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Synthesis and characterization of chitosan Schiff base derivatives

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ABSTRACT

The research on biopolymers and its derivatives has increased much attention towards the researchers in preparing a novel material. The biopolymers and its derivatives have vast applications due to its biodegradability, non toxicity and biocompatibility. The present study aimed to synthesis and characterizes novel chitosan Schiff base compounds using vanillin and O-vanillin. The prepared compounds were characterized under advanced analytical tools such as Fourier transform infrared spectroscopy (FTIR), X-ray diffraction studies (XRD), Thermal analysis (TGA and DSC) and SEM analysis. The results of FT-IR studies clearly indicate that chitosan Schiff base complex were effectively formed during blending. From the results of the XRD pattern, the change in crystallinity of the samples was elucidated. The thermal stability of the polymer complex was determined from the TGA and DSC studies. The SEM images showed the increased porosity of the chitosan derivatives.

INTRODUCTION

Schiff base compounds containing an imine group are usually formed by the condensation of a primary amine with an active carbonyl. Its attractiveness as analytical reagent rises from the fact that they enable simple and inexpensive determinations of various organic and inorganic substances [1]. Also they have better physiological activities and applications in antibacterial and antiviral fields. Among the substituted biopolymers, particularly noteworthy are the Schiff bases obtained by the reactions of the free amino groups of chitosan with an active carbonyl compound such as aldehyde or ketone [2]. Santos et al.,[3] have investigated not only Schiff base reaction with chitosan and salicylaldehyde, but also the degree of substitution of chitosan Schiff base using ¹H NMR.

These bases offer an efficient approach to protect the C-2 amino groups [4] or to coordinate with metal ions for enhancing the adsorption / complexation properties of the biopolymer yielding a complexing material with potential analytical and environmental applications [5]. The Schiff base reaction between amine groups and aldehyde groups increases the stability of the biopolymer [6].

The extension of Schiff base formation is called degree of substitution (DS). It is the number of free amino groups in relation to the Schiff bases on the substituted biopolymeric matrix. This is an important parameter that plays an important role in the application of Schiff bases.

Several chitosan Schiff base derivatives have been reported in literature. Thermal analysis of some chitosan Schiff bases was studied by Tirkistani [7], where the reaction of chitosan with aromatic aldehydes was studied. The main thermal process of the prepared polymer takes place at temperatures lower than the second degradation stage of

chitosan indicating that all the Schiff base polymers are less stable than chitosan. It seems that the instabilities of the Schiff base polymers compared with chitosan are due to the absence of the free amino group in the prepared polymers as they are replaced by the aromatic aldehyde.

Vanillin (chemical name: 3-methoxy-4-hydroxy benzaldehyde) is one of the most widely used flavorings in food, pharmaceuticals and daily chemicals [8]. Natural vanillin is produced by bioconversion or physical methods from natural materials. Even if vanillin occurs in trace amounts in different plants, the pods of the tropical *Vanilla* orchid still remain the only commercial source of natural vanillin. However, as a comparison, a hypothetical production of pure natural vanillin extracted from pods would lead to a cost variously calculated as being between 1200 and 4000 US\$ kg⁻¹, whereas, the price of the vanillin obtained by chemical synthesis is less than 15 US\$ kg⁻¹ [9,10].

Currently, approximately 50% of the worldwide production of synthetic vanillin is used as an intermediate for the production of herbicides, antifoaming agents or drugs [11, 12]. Besides, it is also used in household products, such as air-fresheners and floor polishes [13]. Because of its antioxidant and antimicrobial properties, vanillin could be used as food preservative [14, 15].

The scope of this study is the development of new Schiff bases. In the present work, bio- polymeric Schiff bases were prepared by reacting chitosan with benzaldehyde and its three derivatives, 4-methoxy, 4-methyl and 4-chloro and salicylaldehyde under mild acidic conditions. The uncrosslinked derivatives were characterized by FTIR spectroscopy, TGA, DSC, XRD and SEM and tested towards the cell uptake. The uncrosslinked chitosan Schiff base derivatives were studied for their antimicrobial activities.

