EFFECT OF MALEIC ANHYDRIDE ON THE PHYSICOCHEMICAL PROPERTIES OF CHITOSAN

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Abstract

Chitosan (CS) has been explored in various fields due to its specific properties. Modifications to the glucopyranoside ring of chitosan expand its applicability, improving its existing characteristics and enabling new applications. This study aimed to modify CS with maleic anhydride (MA) at two different temperatures (30°C and 60°C) to investigate the influence of reaction conditions on the properties of the resulting complex.The effect of maleic anhydride on chitosan has been studied using Infrared Spectroscopy (ATR-FTIR), Tensile tests and Contact Angle Measurements. The attachment of MA to the CS backbone has been confirmed by infrared spectroscopy. The mechanical properties and surface free energy values show considerable differences compared to those of pure CS. The results demonstrate that MA incorporation significantly alters the structure–property relationships of CS films. The Young's modulus values were higher, and the contact angle results indicate the improved hydrophilicity of the grafted samples. The physicochemical properties were significantly improved after the incorporation of MA, due to hydrogen bonds formed within the CS matrix. This work establishes a foundational understanding of the basic physicochemical properties of CS–MA complexes and demonstrates how these properties can be tailored through controlled modification toward developing advanced functional systems for biomedical applications such as wound dressing, tissue engineering scaffolds etc.

Keywords: *Chitosan, Maleic Anhydride, Modification, Mechanical properties, Structure*

Introduction

Chitosan (CS) is a biopolymer widely available from the shells of marine animals, such as shrimps and crabs [1-3]. Chitosan, extracted from shrimp waste, has attracted significant interest, particularly in biomedical fields. It is a cationic biopolymer, soluble in organic acids such as acetic and lactic acids, with specific properties due to the presence of amine (-NH_2) and hydroxyl (-OH) groups [4]. It is also an alkaline polysaccharide, a copolymer of glucosamine and N-acetylglucosamine, bridged by a β(1-4) linkage [5, 6], with properties including non-toxicity, biodegradability, biocompatibility, and excellent film-forming capacity [7, 8]. Due to the presence of -NH_2 groups, it exhibits strong crosslinking properties and can be processed into various forms, including films, hydrogels, xerogels, and tablets. The properties of CS based complexes depend on some major factors, such as the molecular weight and degree of deacetylation of chitosan and the solvent used [9]. Despite these advantages, chitosan has drawbacks, including brittleness and low mechanical strength [10-12]. To address the challenge, several strategies have been developed to date. One of the most important steps is the chemical modification of chitosan by crosslinking with low-molecular-weight compounds, such as plasticisers [13, 14]. This modification of the CS matrix can increase its mechanical properties, as additives within the matrix can form a three-dimensional network. This approach can yield new CS derivatives with improved functional properties and expand their application range. One such peculiar compound that can be used for crosslinking with chitosan is Maleic Anhydride (MA). MA is not a typical phenyl monomer; it can provide carboxyl groups and double bonds, which enhance interactions with the CS matrix and can directly improve chitosan's mechanical performance [15, 16]. Some reports show that crosslinking CS with MA, along with other components, improves mechanical properties and biological responses [17-19]. Pan Xingyu et al. [7] reported that maleic anhydride incorporated into CS, and that a composite film made from CS, MA, and Polybutylene adipate terephthalate (PBAT) exhibited better mechanical properties and cross-sectional morphology. Muhammad Ridwan Septiawan et al. [20] reported that functionalizing chitosan with maleic anhydride using both heterogeneous and blending methods improved the chitosan membrane's proton exchange membrane performance. In another report, Janete M. Sousa et al. [21] reported that maleic anhydride grafted CS with ethylenediamine showed cytotoxicity against normal human lung fibroblast cells, with a significant decrease after incorporation of the amino group.

