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Preparation of Schiff Bases Derived from Chitosan and Investigate their Photostability and Thermal Stability

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This study intends to synthesize Schiff bases derived from chitosan and aromatic aldehyde to investigate their photo-stability. The surface morphology and chemical structure of modified polymer were characterized using different techniques such as infrared spectroscopy (FTIR), scanning electron microscope (SEM), microscopic images, atomic force microscopy (AFM), and energy dispersive X-Ray (EDX) mapping. The thermal stability of synthesized materials was determined using thermogravimetric analysis (TGA). The modification in the chemical structure and morphology of new Schiff bases were verified using FT-IR, NMR, AFM, and SEM, whereas the thermal properties were investigated by TGA**.** Thus it was demonstrated that the thermal stability of chitosan has improved after the modification with the corresponding aldehyde. The decomposition temperature (Td) of pure chitosan is about 220 °C while it is between 250-256 °C for modified Schiff bases. Two approaches were applied to investigate the physical photo-stability of modified chitosan the weight loss percentage, and monitoring of the functional group by FTIR. The weight loss percentages of blank films are much higher than modified chitosan polymeric films. This is because the photo-degradation of blank chitosan is faster when irradiated by UV light. The main reason is attached aldehydes groups are aromatic moieties that absorb light in the UV region and convert it to harmless heat. Compound 3 showed the best results this might be because of the existence of the phenol group which is known as an excellent free radical scavenger. Chitosan modification with aromatic aldehydes would have an accelerating effect on thermal decomposition and they are photo-stabilizers, we used many techniques to prove that like FESEM, AFM, weight loss, EDX, TGA.

Keywords: Chitosan, Schiff bases, Photo-stability, Photo-degradation, Weight loss

INTRODUCTION

Plastic goods are generally non-biodegradable and produced from non-renewable fossil resources [1,2]. Due to the rapid rise of the global population, the manufacturing of plastic materials has increased significantly. The incorrect disposal of a massive number of petroleum-derived plastics pollutes the environment, prompting the issue of how to replace them with biodegradable and renewable natural polymers [3]. The recycling of biological polymers should be regarded as an alternative to more typical recycling processes which have been prompted by scientists to develop novel polymers that can be returned to the biological cycle after usage. As a result, using readily biodegradable agricultural biopolymers would overcome these issues [4]. Biodegradable films and packaging materials created from renewable and natural polymers have grown in popularity over the last decade. Scientists have recently focused their efforts on creating innovative biodegradable hydrogels for many applications such as purification [9], drug delivery [5], and sensors [7]. Chitosan, which is made from chitin, one of the most common natural biopolymers, is becoming more commonly employed in a variety of industries due to its beneficial qualities. Chitosan

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is utilized in anticancer, immune-stimulating, and anti-cholesterol treatments, as well as microcapsules, stitch materials, and analysis membranes in medicine and pharmacy. Chitosan is available as a gel or a powder that is made from chitin that has been chemically N-deacetylated. Both have been shown to have biological roles [11]. It's a glucosamine and N-acetyl glucosamine copolymer connected by 14 glucosidic linkages formed via chitin N-deacetylation [12]. It is a semi-crystalline polysaccharide that is insoluble in water at neutral pH, unlike many biodegradable polymers [13]. Chitosan's film qualities are determined by its shape, which is influenced by molecular weight, N-acetylation degree, solvent evaporation, and the free amine regenerating mechanism [14]. Generally, chitosan films are strong and flexible, according to the manufacturer [15]. This opens up the possibility of making a variety of films with crawfish chitosan and organic acid solvents. A thorough examination of these films' sorption properties would enable the efficient selection of crawfish chitosan films that are less susceptible to dampness. As a result, research was carried out to identify the impacts of various chitosan and solvent types on the sorption behavior of crawfish chitosan films, as well as to develop models to propose their sorption behavior of them [16]. Chitosan has reactive groups at positions C-2 (-NH_2), C-3, and C-6 (-OH), which can be exploited to chemically modify its physico-chemical characteristics under moderate reaction conditions [17,18]. Several chemical alterations are conceivable due to the presence of amino groups in its structure, such as the formation of Schiff bases from different aldehyde and ketone molecules [19-21]. In this study, we prepared Schiff bases from the reaction between chitosan and some aromatic aldehydes in an aqueous acetic acid solution. The synthesized polymer was analyzed by FTIR, (AFM), (SEM), (EDX), and thermogravimetric analyses (TGA-DTG). The main purpose of this study is to improve the thermal stability and photostability of chitosan to make it better for daily use