MATERIALS AND METHODS

Materials

Chitosan was purchased from India Sea foods, Cochin, Kerala. O-Vanillin and Vanillin from Sigma Aldrich, India and all other chemicals used are of analytical grade. Millipore water was prepared in the laboratory by double distillation of deionised water in quartz distillation plant.

Fourier transform infrared studies

Fourier transform infrared spectra of chitosan Schiff base derivatives using KBR pellet method were recorded in the frequency range of 400 – 4000 cm⁻¹ using Thermo Nicolet AVATAR 330 spectrophotometer.

X – ray diffraction studies

X – ray diffractograms of samples were obtained using an X – ray powder diffractometer (XRD – SHIMADZU XD – D1) with Ni – filter and Cu K α radiation source. The relative intensity was recorded in the scattering range 2 θ , varying from 10° to 90°.

Thermogravimetric analysis

Thermogravimetric analysis of the chitosan Schiff base derivatives was conducted using the instrument SOT Q600 V8.0 Build 95, to measure their weight loss at different temperatures in the heating range 20° - 850 °C at a heating rate of 20 °C per minute.

Differential scanning calorimetric analysis

The thermal behavior of the chitosan Schiff base derivatives was studied using NET 2 SCH DSC thermal analyzer. The samples were inserted into the Al pan and DSC scan was made from 30°–300°C in nitrogen atmosphere at a heating rate of 20°C per minute. The results were recorded and analyzed.

Scanning Electron Microscopy (SEM)

The surface morphology and cross section morphology of chitosan Schiff base derivatives were observed with scanning electron microscopy to verify the compatibility of the mixtures of chitosan Schiff base derivatives. To analyze the samples, the films were cut into pieces of various sizes and wiped with a thin gold – palladium layer by a sputter coater unit (UG – microtech, UCK field, UK) and the cross section topography was analyzed with Cambridge Stereoscan 440 Scanning Electron Microscope (Leica, Cambridge UK).

RESULTS AND DISCUSSION

FTIR studies

Infrared (IR) spectroscopy is based on the absorption of IR-radiation in the chemical bonds, if the vibration of the bond is associated with change of permanent dipole moment (e.g. stretching, bending). FTIR has often been used as a useful tool in determining specific functional groups or chemical bonds that exist in a material. The presence of a peak at a specific wave number would indicate the presence of a specific chemical bond. The FTIR spectra of all prepared derivatives showed the characteristic peaks as discussed below.

