

# ***Facile Preparation of Chitosan/Clay Biocomposites and their Characterizations***

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## Summary and conclusion

This thesis details the synthesis of MCS, which involved the interaction between CS and BPB in the presence of TEA and DMF. Various characterization techniques, including FT-IR, UV/Vis, XRD, SEM, TGA, DSC, and NMR, were employed. The FT-IR analysis revealed a shift in the absorption peak of the secondary -OH groups on the CS molecule to  $1085\text{ cm}^{-1}$ . Additionally, the absorption peak of the primary amine group moved to a lower wavenumber in the case of the MCS molecule, indicating a reaction between the secondary -OH group and primary -NH<sub>2</sub> group of CS molecules with BPB. Furthermore, a new carbonyl peak at  $1742\text{ cm}^{-1}$  emerged in the MCS, suggesting the successful grafting of BPB onto CS. Notably, MCS displayed a broad UV-Vis absorption band ranging from 450 to 650 nm, a feature absent in CS, highlighting the occurrence of the reaction between CS and BPB. The XRD pattern confirmed a modification in the crystallinity of CS due to the inclusion of the BPB group. SEM micrographs indicated that the surface roughness of MCS surpassed that of pure CS, possibly attributed to interactions involving the amine or hydroxyl groups of CS. The introduction of the BPB group resulted in decreased thermal stability compared to pure CS, providing clear evidence of a significant chemical modification in CS. The reduced thermal stability strongly suggests the formation of a chemical bond between these molecules, corroborating the presence of the reaction. Additionally, the DSC study demonstrated that the establishment of a chemical connection between CS and BPB led to a reduction in the thermal stability of MCS. The NMR study suggested the existence of the carbonyl carbon from BPB, potentially indicating grafting through the N-atom. The antibacterial efficacy of both CS and MCS was assessed, revealing heightened inhibition for MCS in comparison to pure CS against both gram-negative and gram-positive bacteria. Utilizing the B3LYP functional, a quantum chemical investigation was carried out to explore the two potential reaction pathways when the CS monomer reacts with BPB. The calculated IRC paths and energy barriers consistently point towards the more probable occurrence of the formation of product P2 in reaction R-2. Thus, the collective analyses strongly support the occurrence of the reaction between CS and BPB. Both FT-IR and SEM analyses suggest that the secondary -OH group and primary -NH<sub>2</sub> group of CS molecules underwent a reaction with BPB. Furthermore, NMR analysis indicates the presence of carbonyl carbon from BPB, potentially through the N-atom. The theoretical investigation suggests that both the primary and secondary -OH groups of CS molecules have the potential for a reaction with BPB, with a higher likelihood of the reaction occurring with the secondary -OH group.

In summary, it can be confirmed that the BPB group is capable of undergoing grafting onto CS through the primary O-atom, secondary O-atom, and primary N-atom.

The thesis also reports the preparation of four films comprising CS and KAO clay at varying weight ratios in a 2% acetic acid solution. The weight ratios of the biocomposite films were maintained at approximately 10:01, 10:02, 10:03, and 10:04, respectively. Comprehensive characterization of all biocomposite films was conducted through various physicochemical methods, including FT-IR, UV/Vis, XRD, SEM, UTM, TGA/DTA, and DSC. Antibacterial activities against *Escherichia coli* and *Bacillus subtilis* were assessed for the biocomposite films. Additionally, swelling tests were performed on the biocomposite films to evaluate their solvent uptake behaviour. FT-IR analysis indicates a notable shift in the absorption band from  $1639\text{ cm}^{-1}$  in the CS film to  $1624\text{ cm}^{-1}$  in the CS/KAO clay biocomposite films. The biocomposites exhibit higher UV/Vis absorption compared to the pure CS matrix. The XRD pattern verifies the effective incorporation of KAO clay into CS at four different concentrations. SEM micrographs reveal that in the CS/KAO-1 biocomposite, clay particles are uniformly dispersed, resulting exfoliated structure. Conversely, in CS/KAO-2 and CS/KAO-3, the interaction between filler and matrix is more pronounced. The presence of a fibrous network and a rough surface in CS/KAO-4 can be attributed to the elevated concentration of KAO clay within the CS matrix. The gradual incorporation of filler accounts for the enhancement in the mechanical properties of the biocomposites. Notably, the biocomposite films demonstrate superior thermal stability compared to the CS matrix, and this stability further improves with an increase in the amount of clay incorporated into the CS matrix. DSC results suggest that the composite formation contributes to the enhanced thermal stability of CS. The antibacterial activity of the biocomposite films was assessed, revealing a substantial inhibitory effect against *Escherichia coli*, surpassing their impact on the *Bacillus subtilis*. The swelling experiment reveals distinct water absorption capacities for CS and CS/KAO clay biocomposites, and the increase in clay content is inversely proportional to the swelling of the films. Literature analysis suggests various applications for CS/KAO clay biocomposites. Due to the favourable combination of robust tensile strength and notable antibacterial properties exhibited by the synthesized biocomposites, they present a promising potential for utilization in food packaging applications. While all biocomposites exhibit potential as food packaging materials, CS/KAO-2 stands out by displaying the highest zone of inhibition against *Escherichia coli*. Hence, among the biocomposites, CS/KAO-2 is identified as the most promising material for food packaging

applications. Additionally, it is noteworthy that among all the biocomposites, CS/KAO-2 exhibits a more uniform and smoother surface, making it particularly well-suited for industrial applications. Moreover, the biocomposites, being rich in clay, may demonstrate enhanced performance in the absorption of various cationic dyes and heavy metals. Based on literature investigations, it is suggested that CS/KAO-4 could potentially show superior performance in cationic dye uptake, given its highest KAO clay content, while CS/KAO-1 may be more effective in adsorbing heavy metals due to its lower amount of KAO clay. The results indicate that CS/KAO clay biocomposites possess exceptional properties, showcasing versatility for a wide range of applications. This suggests that they have the potential to capture a substantial market share globally.