MATERIALS AND METHODS

Materials

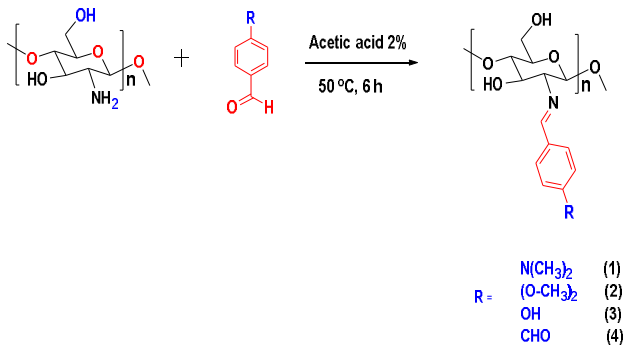
Chitosan (MW. 50,000-100,000Dalton) was obtained from CDH. All aldehydes, NaOH, and acetic acid (purity 99%) were purchased from Sigma Aldrich Company.

Characterization of Samples

SHIMADZU UV-1650PC instrument was used to measure FTIR in the wavenumber range of 400-4000 cm^{-1}. The surface morphology of materials was examined using a HITACHI S-4160 Field Emission Scanning Electron Microscope (FE-SEM). In 1% HCl per D_2O volume at a concentration of 10 mg ml^{-1} the synthesized compound (1-4) was dissolved to obtain ^1H NMR spectra using BRUKER (500 MHz) spectrometer. DuPont 2000 thermal analysis equipment was used to perform TGA/DTA analysis at an increasing rate of the temperature of 5 °C per min with a heating rate from 30 to 800 °C in an air environment. AFM-Ara Pajohesh-0102/A microscopy was used to capture two- and three-dimension atomic force microscopy images of polymeric films before and after irradiation.

Preparation Schiff Bases Derived from Chitosan

The novel Schiff base derivatives were prepared by dissolving 0.5 g of chitosan in 25 ml of acetic acid (2%) with continuous stirring at room temperature for 6 h. The aldehyde was then dissolved in 10 ml ethanol and dropped into the chitosan solution, stirring constantly at 50 °C for another 6 h. The deep yellow gel was then filtered and rinsed with ethanol many times to eliminate any remaining aldehydes. We used NaOH (5%) to neutralize the finished result before washing it several times with distilled water. Finally, we dried the product overnight in a vacuum oven at 60 °C to get the target Schiff bases as shown in Scheme 1 [22].



Scheme 1. Modification of chitosan to form Schiff base compounds (1-4)

RESULTS AND DISCUSSION

Synthesis of Modified Chitosan Schiff Base Compounds (1-4)

The new four chitosan Schiff bases (1-4) were synthesized by reacting chitosan with corresponding benzaldehydes using 2% acetic acid to dissolve chitosan and ethanol to dissolve the aldehydes (see Scheme 1). Since these two solvents are miscible and chitosan is insoluble in ethanol at a percentage more than 50%. It was used in moderate conditions for this reaction hence the aldehyde was added dropwise to the reaction mixture and stirred at 50 ℃ for 6 h. The crude product was precipitated by adding ethanol to the reaction mixture and it was purified by washing it many times with ethanol to remove any unreacted aldehydes and traces amount of water. NaOH (5%) was also used to neutralize the product and then washed several times with distilled water. Lastly, we dried the product overnight in a vacuum oven at 60 ℃ to get the target Schiff bases as shown in Scheme 1 [23].

