Chapter 1:

Introduction

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1. Polymer

The term "polymer" originates from Greek, where 'poly' signifies many, and 'meros' translates to parts. In contemporary times, polymers have evolved into a pivotal component of our daily lives. Its ubiquitous use in various applications has led to the current era being aptly referred to as the age of polymers. The term "polymer" was initially coined by Jons Jacob Berzelius in 1833 [1]. Herman Staudinger introduced the concept of macromolecules in his published work titled 'Uber Polymerization' in 1920. According to Staudinger, polymers are formed through the linkage of small repeating units [2]. Following this breakthrough, progress in this field has been exceptionally rapid, resulting in our surroundings being predominantly composed of materials consisting of either polymers or polymeric materials.

Polymers can be categorized into two main types based on their origin: (a) Natural polymers and (b) Synthetic or man-made polymers. Advancements in both classes have been observed to progress rapidly. These polymers also find extensive applications in various fields such as electronics, consumer products, transportation, medical, construction, etc. [3]. In the present day, synthetic polymers are manufactured on a large scale, where United States alone producing approximately 45 million tons of synthetic polymers annually [2].

Most of the natural polymers are biodegradable in nature. They often exhibit shortcomings in terms of water resistance and physical as well as mechanical properties. Scientists are actively working to enhance the properties of biodegradable polymers through modifications, aiming to position them as potential substitutes for traditional synthetic polymers. Chemically modified biodegradable polymers are now utilized in various applications across fields such as consumer products, agriculture, medical, etc. [4]. Researchers are actively involved in exploring further in this field to either develop new polymeric material or modify existing ones with good properties and biodegradable characteristics.

1.1. Harmful effects of synthetic polymers

Synthetic polymers are acknowledged for their resistance towards chemical and biological degradation. In applications ranging from surgery, pharmacology, agriculture to environmental settings, the increasing presence of polymeric waste has been creating a significant issue [5]. The severe environmental concerns, coupled with escalating waste management challenges and the imminent threat of global warming due to CO_2 emissions in incineration of polymeric waste [6].

There is a clear demand for polymeric materials as an alternative to existing ones, capable of satisfying the criteria of biodegradability, biocompatibility, and the release of low-toxicity degradation products [7]. In the current context, the utilization of synthetic polymers poses a significant environmental threat. The majority of synthetic polymers are non-biodegradable, contributing to various forms of environmental pollution. Therefore, communities in the materials field are actively investigating different biodegradable polymers as potential alternatives.

1.2. Biodegradable polymers

Polymers that are biodegradable and derived from renewable sources have garnered significant attention in recent years, owing to their appealing properties such as biocompatibility, biodegradability, and natural abundance. In recent times, a range of biodegradable polymers, stemming from both natural and synthetic sources, and exhibiting robust biodegradability and biocompatibility, has surfaced [8]. Several environmentally friendly biodegradable polymers have been developed as alternatives to synthetic polymers. Some of them undergo bacterial decomposition, leading to the formation of different gases and smaller molecules, including water, low molecular weight hydrocarbon molecules, and various inorganic salts. Cellulose, collagen, chitin, silk, starch, and similar materials are frequently cited as prime examples of biodegradable polymers [9]. Among them, chitin stands out as the second-most abundant biodegradable biopolymer, following cellulose [10].

1.2.1. Chitin

Chitin is characterized as a linear homopolymer of N-acetylglucosamine, featuring β (1,4) linkages, and exhibits cationic behavior (Figure 1.1.) [11]. In general, three different polymorphs of chitin are found in nature, and structurally, they are known as α-chitin, β-chitin, and γ-chitin. Among these, α-chitin is the predominant structure observed in most natural chitins [12]. Chitin is primarily sourced from the exoskeletons of crustaceans, mollusks, and certain marine insects such as krill, shrimp, crab, crawfish, and others. Additionally, chitin can be extracted from the cell walls of certain fungi and microorganisms. [13]. There are reports indicating that various marine species serve as a primary source of chitin. Among these, oyster and crab shell waste have been identified as yielding the highest chitin content. Conversely, prawn, mussel shell, pang, and silver scales have lower chitin content [14]. Figure 1.2. illustrates the percentage of chitin production from different marine species.

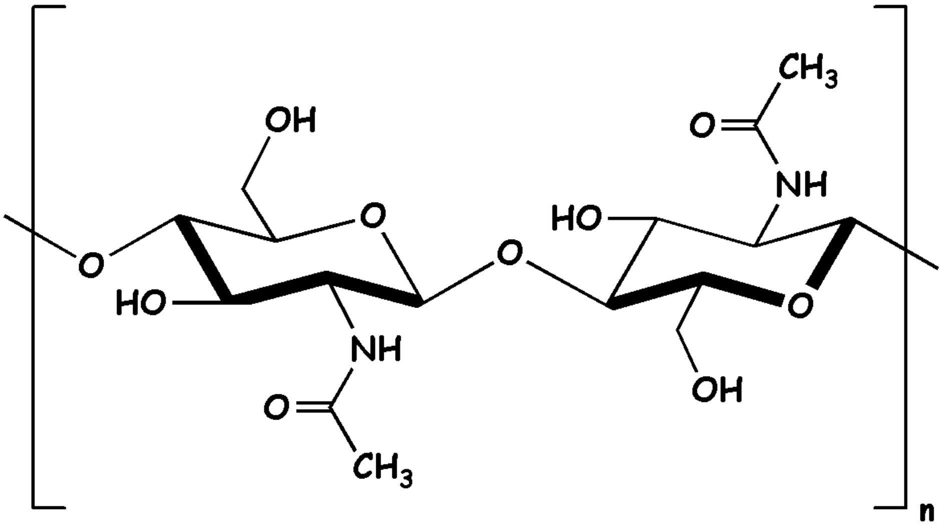

Figure 1.1. Chemical structure of chitin.