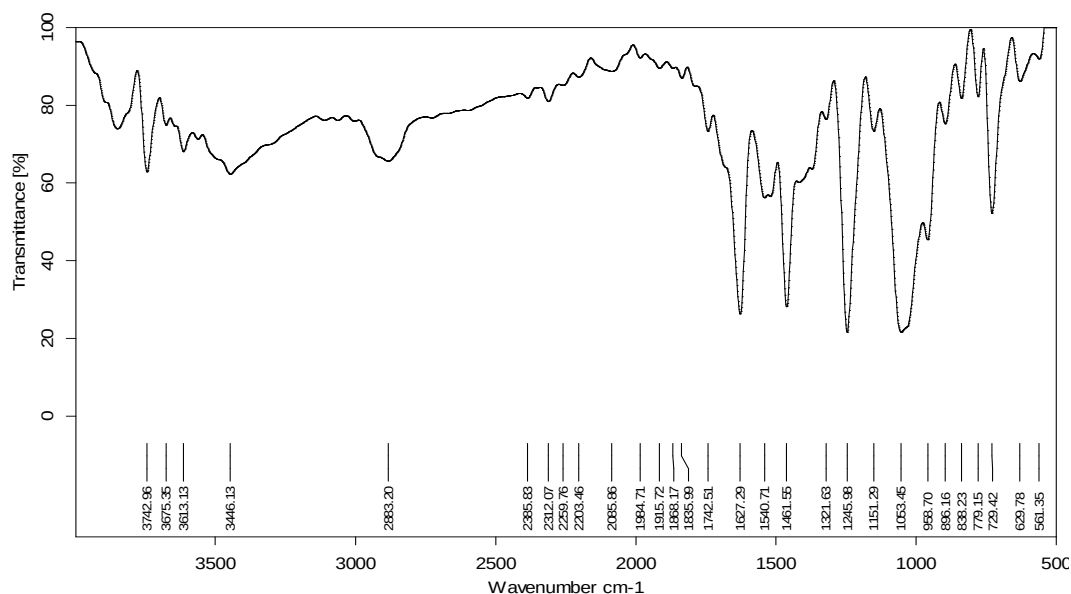


Figure- 1: FTIR spectrum of chitosan/o-vanillin

The FT-IR spectral details of **chitosan/o-vanillin Schiff base** was represented in the **figure-1**. The absorption peak observed at 3446.13cm^{-1} corresponds to the intermolecular hydrogen bonded OH stretching, NH stretching in secondary amides. The peak obtained at 2883.20 cm^{-1} and 1627.29 cm^{-1} confirms the presence of symmetric CH stretching in methylene group and C=O stretching in amides (amide-I band) respectively. Certain absorption bands which were obtained at 1540.71 cm^{-1} , corresponds to the N-H bending in secondary amides (amide II band), and at 1461.55 , 896.16 cm^{-1} OH in-plane bending seen, and symmetrical C-H bending in CH_3 at 1151.29 cm^{-1} , a peak at 1053.45 cm^{-1} corresponds to C-O-C linkage and 1245.98 cm^{-1} , C-O stretching and at 779.15 cm^{-1} C-H bending is seen respectively.

The FT-IR spectra of **chitosan/vanillin Schiff base** was represented in the **figure-2**. The absorption peak observed at 3363.72cm^{-1} corresponds to the intermolecular hydrogen bonded OH stretching, NH stretching in secondary amides. The peak obtained at 2922.79 cm^{-1} and 1645.06cm^{-1} confirms the presence of aliphatic CH stretching in methylene group and C=O stretching in amides (amide-I band) respectively. Certain absorption bands which were obtained at 1587.76 cm^{-1} corresponds to the N-H bending in secondary amides (amide II band), and at 1457.81 , 864.5 cm^{-1} OH in-plane bending seen, and symmetrical C-H bending in CH_3 at 1151 cm^{-1} , a peak at 1017.38 cm^{-1} corresponds to C-O-C linkage and 1274.78 cm^{-1} , C-O stretching and at 781.15 cm^{-1} C-H bending is seen respectively.

Thus the FTIR results clearly shows the interaction which was formed between chitosan matrix and the aldehydes. The formation of new imine linkages was confirmed by the peak at the range of 1627 and 1645 cm^{-1} for both the blends. Also the shifted in peaks were observed in the blends when compared with the FTIR of pure chitosan confirming the formation of chitosan Schiff bases.