Characterization of Compounds (1-4) by FTIR

FTIR technique was used to demonstrate the chemical structure of products hence it was compared the spectra with the FTIR spectrum of pure chitosan. The stretching vibrations of both symmetric and asymmetric NH_2 groups have shown nice sharp doublet peaks at 3250 cm^{-1} and broadband at 3558 cm^{-1} for the OH stretching group, while CH stretching has shown bands at 2828 cm^{-1} of pure chitosan and a peak at 3060 cm^{-1} for C-H aromatic. However, the FTIR spectra of products showed the disappearance of peaks that belongs to the NH_2 group and the appearance of new singlet strong sharp peak at 1790 cm^{-1} which is referees the formation of the Schiff base group, this is clear evidence that demonstrates the synthesis of target products (1-4). The FTIR spectra of compounds 1 and 2 showed an increase of intensity for bands around 2900 cm^{-1} this is due to the presence of methyl groups within the aldehyde units. Thus compound 3 gives a broader and stronger peak at the region between 3200-3600 cm^{-1} the reason for that is the existence of the hydroxyl group at the para position of aldehyde moiety. Finally, compound 4 has an aldehyde group at the *para* position which appears at 1722 cm^{-1} as a sharp strong peak and this is good evidence that almost of aldehyde units have reacted from one side and did not make cross-linking.

Investigation of Chitosan and Schiff Bases Photo-dDegradation through Weight Loss

Cross-linking and cleavage of bonds occur during chitosan photo-degradation, resulting in the generation of gases such as N_2 gas and the development of tiny polymeric fragments [24]. The Chitosan sample loses weight as a result of the irradiation, which rises with increasing the irradiation time. Figure 1 shows the weight loss percentages versus irradiation time for blank chitosan and modified synthesized polymeric films (1-4). It is very obvious that the weight loss percentages of blank films are much higher than modified chitosan polymeric films. This is because the photo-degradation of blank chitosan is faster when irradiated by UV light. The main reason is attached aldehydes groups are aromatic moieties that absorb light in the UV region and convert it to harmless heat. Compound 3 showed the best results this might be because of the existence of the phenol group which is known as an excellent free radical scavenger.

The FTIR spectra of chitosan before and after irradiation by UV light. The exposure to UV light causes a significant change in substance chemical structures which results in consistent alterations in their FTIR spectra. All irradiated materials' spectra show significant alterations in the frequency region 3200-3600 cm^{-1}. For Schiff bases derived from chitosan, there is a change detected in the frequency range of (1550-1650) cm^{-1}, the peaks became

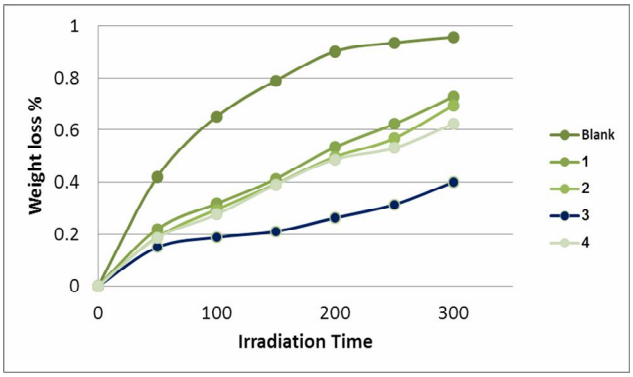


Fig. 1. Changes in weight loss (%) of blank Chitosan and compounds (1-4).

higher and sharper after irradiation, the reaction between chitosan and aromatic aldehydes has decreased the photo-degradation of chitosan and inhibit the creation of small fragments and working as UV-blocker and free radical scavengers.

Investigation Photo-degradation through Surface Morphology

The morphology of the irradiated blank chitosan film Fig. 2a was generally smooth with many dark spots, cracks, grooves, and some surface damage. The dark spots' appearance is generally because of chitosan decomposition [25]. The surface of Schiff bases derived from Chitosan was almost smooth with fewer groves or cracks on Schiff base 1 (b) the reason for these cracks is unknown; it could have something to do with the rate of the elimination of volatiles during the photo-degradation process. In Schiff base 3 (c) the film was very smooth and had few cracks on it, both Schiff bases have a noticeable change in color compared with chitosan

.

Surface Morphology by SEM

The surface morphology was studied by SEM to examine the morphology of both blank chitosan film and Schiff bases generated from it, as well as the porosity of such films. The surface of pure chitosan and chitosan-aromatic Schiff base reveal distinct variances in SEM images [26]. Figure 3 shows the morphology of pure chitosan and Schiff bases films. The pure chitosan film's images revealed that it is nonporous and has a simple