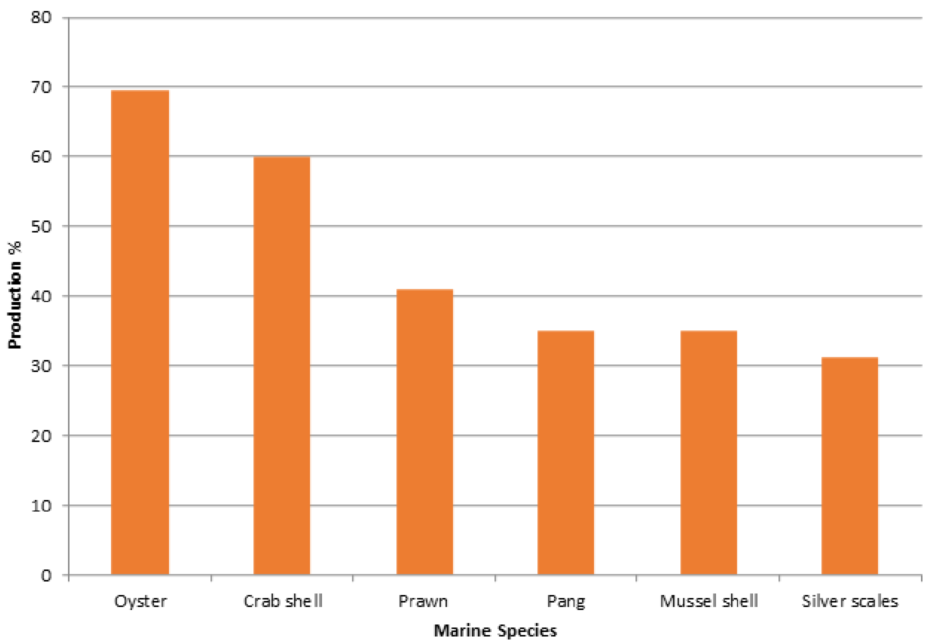

Figure 1.2. Percentage of chitin production from different marine species [14].

Chitin exhibits a poor solubility profile, prompting a need for further improvement. The challenges associated with chitin's solubility have led to an increasing focus on chitosan (CS) as a viable alternative [15].

1.2.2. Chitosan

Chitosan (CS) is regarded as the enhanced and refined version of chitin. This powdery substance, ranging from white to light red, possesses an improved solubility profile compared to chitin. While CS is generally insoluble in water, it demonstrates solubility in various organic acids, including formic acid, acetic acid, tartaric acid, and others. It is recognized as one of the most versatile, unique, and multi-functional biopolymers, possessing inherent biological properties. CS is a linear polysaccharide characterized by randomly distributed β-1,4-linkages of D-glucosamine and N-acetyl-D-glucosamine residues (Figure 1.3.) [11].

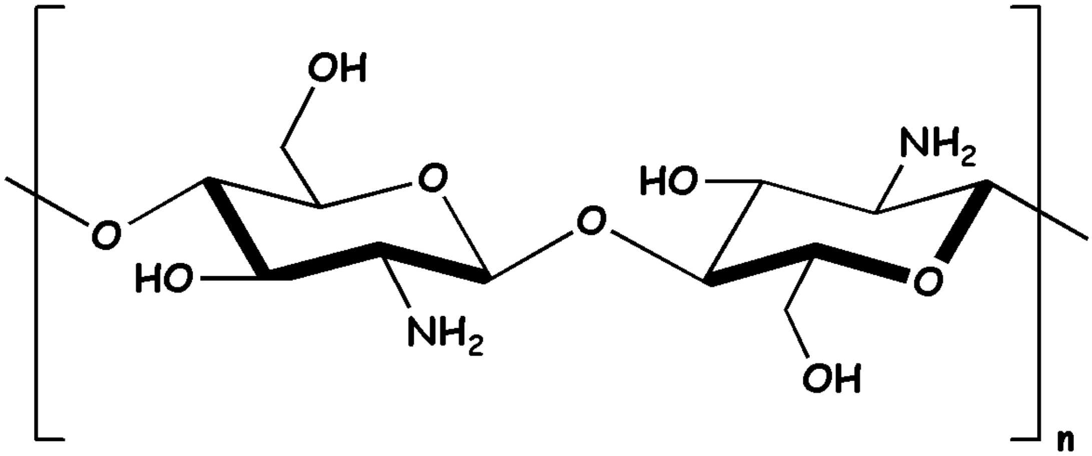

Figure 1.3. Chemical structure of CS.

CS acquires various interesting properties, such as good biodegradability [16], biocompatibility [17], and non-toxicity [18], that depends on factors like the source, method of preparation, molecular weight, and degree of acetylation. Due to these attributes, this linear polysaccharide finds suitability for diverse applications in pharmaceutical drug delivery technology [19]. The Global Strategic Business Report on "Chitin & Chitosan" provides estimates of production and annual sales amounts in metric tons from the year 2010 to 2018 across various geographic regions and countries (Figure 1.4.). Moreover, the report also presents estimates of the annual amount of CS used and consumed in various fields (Figure 1.5.) [20].

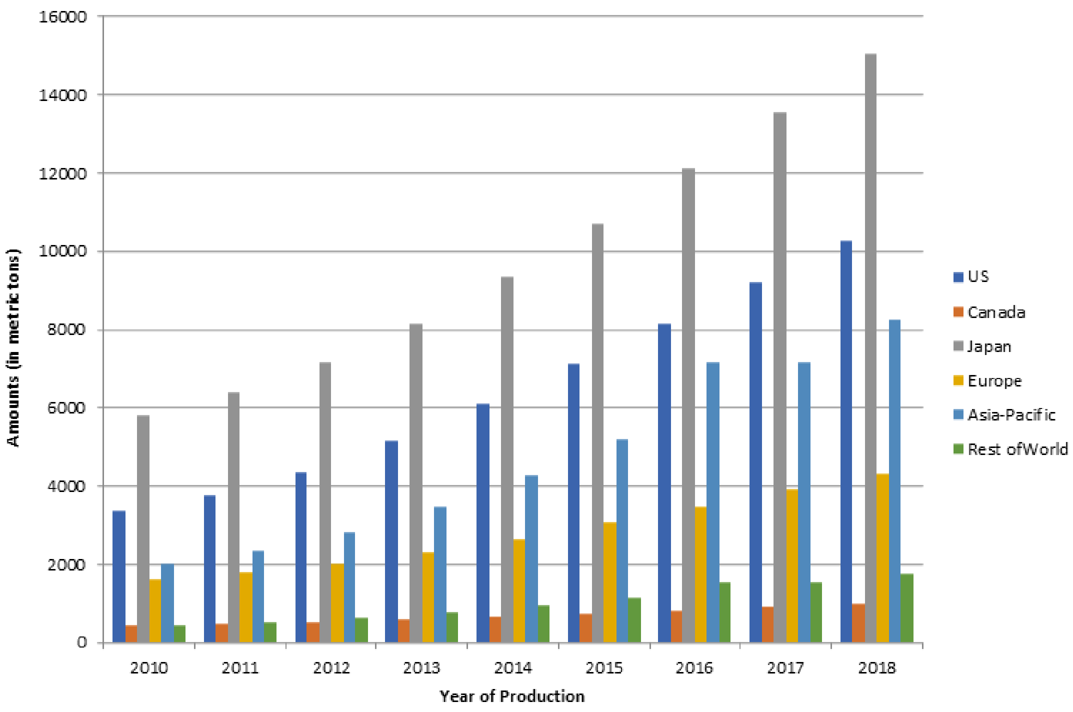

Figure 1.4. Annual sales amounts of CS in metric tons by different geographic regions/countries [20].