In this study, our objective was to examine and compare the effect of MA modification on CS at 30°C and 60°C. The two distinct temperatures were selected to understand the influence of mild versus moderately elevated reaction conditions on the extent of interaction between CS and MA. Temperature plays a major role in controlling reaction kinetics and degree of modification. The previous studies have reported that the modification of chitosan using various anhydrides, including MA, a comparison of temperature dependent modification and its direct effect on mechanical properties and surface characteristics remains limited. This work addresses this gap by correlating reaction conditions with physicochemical performance, thereby providing a clearer understanding of how controlled modification influences the behaviour of the polymers used. The novelty of this study lies in establishing a direct relationship between modification temperature, MA incorporation, and the resulting mechanical and surface properties of CS films. This approach provides a simplified yet effective pathway to tune chitosan-based materials in extending its approach toward advanced applications such as tissue engineering scaffolds, wound dressings, and drug delivery systems, where controlled mechanical strength and surface properties are essential.

Materials and methods

The Chitosan powder with a degree of deacetylation 88% and viscosity-average molecular weight of 972000 g/mol

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was purchased from Pol-Aura (FIG. 1). Maleic Anhydride (98%) was obtained from Sigma Aldrich (FIG. 2). Glacial Acetic acid of 99.9% purity was obtained from Chempur. All chemicals used in this study are of analytical grade.

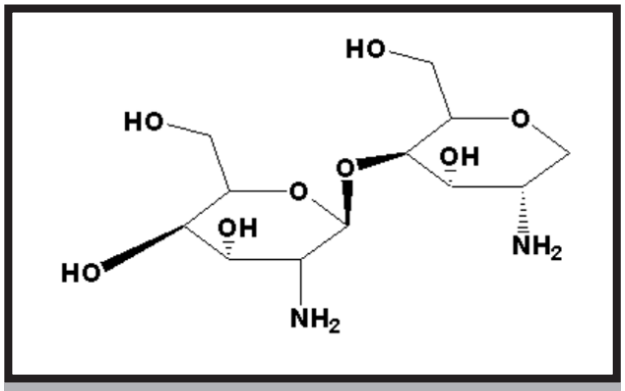

FIG.1. Chemical structure of Chitosan

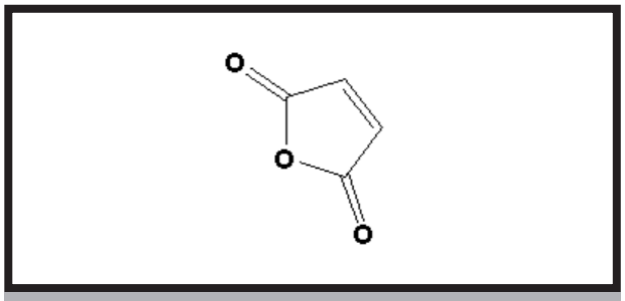

FIG.2. Chemical structure of Maleic Anhydride

Preparation of CS and CS-MA Films

To prepare a 2 wt% solution, 2 g CS powder is dissolved in 1% acetic acid solution at room temperature, and the mixture is stirred with a magnetic stirrer for 6 hours. The 25 ml solution is taken and poured into a 10 cm × 10 cm side Petri dish. The sample was kept inside the oven at 50°C for 24 hours.

To prepare CS-MA films, 1g of MA was used at different temperatures, as shown in Table 1. MA was first dissolved in a 1% acetic acid solution. After complete dissolution, 2 g of chitosan was added to the solution. The solution is stirred for 6 hours using a magnetic stirrer at different temperatures. After stirring, 25 ml of the solution is poured into a Petri dish and kept in the oven at 50°C for 24 hours.

TABLE 1. Abbreviations, amount and temperature of materials used

Chitosan (CS)	Maleic Anhydride (MA)	Temperature (°C)	CS - MA Complex
2G	1G	30°C	MA 1G 30
2G	1G	60°C	MA 1G 60

Infrared Spectroscopy

The infrared spectra of CS and CS-MA films were recorded using a Nicolet iS10 spectrometer (Thermo Scientific, USA) operating in attenuated total reflectance mode with a diamond crystal. A total of 64 scans were performed at a resolution of 2 cm^{-1}. The measurements were recorded over the spectral range of 4000 cm^{-1} to 400 cm^{-1}. The infrared spectra of the films were analyzed using Omnic 9.3.30 software (Thermo Scientific, USA).