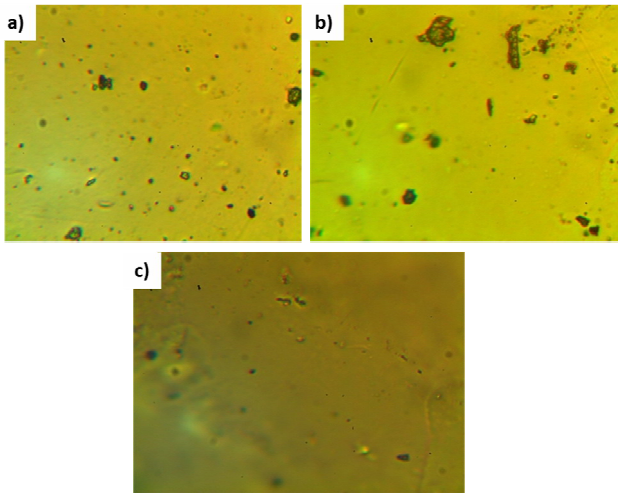


Fig. 2. Microscope image for a) pure chitosan, b) chitosan/1, and c) chitosan/3 films after irradiation.

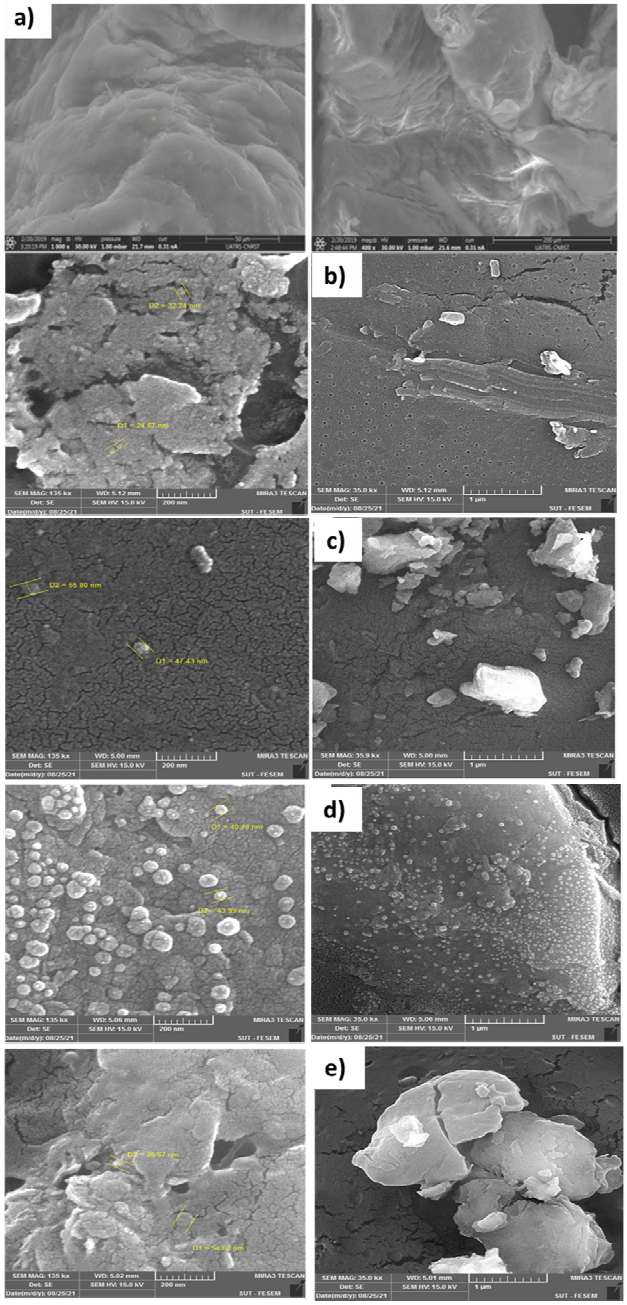


Fig. 3. SEM image (a) for pure chitosan, (b) for Schiff 1, (c) for Schiff 2, (d) for Schiff 3 and (e) for Schiff 4.

texture without clear pores. Surface roughness was higher in modified chitosan than in pure chitosan. Figure 3a shows SEM images of pure chitosan and the materials look more homogenous in comparison to modified chitosan in Figures b-e this is maybe because of the presence of aromatic Schiff bases units. This observation can be explained by the disruption of the backbone of the modified chitosan polymer as a result of the reaction of chitosan's amine groups with aromatic aldehydes, as well as the breaking of hydrogen bonds present in pure chitosan and interaction between the newly introduced hydrophobic phenyl groups.