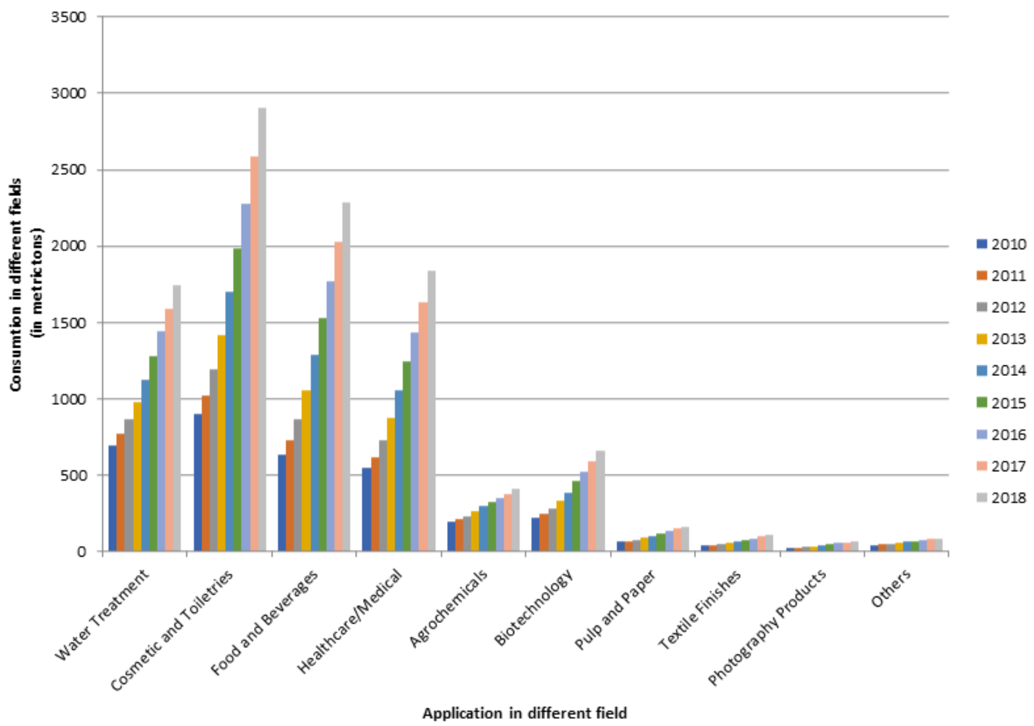

Figure 1.5. Annual consumption of CS in different field [20].

CS is classified into three different qualities based on the degree of deacetylation of chitin. These classifications are known as low purity (low level of degree of deacetylation), medium purity (medium level of degree of deacetylation), and high purity (high level of degree of deacetylation), with the latter also referred to as medical grade. Low purity CS finds applications in various industrial processes for water treatment, as pesticides in agriculture, and in the pulp and textile industries. Medium purity CS is utilized for purposes such as protein precipitation, acting as an aqueous thickener, and serving as an encapsulating agent. High purity CS, often categorized as medical grade, is primarily employed in applications related to wound healing and hemostasis, bio-surgery and ophthalmology, cell therapy, drug delivery, and vaccines [20].

1.3. Conversion of chitin to chitosan

CS can be derived from chitin through either enzymatic or chemical modification processes [21]. Kafetzopoulos *et al.* documented a method for the biosynthesis of CS from chitin, employing the enzyme chitin deacetylase. The enzyme employed in the conversion was extracted from the mycelial extracts of the fungus *Mucor rouxiia*, which catalyzes the hydrolysis of the acetamido groups of N-acetyl-glucosamine in chitin [22]. Alternatively, the conversion can be achieved chemically through the process of deacetylation, where chitin is subjected to treatment with sodium hydroxide (NaOH) at temperatures exceeding 80 °C (Figure 1.6.) [23]. The degree of deacetylation of CS can vary between 40% to 98%, and its molecular weights typically fall within the range of 5×10^4 Da to 2×10^6 Da [19].

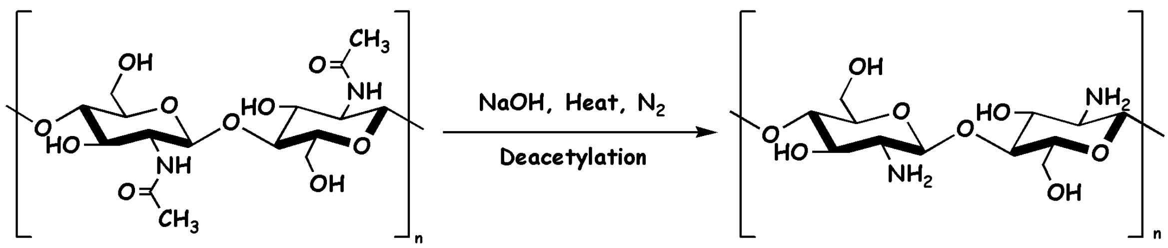

Figure 1.6. Chemical conversion of chitin to CS.

1.4. Modification of chitosan

CS exhibits unique and exceptional properties and applications owing to its distinctive chemical structure. Indeed, CS boasts a range of favorable properties, including biocompatibility, biodegradability [21], non-toxicity, antimicrobial capabilities [24], environmental friendliness, as well as notable adsorption properties, among other attributes

[25]. Essentially, CS consists of three functional entities within its monomer skeleton: a primary amine, and primary and secondary hydroxyl groups (Figure 1.7.) [26]. These groups can undergo substitution or modification with various other groups, resulting in modified chitosan (MCS) with a myriad of fascinating properties. This versatility opens up a wide range of possibilities for applications across diverse fields. During various modification processes, it is ensured that the degree of polymerization remains intact, preserving the polymeric properties of CS.