Furthermore, the synthesized CS/BNTN and CS/SIO biocomposite films were subjected to analysis through FT-IR, UV/Vis, XRD, SEM, UTM, TGA, and DSC methods. FT-IR and UV-Vis analyses highlight the interactions between CS and clay particles in the prepared biocomposite, confirming the successful formation of the biocomposite rather than a mere physical mixture. The XRD and SEM analyses play a crucial role in elucidating the distribution of clay particles within the CS molecule. In comparison, CS/BNTN biocomposite films exhibit a slightly more intricate crystalline structure than the CS/SIO biocomposite films. SEM micrographs depict an intercalated morphology evident in both types of biocomposite films. Across all biocomposite films, there was an observed enhancement in mechanical properties. In comparison to CS/SIO and CS/KAO biocomposite films, CS/BNTN biocomposite films demonstrate a higher tensile strength. The thermal stability of all biocomposite films was noteworthy. Notably, the CS/SIO biocomposite films exhibited superior thermal stability compared to both CS/BNTN and CS/KAO biocomposite films. Antimicrobial activity results indicate strong inhibition of both gram-negative and gram-positive bacterial growth by all biocomposite films. Particularly noteworthy is the CS/BNTN biocomposite film, which displays the highest zone of inhibition against both types of bacteria. Among the synthesized biocomposite films, CS/BNTN-3 stands out with superior mechanical properties and significant antimicrobial efficacy compared to the other two. Hence, based on its superior mechanical properties and significant antimicrobial efficacy, CS/BNTN-3 is considered an excellent candidate for applications in food packaging materials.

## **Future prospective of this study**

CS-g-BPB is likely being explored for its use as a macroinitiator in controlled polymerization reactions, particularly in the synthesis of block copolymers or functionalized CS derivatives. CS, as a natural polysaccharide, has applications in biomedical and pharmaceutical fields. The introduction of BPB may enhance the functionalization of CS, making it suitable for drug delivery systems, wound healing, or tissue engineering. The ability to control polymerization processes using CS-g-BPB as a macroinitiator could lead to the development of smart materials with responsive properties, such as stimuli-responsive hydrogels for controlled drug release or environmental sensors. CS-g-BPB may find applications in surface modification of materials, improving adhesion, and imparting specific functionalities. This can be particularly relevant in the development of advanced coatings or biomaterial interfaces. CS derivatives are known for their biodegradability and biocompatibility. Future research might explore the use of CS-g-BPB in designing eco-friendly materials for environmental applications, such as water purification or soil remediation. The integration of CS-g-BPB into polymer nanocomposites could lead to the development of materials with enhanced mechanical, thermal, or barrier properties. This is crucial for industries such as packaging or materials engineering. The future perspective also depends on collaborative efforts between researchers from various disciplines. Collaborations between polymer chemists, material scientists, and experts in specific application areas could lead to innovative solutions and new applications for CS-g-BPB.

Moreover, CS/clay biocomposites may find increased use in biomedical applications, such as drug delivery systems, tissue engineering, and wound healing. The incorporation of clay nanoparticles could enhance the mechanical properties and controlled release characteristics of CS-based materials. CS, known for its biodegradability and antimicrobial properties, combined with clay nanoparticles, can be explored for developing environmentally friendly food packaging materials. These biocomposites may help extend the shelf life of food products and reduce the environmental impact of packaging waste. CS/clay biocomposites may be employed for water purification purposes. The clay content could provide adsorption properties, while CS contributes antimicrobial features. This combination could lead to the development of efficient water treatment materials for removing contaminants and pathogens. The integration of responsive clay nanoparticles into CS matrices may result in the creation of smart materials with tunable properties in response to environmental stimuli. This could lead to the development of sensors, actuators, or other adaptive devices. CS/clay

nanocomposites could be explored further for the development of thin films and coatings with enhanced mechanical strength, barrier properties, and durability. Such materials could be applied in various industries, including automotive, packaging, and construction. CS/clay biocomposites might find applications in agriculture, acting as environmentally friendly and sustainable materials for controlled-release fertilizers, soil amendments, or seed coatings. The combination of CS and clay could enhance nutrient retention and water absorption. CS/clay biocomposites could be investigated for their potential in sustainable construction materials, such as biodegradable and eco-friendly composites for insulation, panels, or coatings. The unique properties of CS/clay biocomposites, such as their mechanical strength and ion exchange capabilities, may be explored for use in energy storage devices, such as supercapacitors or batteries.

Furthermore, we can also prepare CS-g-BPB/clay biocomposite films and compare them with our prepared CS/clay biocomposite films.