Surface Morphology by Atomic Force Microscopy (AFM)

In order to understand the mechanism of chitosan and Schiff bases derived from it, the topography of the films was observed by AFM Fig. 4. The AFM analysis showed that the chitosan film exhibited a uniform structure, As can be seen, chitosan film was basically smooth [27]. In Schiff bases 1 and 2 have a high level of homogeneity and smoothness existed in the film. The (Rq) of Schiff base 1 film was (1.650) nm and was (1.877) nm in Schiff base III, less than the Rq (2.234) of the chitosan film, indicating that the reaction between chitosan and that aldehydes made the chitosan film smoother. When dimethoxy benzaldehyde and terphthaldehyde were reacted with chitosan, the roughness became more; the Rq for Schiff base 3 was (4.117) nm and Rq for Schiff base 4 was (4.764) nm, which was higher than that of chitosan film.

Energy Dispersive X-ray (EDX) Mapping

The EDX approach is an acceptable technique to recognize the elemental composition of polymeric materials [29]. Figure 5 shows the EDX of chitosan films to determine the C, O, and N elements to characterize the chemical structure of synthesized Schiff bases (1-4). The chemical compositions of modified Schiff bases, found in EDX Fig. 5b, c, and d showed no alteration in their chemical analysis, the only change is in the weight percentage of the elements, which means a reaction occurs between chitosan and aldehydes.

Thermogravimetric Analysis (TGA)

The TGA of pure chitosan and synthesized Schiff bases

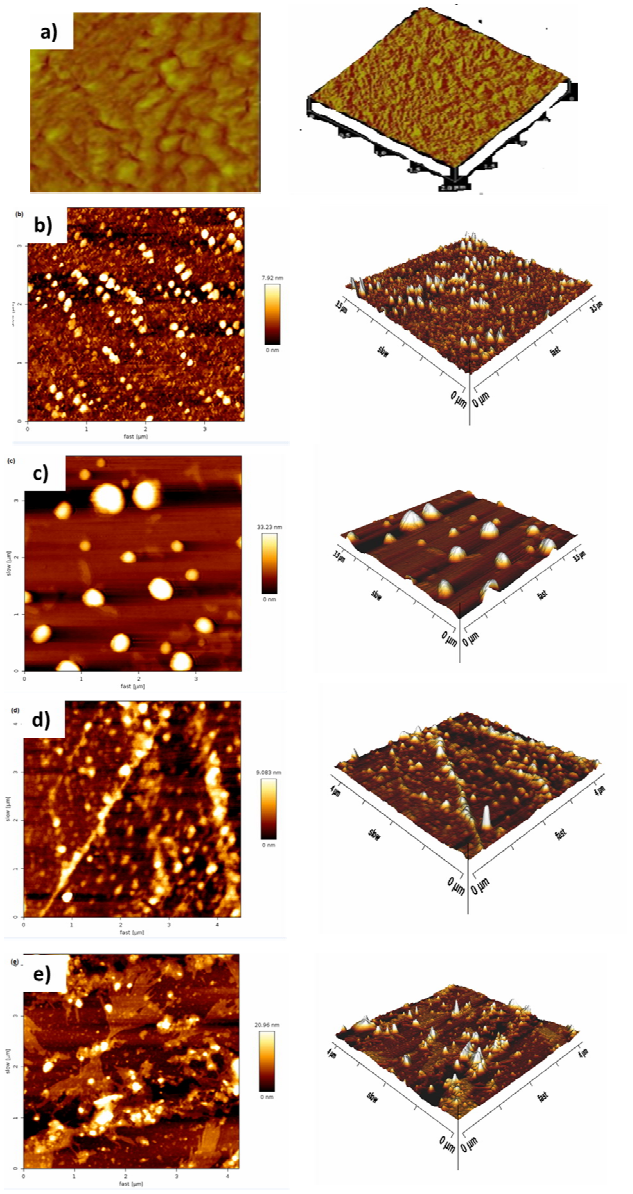


Fig. 4. AFM image (a) for pure chitosan [28], (b) for Schiff 1, (c) for Schiff 2,(d)for Schiff 3 and (e) for Schiff 4.