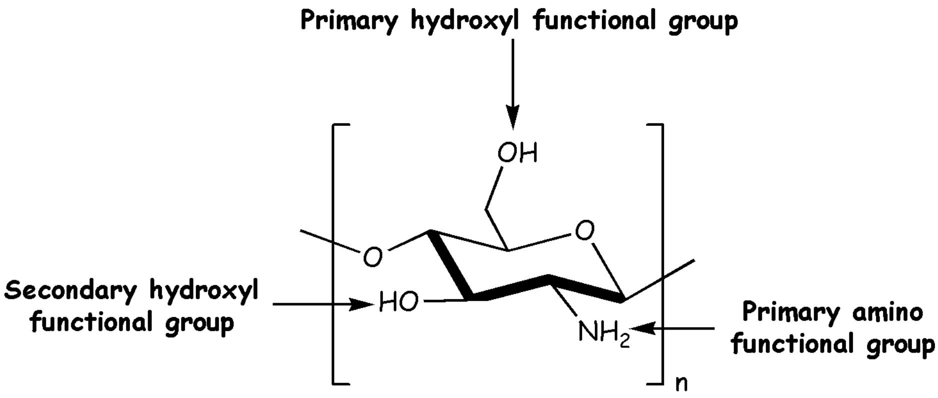

Figure 1.7. Functional groups present in CS.

Despite CS's poor solubility in water and its insolubility in many common organic solvents, its multifunctional nature renders it a unique and remarkable compound. The primary amino group possesses the ability to donate its free lone pair of electrons, rendering CS soluble in various aqueous organo-acidic solvents and allowing it to form coordination bonds [27]. Numerous modifications have been undertaken on CS to enhance its solubility [28] and broaden its applicability. Additionally, these modifications make CS a strong candidate for various applications in pharmaceuticals, biomedicine [24], water treatment [29], cosmetics [30], agriculture [31], etc. The dissolution property of CS is influenced by its average degree of acetylation [29].

The chemical modification of CS with 2-Bromopropionyl bromide (BPB) has also been reported in this thesis.

1.4.1. Chemical modification of chitosan with 2-Bromopropionyl bromide

2-Bromopropionyl bromide is a chemical reagent (Figure 1.8.) which is often used in chemical reactions for the modification of polymers, such as grafting reactions [32, 33]. According to the literature survey, the modification of CS with BPB has never been reported.

To introduce functional groups or side chains onto the CS polymer chain BPB can be used. This can be done by a grafting process that involves the reaction of BPB with CS. The Br-atom in BPB reacts with either amino group or hydroxyl groups on the CS polymer chain through an amide or ester linkage. This covalent attachment alters the chemical structure of CS. The introduction of functional groups can impart specific properties in CS, making it suitable for some particular applications.

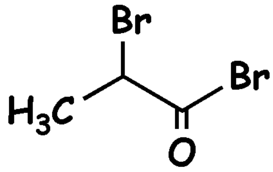

Figure 1.8. Structure of BPB.

1.4.2. Modification of chitosan by incorporation of clays

Modifications through the formation of a biocomposite with clay may be attempted to enhance the characteristics of pure CS. Biocomposites introduce new dimensions to the inherent properties of biodegradable polymers, creating an interdisciplinary realm that brings together biology, chemistry, and material science [34]. Biocomposites derived from waste and naturally occurring materials show great promise as candidates for various industrial applications. In this context, the biodegradable polymer CS stands out as an excellent choice due to its distinctive characteristics. It is cost-effective, readily available, biocompatible, biodegradable, hydrophilic, non-toxic, easily amenable to chemical modification, and exhibits good adhesion, ion-exchange, and adsorption properties [35]. Nevertheless, the industrial applications of CS are limited due to certain drawbacks. The limitations include a tendency for gel formation and softening in aqueous media due to hydrophilicity, low specific surface area, low specific gravity, swelling and floating in water, weak mechanical properties, and higher solubility in acidic media [36]. Despite the development of various CS-based composites in recent years to address these drawbacks, there has been a notable emphasis on immobilizing CS on clay minerals [37]. Clay minerals can substantially enhance the properties of CS by offering excellent surface interaction attributed to their smaller particle size, higher surface area, aspect ratio, and improved dispersion properties [38]. Moreover, clay minerals exhibit excellent properties including good biocompatibility, non-toxicity, and significant potential for controlled release. These attributes provide a solid foundation for their applications in various fields such as food, medicine, pharmacy, cosmetics, etc. [39]. Since CS is a naturally occurring polycation with numerous favorable properties and clay serves as a natural inorganic filler used in various applications such as medicine, ceramics, and food additives, the combination of these two biomaterials — a natural polycation (CS) and a natural filler — may result in the formation of a biocomposite, CS/clay, with a range of interesting properties. In this thesis, we report the findings on the modification of CS using three distinct types of clay, namely kaolin (KAO), bentonite (BNTN), and silica (SIO) clay.

1.4.2.1. Kaolin clay

Kaolin (KAO) is obtained from kaolinite mineral. It is recognized as one of the most prevalent natural inorganic clays [40]. KAO is hydrated aluminum silicate (Figure 1.9.) with a two-layer 1:1 silicate structure [41]. KAO is an essential material in various industrial processes due to its outstanding properties, including abundant availability, environmental friendliness, low-cost production, high surface area, strong bonding ability, high whiteness, low-cost, and excellent thermal stability [42]. However, the most common disadvantages limiting the large-scale application of KAO as an adsorbent material are aggregation and its limited adsorption capability towards anionic species [43]. Therefore, numerous reports have concentrated on modifying KAO to overcome these weaknesses, employing approaches such as surface modification and composite formation [44]. CS can be intercalated with KAO through cationic exchange and hydrogen bonding. The resulting biocomposites display fascinating features [45].

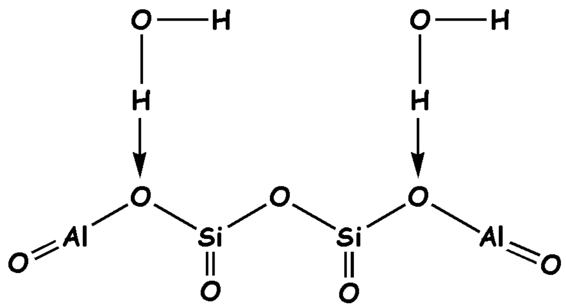

Figure 1.9. Structure of KAO clay.

1.4.2.2. Bentonite clay

Bentonite (BNTN) is a significant natural clay material extensively utilized in numerous industries. It is composed of hydrous aluminosilicates, predominantly montmorillonite, and contains lesser amounts of other clay minerals [46]. It possesses a layered structure with exchangeable cations within the spaces, exhibiting certain dispersibility, chargeability, and hydration in aqueous solutions (Figure 1.10.) [47]. BNTN is widely recognized as an economical and environmentally friendly clay mineral with notable adsorbent qualities [48]. It emerges as a favorable support material, attributed to its mechanical strength, chemical stability, and availability [49]. Natural BNTN exhibits high hydrophilicity, readily associating with water molecules, thereby impeding the diffusion and adsorption of organic substances on its surface. Modification can enhance its adsorption performance by augmenting its lipophilic hydrophobicity. Nevertheless, the use of BNTN comes with drawbacks, including low adsorption efficiency, lack of selectivity, and low binding coefficients [50]. As CS exhibits a polycationic nature in acidic environments, it can be intercalated into BNTN through cationic exchange mechanisms and hydrogen bonding interactions. The resulting biocomposites showcase intriguing features [45].