Mechanical Tests

Mechanical properties were measured using a mechanical testing machine (Z.05, Zwick/Roell, Germany) for each film (ASTMD 638). Paddle-shaped samples were produced for mechanical testing. The Young's modulus, tensile strength and elongation at break were measured under room conditions using a Zwick Roell Z.05 materials testing machine (Zwick Roell, Ulm, Germany) with the speed starting position of 50 mm/min, the speed of the initial force of 5 mm/min, and the initial force of 0.1 MPa. The sample was 4 mm wide and 25 mm long. A total of 5 samples of each film type were tested.

Contact Angle Measurement

The contact angles of two liquids (water and diiodomethane) on the films were measured using a goniometer equipped with a drop shape analysis system (The Ossila Contact Angle Goniometer, Ossila BV, Leiden, Netherlands). Each contact angle represents an average of 10 measurements. The contact angle measurements were utilized to calculate the surface free energy (SFE) and its polar (SFE (s, P)) and dispersive (SFE (s, D)) components using the Owens–Wendt method [22].

Results and discussion

FTIR Spectroscopy Analysis

The effect of the MA addition on the CS films is examined by infrared analysis (ATR-FTIR). When components are mixed and reacted at the selected temperature, interactions and new bonds in the polymer matrix (FIG.3.) are reflected by changes in characteristic bands. FIG. 4. shows infrared spectra of the pure CS and MA and the modified films (MA-1G-60 and MA-1G-30) at two different temperatures. The broad band in the 3000–3500 cm^{-1} region found in the CS, MA-1G-60 and MA-1G-30 is due to the stretching of OH and NH groups [23]. The peak at 1589 cm^{-1} corresponds to the C=C stretching of maleic anhydride groups in the MA-1G-60 and MA-1G-30 samples [24]. The appearance of a new strong peak around 1705 cm^{-1} indicates the occurrence of a grafting process on the hydroxyl groups. The peaks at 1635 cm^{-1} and 1558 cm^{-1} in the MA-1G-30 and MA-1G-60 samples indicate the presence of amide I and amide II groups, suggesting amidation during the reaction [24]. At higher temperature (60°C), increased