(1-4) was investigated hence the x-axis represents the increase of temperature by degree centigrade (°C) and the y-axis shows the weight loss percentage [30]. In general, for pure chitosan and Schiff bases' chitosan (1-4) there is a decrease in weight of about 10% this is due to the evaporation of water at temperatures between 100-150 °C. The most important outcome has been got from this

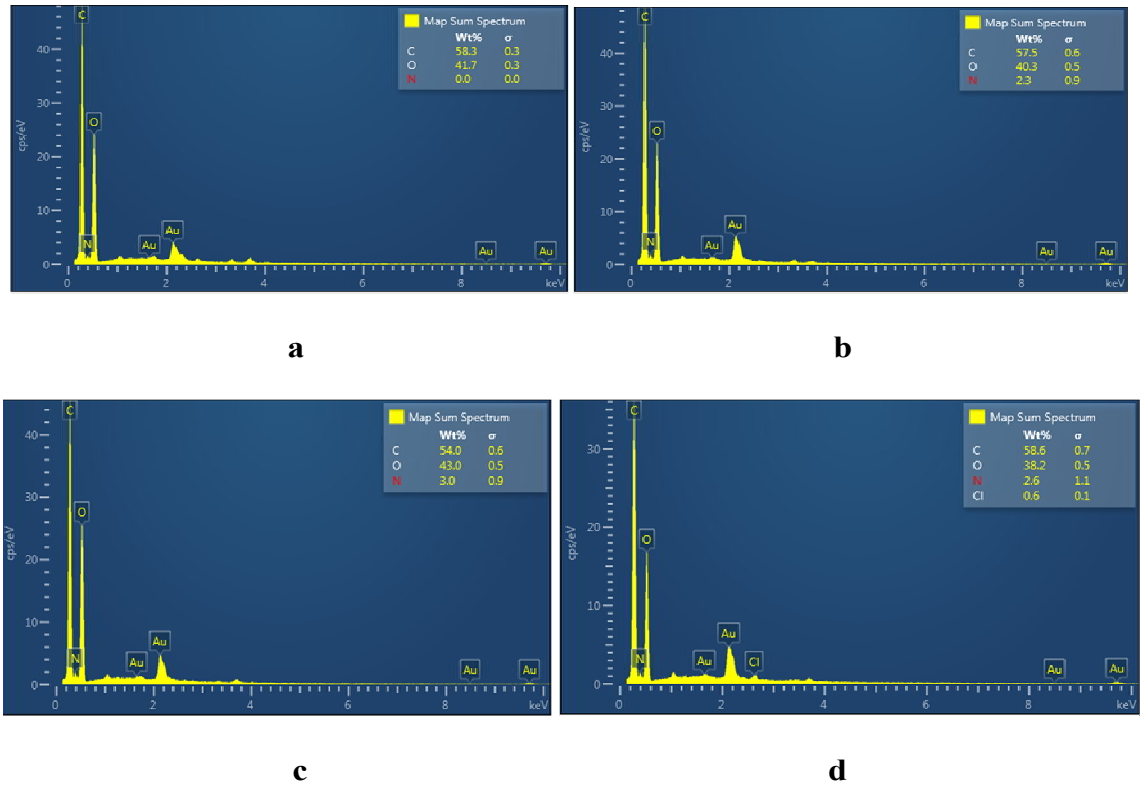


Fig. 5. EDX analysis (a) for pure chitosan, (b) for Schiff 1, (c) for Schiff 2, (d) for Schiff 3 and (e) for Schiff 4.

experiment is that the thermal stability of chitosan has improved after the modification with the corresponding aldehyde. This is because the decomposition temperature (T_d) of pure chitosan is about 220 °C while it is between 250-256 °C for modified Schiff bases. Almost of the materials were decomposed between 250 °C and 350 °C and the weight loss percentage reached 70%. It also noticed that even with increasing the temperature up 600 °C there are still some materials in the crucible weighing about 20% this is the remaining char. Table 1 summarized the thermal decompositions temperature of pure chitosan and synthesized Schiff bases (1-4).