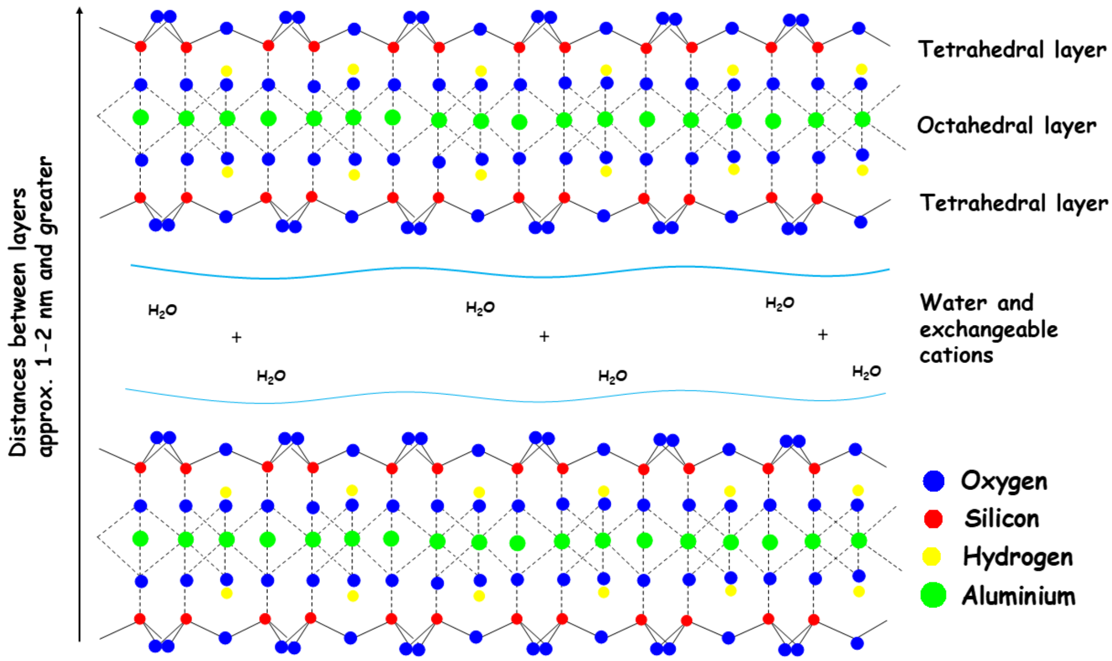

Figure 1.10. Structure of BNTN clay.

(Source: https://scottlab.com/bentonite-clarification-heat-protein-stabilization)

1.4.2.3. Silica clay

Silica (SIO) clay is composed of silicon and oxygen. It is a ubiquitous mineral present in the Earth's crust and serves as a fundamental component of various minerals, including quartz. It lacks a specific arrangement, resulting in a three-dimensional, porous network (Figure 1.11.). SIO are distinguished by their enhanced surface stability in acidic mediums, well-developed surfaces, favorable kinetics, thermal stability, resistance to microbial attack, and cost-effectiveness [51]. SIO stands out as a highly representative porous inorganic material, finding extensive use in industries such as rubber, pesticides, papermaking, plastic processing, and others. Its widespread adoption is attributed to its advantages, including a large pore volume, diverse pore structure, and numerous modification methods [52]. SIO clay holds significant potential for diverse industrial applications owing to its distinctive properties. Recently, numerous technologies for hybrid materials combining silica and CS for versatile applications have been reported [53].

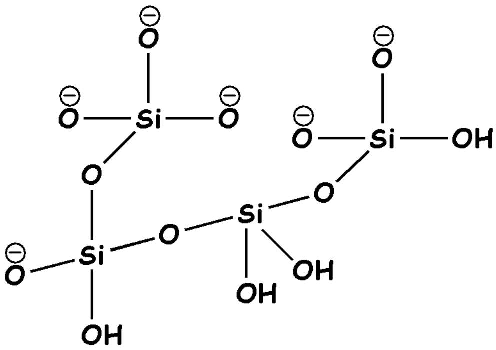

Figure 1.11. Structure of SIO clay.

1.5. Literature review

1.5.1. Chemical modification of chitosan

Various modifications such as quaternization [54], alkylation [55], acetylation [56], graft copolymerization [57], phosphorylation [58], reversible-deactivation radical polymerization [28], etc. were performed on CS to increase its solubility [28] and applicability. These modifications make CS a strong candidate for different applications like pharmaceuticals, biomedicine [24], water treatment [29], cosmetics [30], agriculture [31], etc. There have been several reports that focuses on the modification of CS with 2-bromoisobutyryl bromide (BIBB). Bao *et al.* initiated the synthesis of a CS macroinitiator using BIBB and subsequently developed a graft copolymer by incorporating poly[(2-dimethylamino)ethyl methacrylate] onto the CS backbone [59]. In another investigation, Liu *et al.* achieved the synthesis of quaternary phosphonium graphene oxide through the treatment of graphene oxide with BIBB in the presence of triethylamine (TEA). This quaternary phosphonium graphene oxide was then graft-copolymerized into the CS matrix to fabricate anion exchange membranes [60]. In an alternate study carried out by Tahlawy *et al.*, a CS macroinitiator was prepared by reacting CS with BIBB in the presence of pyridine. This macroinitiator was subsequently employed to catalyze the polymerization of methoxy-poly(ethylene glycol) methacrylate [61]. Using a similar approach, Chen *et al.* developed a comb-shaped copolymer, CS-*graft*-poly(N-isopropylacrylamide), by utilizing bromoisobutyryl-terminated CS [62]. In another study, Li *et al.* commenced polymerization by reacting the surfaces of CS with BIBB. They subsequently fabricated CS-*graft*-polyacrylamide, aiming for improved and selective removal of mercury ions from aqueous solutions [63]. In another study conducted by Dryabina *et al.*, CS was utilized as a macroinitiator. In this research, CS underwent a reaction with BIBB in the presence of dimethylformamide (DMF). The resulting macroinitiator was then employed to polymerize trimethyloxyethylmethacryloyl ammonium ethyl sulfate [64]. Moreover, Huang *et al.* carried out a reaction in which functionalized cross-linked CS was treated with BIBB in the presence of TEA and tetrahydrofuran (THF). This reaction led to the synthesis of poly(methacrylic acid), which was utilized for the removal of Cd^{2+} ions from an aqueous solution containing sodium methacrylate [65]. Tang *et al.* introduced an innovative method for modifying CS by generating CS nanospheres (NS). In this process, CSNS were first prepared from CS, and then treated with BIBB in the presence of TEA and DMF. The resulting macroinitiator was subsequently used in the synthesis of CSNS-*graft*-polymethylmethacrylate-*block*-poly(polyethyleneglycol methyl ethyl methacrylate) [66]. We were thus keenly interested in modifying CS with BPB. Table 1.1. summarizes the modified version of CS achieved through the use of the reagent BIBB, along with their corresponding properties and applications.