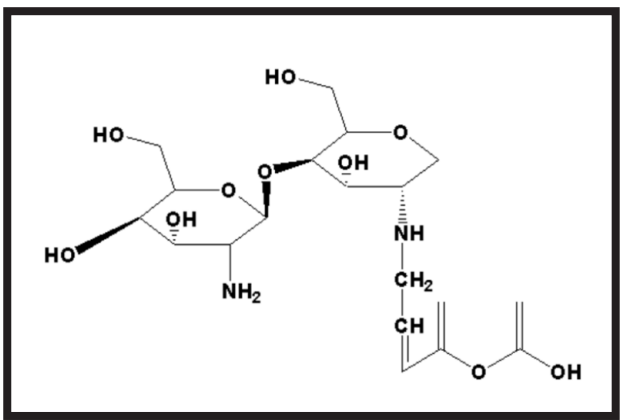

FIG.3. Chemical structure of Chitosan Maleic Anhydride Complex

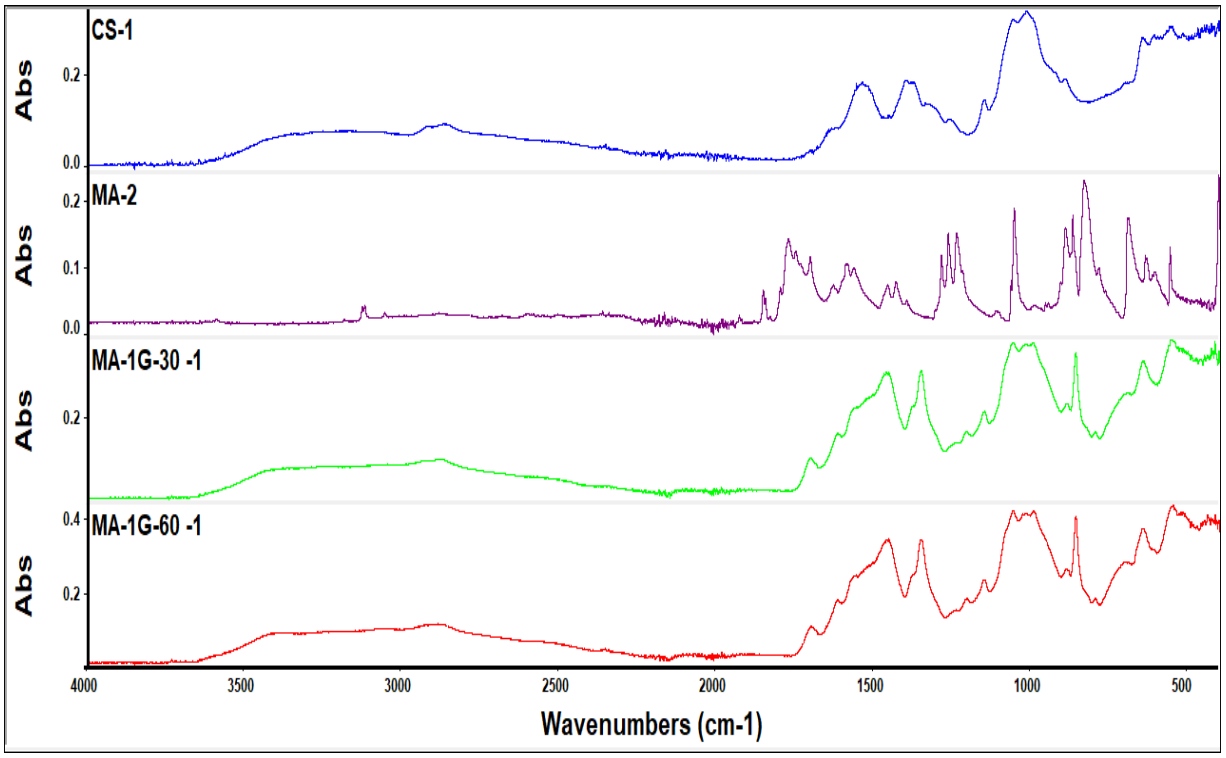

FIG.4. FTIR Spectra of films made of pure CS, MA -1G-30, MA-1G-60 and MA Flakes

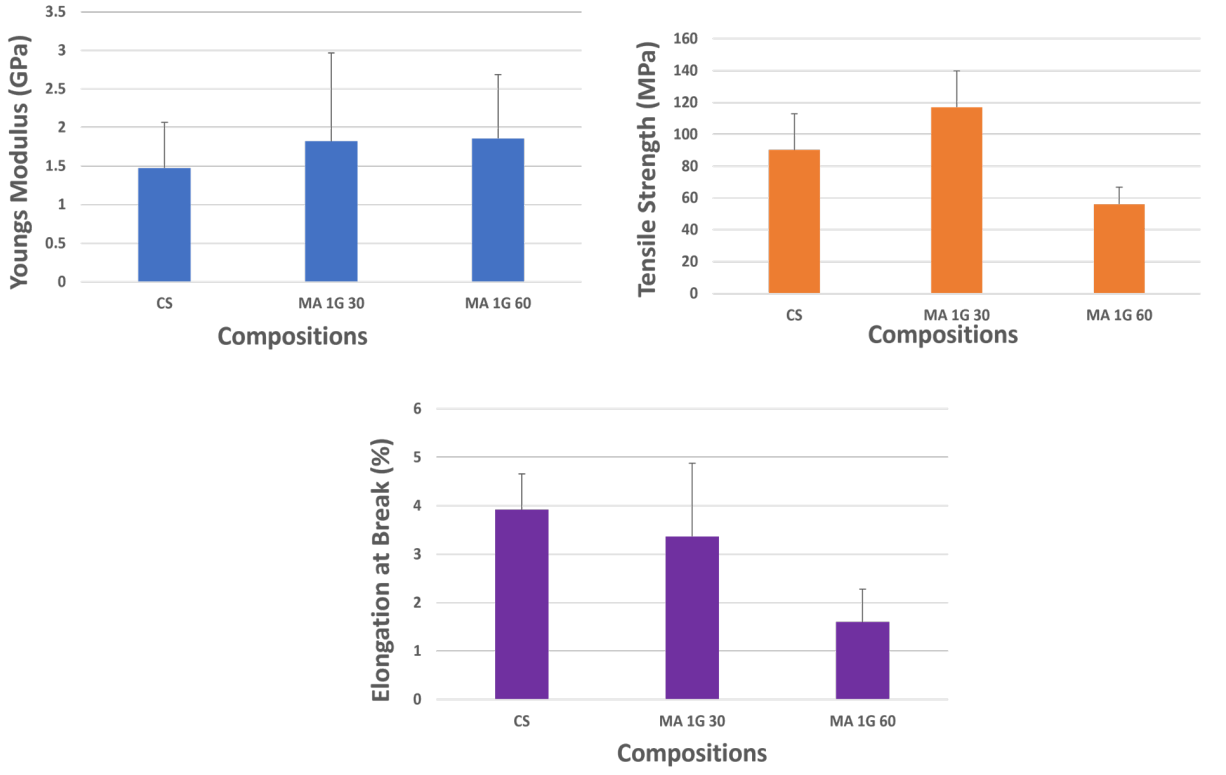

FIG.5. Young's modulus, Tensile Strength and Elongation at break values of CS, MA-1G-30 and MA-1G-60 samples

reaction kinetics may promote a higher degree of interaction between CS and MA, leading to changes in its physicochemical properties. The changes in the peak positions indicate successful MA grafting onto the CS backbone (FIG. 4).

Mechanical Test Analysis

The mechanical properties were measured for the three samples and are shown in FIG.5. The results of mechanical properties of CS as well as the MA grafted samples indicates that MA-1G-60 sample showed Young's modulus of 1.8 GPa and MA-1G-30 sample showed a Young's modulus of 1.9 GPa, while the pure CS sample exhibits a Young's modulus value of 1.5 GPa (FIG.5). It shows that adding 1 g MA at 60°C and 30°C shows increase in Young's modulus values as compared to pure CS and also exhibits less difference in the values at both the temperatures. A similar trend is also evident in the samples regarding their flexibility. The elongation at break values show the lowest values for MA-1G-60 and MA-1G-30 compared to the pure CS sample. Both the temperatures reflect conditions where consistent improvements in physicomechanical performance were observed without compromising material integrity. The mechanical property values obtained suggest that these samples can be used in medical applications, provided suitable crosslinking agents are added in the future, as the current values indicate a positive impact on CS mechanical performance, particularly after the addition of MA at higher temperatures. Moreover, these results indicate the potential of the MA grafted CS samples to advance in the biomedical applications, by the incorporation of suitable additives that can enhance their mechanical as well as biological response. These topics will be investigated in our upcoming research.

