and environmental remediation.Lastly , the review highlights the significant progress and future prospects of using modified chitosan as a versatile and sustainable material for a wide range of chemical technology applications.

RECOMMENDATIONS

The following are recommended:

i. Continued research and development to optimize the chemical modifications and tailor the properties of chitosan for specific applications.
ii. Exploration of novel modification techniques and combinations to expand the functionality and versatility of chitosan-based materials.
iii. Scale-up and commercialization of the most promising modified chitosan technologies to enable their widespread adoption in the chemical industry and beyond.
iv. Addressing any remaining challenges, such as large-scale production, and regulatory approvals, to facilitate the broader implementation of

modified chitosan in chemical technology applications.

v. Continued interdisciplinary collaboration between chemists, materials scientists, engineers, and end users to drive innovation and unlock the full potential of modified chitosan as alternative novel materials.

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