Table 1.1. Modified CS and their properties/applications.

Modified form of CS	Properties/Applications	Reference
Poly[(2-dimethylamino)ethyl methacrylate]-*g*-CS	Shows pH-responsive association behavior Used for gene/drug delivery and controlled release	[59]
CS/ Quaternary phosphonium graphene oxide	Used in drug delivery and controlled release High mobility and activity Promotes hydroxide conductivity Higher fuel cell performance	[60]
CS-macroinitiator	Helps in the formation of CS-*g*-methoxy-poly(ethylene glycol) methacrylate via atom transfer radical polymerization (ATRP)	[61]

	Helps in the formation of CS-*g*-trimethyloxyethylmethacryloyl ammonium methyl sulfate via ATRP	[64]
CS-*g*-poly(N-isopropylacrylamide)	Suitable for delivery of hydrophobic drug molecules	[62]
CS-*g*-polyacrylamide	Greater absorption capacity and faster absorption kinetics for mercury ions	[63]
Cross linked CS	Helps in the removal of Cd(II) ions from aqueous solution	[65]
CSNS-*g*-polymethylmethacrylate-*b*-poly(polyethyleneglycol methyl ethyl methacrylate)	Good biocompatibility Low toxicity Used for the synthesis of materials for *in vivo* biomedical applications as well as polymerization for industrial-scale production	[66]

1.5.2. Chitosan/clay composites

There are only a limited number of CS-based products due to its inferior properties. However, these properties get improve in its composites [36]. In recent years, various types of CS-based composites have been developed to address these issues [67]. For this purpose, the immobilization of CS on clay minerals has garnered significant attention [21]. The electrolytic and chelating properties of CS arise from the acidity of the $-NH_3^+$ groups. Additionally, owing to its polycationic nature in acidic environments, CS can be intercalated into various clays through the cationic exchange mechanism and hydrogen bonding interactions. Therefore, the composite form exhibits intriguing structural and functional characteristics [68]. Recent literature provides a detailed exploration of the various characteristics and applications of hybrid materials involving clay and CS. Hence, our strong interest lay in the synthesis of environmentally friendly green biocomposite materials based on CS/clay, ensuring their ecological sustainability.

1.5.2.1. Chitosan/kaolin clay composites

As far as we know, the CS biocomposite utilizing KAO clay has garnered minimal attention and has been the focus of relatively fewer scholarly articles. Ma *et al.* developed a magnetically separable adsorbent (CS/KAO/Fe_3O_4) through emulsion cross-linking. These microspheres were employed as an adsorbent for the removal of ciprofloxacin [70]. Dey *et al.* prepared pH-triggered bicomposites by employing various proportions of KAO and CS. These biocomposites have numerous industrial applications, including uses in leather, textile, food, pharmaceuticals, etc. [34]. In another investigation, Zhu *et al.* conducted the synthesis of CS/KAO/nanosized γ-Fe_2O_3 composites through a micro-emulsion process. These composites can serve as a cost-effective alternative for removing anionic dyes from industrial wastewater [44]. Biswas *et al.* synthesized high-performance composites by using CS and modified KAO clay in various combinations [71]. In a separate investigation, Chen *et al.* developed CS-coated KAO beads utilizing hydrochloric acid without the incorporation of any cross-linking agent [72]. Mohamed *et al.* investigated the production of aminated CS/KAO composite beads for the adsorptive removal of harmful anionic dyes [73]. In another study, Sun *et al.* enhanced the hemostatic performance of CS by blending it with KAO to create porous composite microspheres through the inverse emulsion method combined with thermally induced phase separation [41]. Lefatle *et al.* produced a magnetic adsorbent composed of a CS/KAO nanocomposite through a one-pot co-precipitation method. The nanocomposite was employed as an adsorbent in the magnetic solid-phase extraction of tetracycline from wastewater and surface water [74]. In an additional investigation, Yarangsee *et al.* utilized the spray drying technique, specifically the rotary atomizer spray dryer, to develop co-processed CS/KAO, focusing on the characterization of its excipient properties [75]. Rekik *et al.* fabricated composite porous membranes of CS/KAO through a solvent casting and evaporation process. The suspensions with varying concentrations of KAO and CS exhibited Newtonian behavior [76].