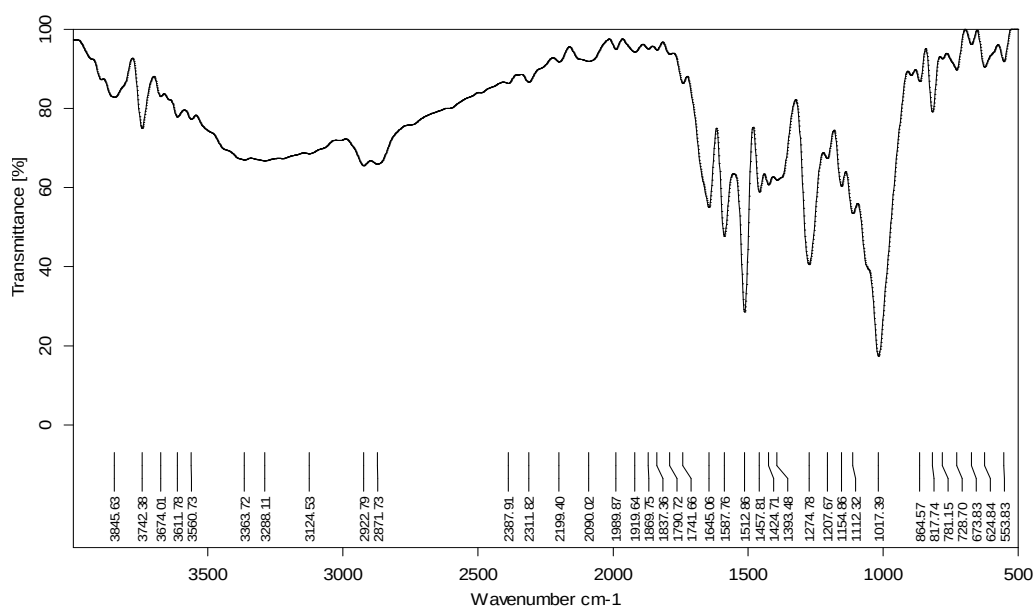


Figure- 2: FTIR spectrum of chitosan/vanillin

Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. TGA is a useful technique to assess the thermal stability of polymer and its blends. It is an important technique in which the mass of the substance is measured as a function of temperature, while the substance is subjected to controlled temperature programme. In any polymer analysis, the TG trace follows a relatively simple pattern. Thus the sample weight decreases slowly as the reaction begins, then decreases rapidly over a corresponding narrow temperature range and finally comes to a minimum as the reactants are spent.