DSC is a useful tool to characterize the thermal properties of chitosan and Schiff bases derived from it. DSC/TGA curve for pure chitosan film shows that this film lost about 10.35% of its weight at 194.47 °C, which may be due to the removal of the adsorbed solvent on the compound [31]. Then, in a fast stage at 349.14 °C, it shows a weight loss of 34.73%. The residual amount of the compound at 600 °C is about 15.57%. TGA/DSC curve for Schiff base 1 fig. shows that the film lost 12.84 at 150 °C, another peak showed 53.69% weight loss at 445.11 °C and 17.54% weight loss at 600 °C, the residual amount at 800 °C is 15.93%, for Schiff base 2 a peak shows 13.04% weight loss at 130.25 °C and 52.07% weight loss at 427 °C, and 610 °C 12.64% weight loss. The residual amount is 22.26%,

Table 1. Thermal Decomposition (T_d) Data for Pure Chitosan and Synthesized Schiff Bases (1-4)

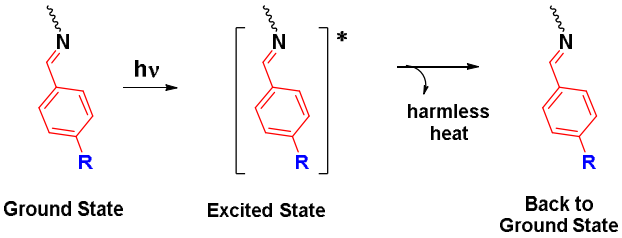
Compound	T_d (°C)
Pure chitosan	220
1	250
2	256
3	255
4	250

for Schiff base 3 DSC/TGA curve shows a weight loss of 19.35% at 221.57 °C, 38.53% at 410.97 °C and 19.60% at 610 °C, residual amount 22.53%, Schiff base 4 fig. show a weight loss of 6.902% up to 150 °C. After that, in one step and up to 420 °C, it loses another 38.21% of its weight, at 600 °C, this film also loses about 9.838% of its own weight. The residual amount of the compound was 45.05%

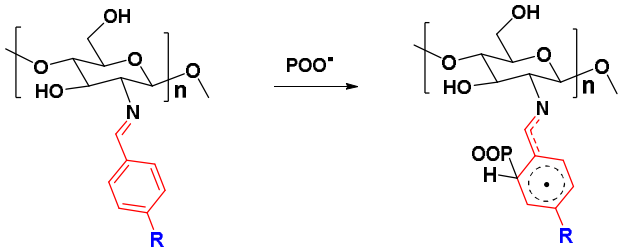
Synthesized Modified Chitosan: Proposed Stabilization Mechanisms

The results of the investigations above show that the novel synthesized modified chitosan is effectively stabilized for the chitosan films. In this part, several proposed processes for how modified aromatic units can work as photo-stabilizers of chitosan films will be presented [32]. As previously stated, the modified aromatic unit achieves the greatest results owing to the strong conjugated system including the Schiff's base and phenyl group. As a result, this complex has a strong capacity to absorb UV light through the aromatic system's π-bonds and transfer it from the ground state to the excited state [33]. Then the electrons go back again to the ground state with release harmless heat as shown in Scheme 2.

The peroxide radical (POO•) has a negative impact on chitosan polymeric films by forming various photo-oxidative compounds. The novel modification of chitosan by aromatic unit indicates excellent stability as it works as a radical scavenger [34]. Scheme 3 illustrates how the Schiff's base and aromatic ring can deal with peroxide free radicals without harming the chitosan backbone.



Scheme 2. Modified Schiff's base and phenyl group act as a UV absorber, proposed mechanism



Scheme 3. Schiff's base and aromatic ring stabilize the peroxide free radicals

CONCLUSIONS

To conclude, it was synthesized novel Schiff bases from chitosan and aromatic aldehyde and test their photo-stability. Different methods were used to assess the surface morphology and chemical structure of the modified polymer, including FTIR, SEM, microscopic images, AFM, and EDX mapping. Thermogravimetric analysis was used to assess the thermal stability of synthetic materials (TGA). The thermal characteristics of novel Schiff bases were examined using TGA. As a result of the alteration with the matching aldehyde, it was proven that chitosan's thermal stability has been enhanced. Pure chitosan decomposition temperature (Td) is at 220 °C, whereas modified Schiff bases decomposition temperature (Td) is between 250 and 256 °C. To evaluate the physical photo-stability of modified chitosan and the weight loss%, two methodologies were used: FTIR monitoring of the functional group and physical photo-stability of modified chitosan. Blank film degradation is considerably greater rate than modified chitosan. This is due to the fact that when exposed to UV radiation, blank chitosan degrades more quickly. The fundamental reason for this is because connected aldehydes groups are aromatic moieties that absorb UV radiation and convert it to safe heat. Compound 3 had the greatest results, which might be due to the presence of the phenol group, which is a good free radical scavenger.

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