1.5.2.2. Chitosan/bentonite clay composites

Recent literature provides in-depth insights into the various features and uses of hybrid materials comprising BNTN clay and CS. Lin *et al.* presented a report outlining a pioneering technique for synthesizing nanocomposites of CS and montmorillonite. Their study delved into the mechanical properties and biodegradable characteristics of the synthesized materials. They indicated that the tensile properties could be improved by synthesizing nanocomposites with CS, thereby preventing degradation *in vitro* tests [77]. In alternative studies, Tan *et al.* synthesized CS/montmorillonite nanocomposites using hydroxy-aluminium oligomeric cations and investigated the resulting nanocomposite. The nanocomposites were employed for absorbing organic and metal ions from both dyes and finishing effluent [69]. Darder *et al.* explored the intercalation process of the cationic biopolymer CS in Na^+-montmorillonite, yielding compact and sturdy 3D nanocomposites exhibiting intriguing functional properties [45]. Laaraibi *et al.* formulated nanocomposite films of CS and montmorillonite, demonstrating promising applications in both the food and environmental domains [78]. Cankaya *et al.* created CS/montmorillonite nanocomposites using three primary types of montmorillonites and their organo-clay derivatives, then examined the thermal, antimicrobial, and swelling properties of these biocomposites [79]. Cacciotti *et al.* evaluated the potential applications of CS/Montmorillonite systems as innovative carriers for the covalent immobilization of enzymes [80]. Benucci *et al.* crafted biopolymeric nanocomposite films by incorporating CS and nano clay, intending to utilize them as carriers for the covalent immobilization of a proteolytic enzyme through glutaraldehyde crosslinking. The aim was to apply these films in the winemaking process [81]. Furthermore, in a separate experiment, the incorporation of two nanoclays into the CS-based nanocomposite films resulted in improved mechanical properties. This enhancement renders the films suitable for applications in both synthetic and actual white wine scenarios [82]. Jia *et al.* synthesized CS/BNTN composites through physical gelation and assessed their effectiveness in adsorbing Cr (VI) from aqueous solutions [47]. Bensalem *et al.* generated CS/BNTN composite beads by gradually introducing a solution containing CS and BNTN into an alkaline NaOH solution. These composites hold potential for adsorbing certain anionic dyes and heavy metals, making them of interest for environmental applications [46]. Huang *et al.* synthesized a cross-linked CS/BNTN composite through the intercalation of CS in BNTN and the subsequent cross-linking reaction of CS with glutaraldehyde. These composites demonstrated potential for effectively removing methyl orange from aqueous solutions [83]. Devi *et al.* developed a series of innovative CS/BNTN nanocomposite films using the solvent casting method, with a focus on their application in wound healing [84]. Savitri *et al.* synthesized a CS/BNTN composite with the goal of modifying and enhancing its characteristics to facilitate the adsorption of both anionic and cationic substances [85]. Teofilovic *et al.* treated BNTN with the surfactant cetyltrimethyl ammonium bromide prior to composite preparation. The resulting CS/BNTN composite beads were then synthesized and employed for the treatment of colored wastewater [86]. In another study reported by Marey, the efficacy of combining CS and BNTN as a coagulating agent in the Ismailia Canal was demonstrated for wastewater treatment processes [87]. Jatrana *et al.* employed a sonication-assisted technique to synthesize environmentally acceptable composites utilizing CS and BNTN. The resulting composite holds promise as a cost-effective and environmentally friendly adsorbent for the removal of pesticides from water environments [88]. Nie *et al.* introduced an environmentally friendly and sustainable 3D porous aerogel derived from citrus peel, CS, and BNTN. This aerogel is fabricated through a straightforward sol-gel and freeze-drying process, specifically designed for the efficient capture of Cu(II) ions from water matrices [89]. Li *et al.* constructed a composite physical hydrogel, CS/calcium alginate/BNTN, to mitigate the risk of secondary pollution associated with toxic residues from chemical crosslinking agents in chemical hydrogel adsorbents. This design aimed to enhance the adsorption performance of the physical hydrogel [90].

1.5.2.3. Chitosan/silica clay composites

Current literature provides a comprehensive exploration of the diverse characteristics and applications associated with hybrid materials incorporating both SIO clay and CS. In a study conducted by Salama *et al.*, a novel adsorbent material was synthesized through the ionic interaction of CS and anionic silica clay, followed by a sol-gel process. The findings indicated that the CS/SIO nanocomposite proved to be a suitable material for the adsorption of organic pollutants in wastewater [91]. Mohammed *et al.* conducted a study wherein they synthesized CS/SIO nanocomposite materials specifically designed for the removal of methyl orange dye from water [92]. In a study explored by Sagheer *et al.*, hybrid films of CS and SIO were fabricated through a sol-gel process, utilizing tetraethoxysilane as a precursor material [93]. Furthermore, in a distinct study, Budnyak *et al.* detail the synthesis of the nanocomposite material CS/SIO, aiming for its application as a biosorbent. The hybrid material was acquired through the sol-gel method, employing tetraethoxysilane as the precursor for SIO [51]. Zhong *et al.* employed a triblock co-polymer as a structure-directing agent, ethyl orthosilicate as the silicon source, and CS as a carrier to synthesize distinctive CS/SIO composites with different mass ratios. Consequently, the formulated composites demonstrated significant efficacy in removing dyes from wastewater, and the material exhibited excellent reusability for up to six cycles [53]. Blachino *et al.* similarly synthesized a CS/SIO hybrid composite using both physical adsorption and the sol-gel method. These materials were subsequently employed for the removal of sulfonated azo dyes from aqueous solutions [94]. Ma *et al.* studied the co-action behavior of a hybrid material composed of CS and SIO by incorporating it into an epoxy resin. The goal was to induce an active barrier effect on the metal surface [95]. Sumarni *et al.* examined the impact of varying SIO composition on the physical characteristics of CS/SIO membranes made from rice husk ash [96]. Wang *et al.* produced a range of aerogels using varying feeding ratios of CS and SIO [97]. Table 1.2. outlines different CS/clay composite types, presenting their respective properties and applications.

Table 1.2. CS/clay composites and their properties and applications.

CS/clay composites	Properties/Applications	Reference
CS/KAO/Fe_3O_4	Used as a low-cost alternative for anionic dyes removal from industrial wastewater	[44]
	Employed as an adsorbent for the removal of ciprofloxacin	[70]
	Used as an adsorbent in magnetic solid-phase extraction of tetracycline in wastewater and surface water	[74]
CS/KAO	Play a vital role in advanced research in analytical and environmental science	[34]
	A potential quick pro-coagulant agent for traumatic hemorrhaging control	[41]
	Removal of Cu(II) from aqueous solution	[72]
	For adsorptive removal anionic dyes from polluted aquatic bodies	[73]
	Enhanced the flowability and tableting performance	[75]
	Play an important role in advanced research in water treatment and environmental science	[76]
CS/Montmorillonite (BNTN)	Used in the development of bulk-modified electrodes exhibiting numerous advantages as easy surface renewal, ruggedness, and long-time stability	[45]

CS/Montmorillonite (BNTN)	Used in absorption of organic and metal ions from dyeing and finishing effluent	[69]
	Improved the tensile properties of CS and also hindered the degradation in the vitro test	[77]
	Show a good tensile strength due to the reinforcement of CS intercalation in the silicate, which is an interesting mechanical property needed for food packaging applications	[78]
	Used in many fields, such as textile, furniture, paints and electronics	[79]
	Used as carriers for enzymes covalent immobilization	[80]
	Used as innovative supports for the covalent immobilization of pineapple stem bromelain	[81]
	Used as carriers for the covalent immobilization of papain	[82]
CS/BNTN	Adsorb some anionic dyes, cationic dyes and heavy metals	[46, 84]
	Used as eco-friendly bio adsorbents for the removal of Cr (VI) from aqueous environments	[47]
	Used for the removal of methyl orange from aqueous solutions.	[83]
	Used as potential candidates for wound healing application	[84]
	Used as a coagulating agent for wastewater treatment.	[86, 87]
	Used as a potential adsorbent for thiomethoxam removal	[88]
CS/BNTN/ Citrus peel	Considered as a viable alternative for the green and efficient removal of toxic Cu(II) ions from wastewater	[89]
CS/ BNTN/ calcium alginate	Used for removal of heavy metal ions from water	[90]