Contact Angle Analysis

The contact angles of two different liquids, water (W) (FIG.6.) and diiodomethane (D), on the film surface were studied. The surface free energy and its components were calculated using the Owens–Wendt model, which separates the total surface energy into dispersive and polar contributions. TABLE 2 presents the surface free energy (SFE (s)), and its dispersive (SFE (s, D)) and polar (SFE (s, P)) components. Analysis of the wetting angles with water (FIG.6) indicated that incorporating MA into CS decreased the water contact angle, suggesting that the samples became more hydrophilic. In contrast, the MA-grafted samples for diiodomethane showed irregularity. Among the CS and MA-1G-60 samples, the dispersive component of surface free energy prevailed (TABLE 2). The results indicate that incorporating maleic anhydride and varying the temperature influences both the wettability and the surface free energy of the films. The reduction in the water contact angle of the modified samples suggests enhanced hydrophilicity and greater wettability. At the same time, changes in the dispersive and polar components reflect modifications in intermolecular interactions within the CS–MA matrix. This corresponds to the result for the polar component of the surface free energy. The sample's increased hydrophilicity is an advantage for its cellular applications. However, this can be further advanced by the addition of suitable crosslinking agents, which can affect its hydrophilicity, thereby expanding its application area.

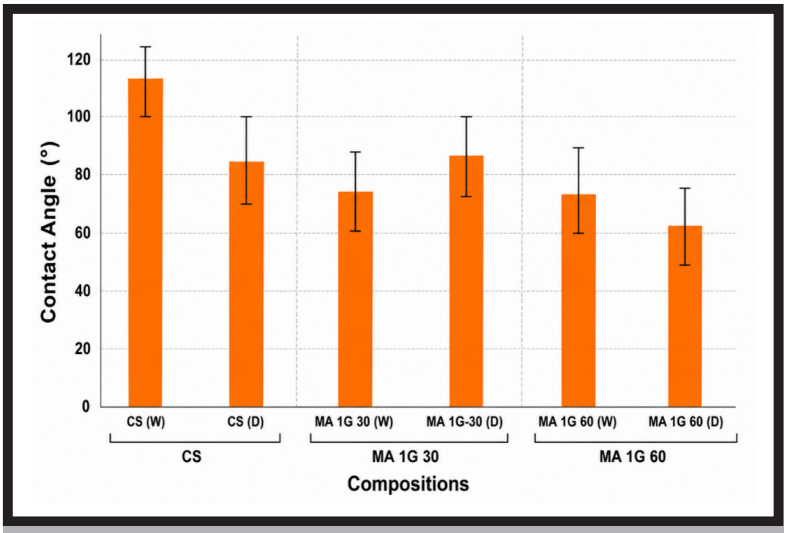

FIG.6. Comparison of Contact Angle Values of CS, MA 1G 30 and MA 1G 60 in water (W) and diidomethane (D) medium

TABLE 2. Values of surface free energy (SFE) and its dispersive (SFE (s, D)) and polar (SFE (s,P)) components for CS, MA-1G-30 and MA-1G-60

Samples	SFE (s) (mJ/m²)	SFE (s, D) (mJ/m²)	SFE (s,P) (mJ/m²)
CS	33.78±5.11	29.88±4.28	3.90±0.58
MA -1G-30	27.63±4.15	25.22±3.78	2.42±0.36
MA-1G-60	43.39±5.80	36.67±5.49	6.72±1.01

Conclusion

In this study, MA grafted CS films were synthesised by optimising the parameters under different temperatures. The pure and grafted samples in film form were analysed by IR spectroscopy, subjected to mechanical tests, and evaluated for contact angles. The research findings reveal the incorporation of MA into the CS matrix and the intermolecular interaction between the MA and CS molecules. This subsequently led to changes in the results of the MA-grafted samples, including their mechanical performance and surface free energy analysis. The Young's modulus was higher for the MA-1G-30 sample, followed by the MA-1G-60, while the elongation at break was higher for the CS sample than the grafted samples. The contact angle results reveal the improved hydrophilicity of the grafted samples. These changes are due to the chemical crosslinking of MA within the CS matrix, likely via hydrogen bonding, and these results have the potential to further enhance the properties of the grafted samples by crosslinking other suitable additives. There is a need to expand research on the CS-MA complex further to improve its biomedical applications, and these results could be a simple way to enhance current research.

Acknowledgments

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