CS/SIO	Used as a biosorbent	[51]
	Shows good reusability at six cycles	[53]
	An appropriate material for the adsorption of organic pollutants from wastewater	[91, 92]
	Used for removal of sulfonated azo dyes from aqueous solutions	[94]
	Promotes an active barrier effect to the coating/metal interface to provide long-term protection on the mild steel surface	[95]
	Used as novel adsorbent materials	[97]

1.6. Scope and objectives

CS is a biodegradable polymer extracted from chitin, which is abundant in the exoskeletons of crustaceans such as shrimp and crabs. CS exhibits distinctive structural, physicochemical, and biological characteristics, rendering its applications in pharmaceuticals, biomedicine, and various other fields. The addition of functional groups to CS enhances its hydrophobic, cationic, and anionic properties, thereby increasing its efficiency across a range of applications. Chemical modification is a method employed to boost the functionality of CS. Grafting; a way of chemical modification may be used to generate such functionalities in the CS. BPB can be chosen for this purpose. The procedure entails the interaction between CS and BPB, leading to the bonding of BPB functional groups to the CS polymer chains. This chemical modification has the potential to introduce novel properties to CS, broadening its scope for various applications.

CS-based functional graft copolymers may open up diverse possibilities, including the development of drug delivery systems with controlled release properties, elevating the efficiency and efficacy of drug delivery etc. Furthermore, the modified CS can contribute to the production of biocompatible materials for medical implants, wound dressings, and applications in tissue engineering. In addition, CS, particularly in its modified form, exhibits a notable affinity for heavy metal ions, making it valuable in water treatment processes to eliminate pollutants like lead, cadmium, and mercury. Grafted CS proves effective in adsorbing organic pollutants, presenting practical applications in wastewater treatment. In the textile industry, modified CS plays an important role in removing dyes from wastewater, aiding in the treatment of effluents before discharge.

The versatility of CS-*g*-BPB extends to the food industry, where it can be employed in developing coatings for food preservation. The modified CS may showcase antimicrobial properties, thereby extending the shelf life of specific food products. In agriculture, grafted CS emerges as a biodegradable and environmentally friendly alternative for crop protection, facilitating the controlled release of pesticides or fertilizers. Modified CS can also be integrated into polymer matrices to enhance mechanical and thermal properties. It also finds applications in film production, membrane development, and other polymeric materials. With its heightened antimicrobial properties, modified CS proves suitable for use in antimicrobial coatings, films, or wound dressings. Moreover, CS-*g*-BPB may be harnessed in the formulation of cosmetics and personal care products, owing to its potential skin-friendly and biocompatible characteristics.

The success and suitability of CS-*g*-BPB hinge on various factors, including the degree of grafting, reaction conditions, and the specific needs of the intended application. It is crucial to conduct comprehensive testing and evaluation of the modified CS to assess its properties, toxicity, and performance in relevant environments before considering widespread commercial utilization. This thorough examination ensures a reliable understanding of the modified CS's behavior and characteristics, facilitating informed decisions regarding its practical applications.

Moreover, when CS is combined with clay minerals, the resulting material may demonstrate enhanced properties in comparison to the individual components. The integration of clay into CS matrices yields a hybrid material characterized by improved mechanical strength, enhanced thermal stability, superior barrier properties, and other distinctive features.

The utilization of CS/clay composites extends across diverse applications, showcasing their potential in drug delivery by enabling the controlled encapsulation and release of pharmaceutical agents. The heightened surface area and porosity of clay particles contribute to improved drug loading and release kinetics. These composite materials hold promise for applications in wound dressings and tissue engineering, where the combination of CS's biocompatibility and the structural reinforcement from clay supports cell adhesion and tissue regeneration. CS/clay composites also prove valuable in the development of food packaging materials, offering enhanced barrier properties that effectively inhibit the permeation of gases, moisture, and contaminants. The amalgamation of CS's antimicrobial properties with the barrier effects of clay makes these composites suitable for antimicrobial packaging applications, preserving fresh packaged food items. In the realm of water treatment, CS/clay composites exhibit efficacy in removing heavy metals, dyes, and pollutants due to the adsorption capacity of clay minerals and the chemical reactivity of CS. This versatility positioned the composite as a valuable adsorbent in water treatment processes. Moreover, the application of CS/clay composites spans various industries, including automotive, aerospace, and construction, where the enhanced mechanical strength and thermal stability of these polymer nanocomposites prove advantageous for lightweight and high-strength materials. In agriculture, CS/clay composites serve as soil amendments, improving soil structure, water retention, and nutrient availability. The slow-release properties of the composite benefit plant growth and contribute to reducing the environmental impact of conventional fertilizers. These composites find further use in textiles, acting as coatings to impart flame retardancy, antimicrobial properties, and enhanced durability. Their incorporation enhances the overall performance and functionality of textile materials. Additionally, CS/clay composites are instrumental in the development of biodegradable films and membranes suitable for various applications, including agricultural mulching films and environmentally friendly packaging materials.

The versatility of CS/clay composites is extensive and continuously evolving as researchers delve into novel applications and refine the composition of these materials. Nevertheless, careful consideration of factors such as the type of clay, component ratios, and processing conditions is paramount to customize the composite properties for specific applications. Furthermore, successful integration into various industries necessitates attention to regulatory considerations, biocompatibility, and assessments of environmental impact are crucial aspects to ensure the responsible and effective deployment of CS/clay composites across a diverse range of applications.

The primary objective of this thesis is to engage in a comprehensive exploration of the chemical modification of CS using BPB as a modifying agent and subsequent characterization of the resulting modified CS. This involves a systematic investigation into the structural, morphological, and chemical changes induced by the chemical modification process. By employing various analytical techniques, the aim is to gain insights into the modified CS's unique properties and potential applications in diverse fields.

In addition to the modification of CS, this research endeavors to prepare CS/clay biocomposites and systematic characterization to evaluate their properties. The investigation will delve into the interactions between CS and clay, aiming to understand the resulting structural configurations and enhancements in the material's overall properties. The comprehensive characterizations will encompass various analytical tools, such as spectroscopy, microscopy, and thermal analysis, providing a holistic understanding of the biocomposites' structural and functional attributes.

Overall, this thesis seeks to contribute to the scientific knowledge around chemically modified CS and CS/clay biocomposites. The outcomes of this research hold the potential to advance the understanding of these materials and open avenues for their application in fields ranging from biomedicine to environmental science and beyond.