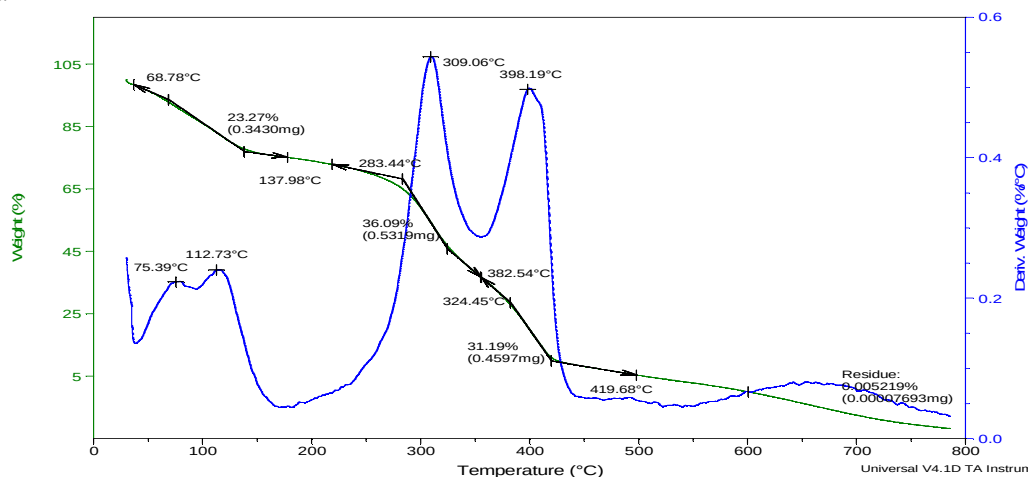


Figure- 3: TGA thermogram of chitosan/o-vanillin Schiff base

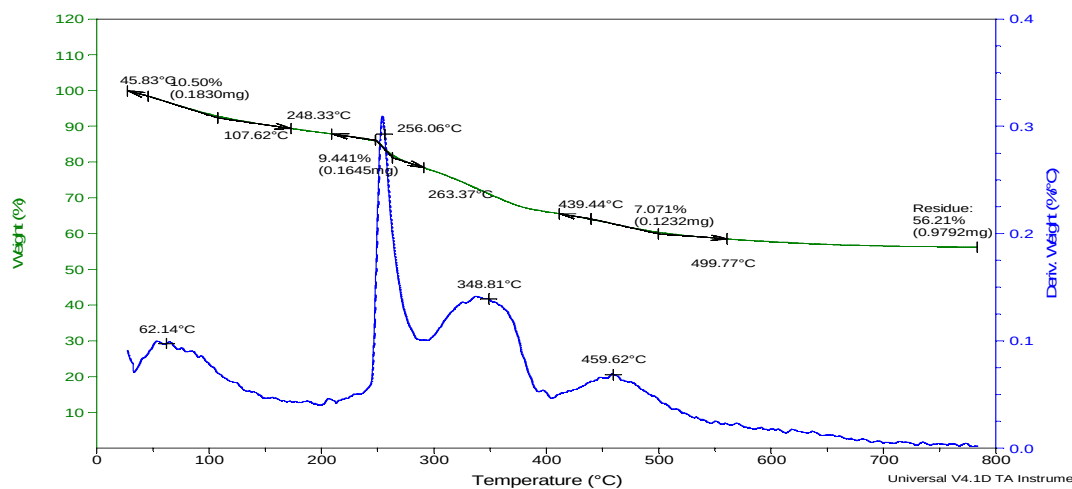


Figure- 4: TGA thermogram of chitosan/vanillin Schiff base

Figure 3 represent the TGA thermogram of chitosan/o-vanillin Schiff base. From the thermogram it is evident that 90% of the sample disintegrated within 410°C. At the end of the experiment around 0.005219% weight of the residue was left. Maximum weight loss occurred at 309°C – 382°C. **Figure 4** represent the TGA thermogram of chitosan/vanillin Schiff base. From the thermogram it is evident that 40% of the sample disintegrated within 460°C. At the end of the experiment around 56.21% weight of the residue was left. Therefore the chitosan derivative chitosan/vanillin Schiff base was found to have high thermal stability.

Differential Scanning Calorimetry

DSC helps in finding the glass transition temperature of polymers, polymer blends and polymer composites. Glass transition temperature (T_g) was taken as the midpoint of the heat capacity change, while the melting temperature (T_m) and crystallization temperature (T_c) were taken as the maximum of endothermic peak and the minimum of exothermic peak, respectively [17].

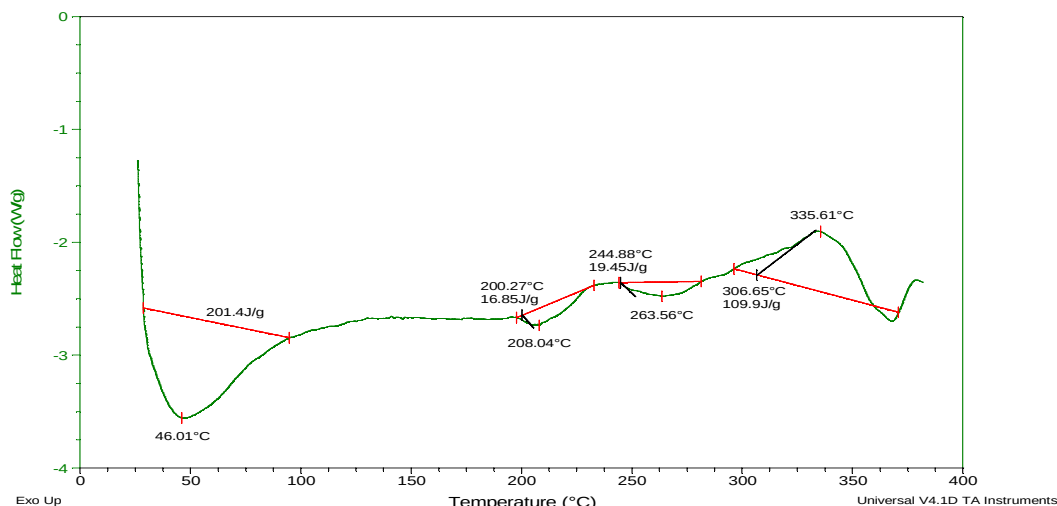


Figure – 5: DSC Thermal Studies of chitosan/o-vanillin Schiff base

The DSC thermogram of chitosan/O-Vanillin Schiff base was represented in **figure-5**. It showed only one endothermic peak (T_m) at 46.01°C showing the crystallization of the Schiff base derivative. The glass transition temperature (T_g) of the blend was observed at 200°C and the exothermic peak (T_c) at 335.61°C. **Figure 6** represents the DSC thermogram of chitosan/vanillin Schiff base. It showed only one endothermic peak (T_m) at

95.82°C showing the crystallization. The glass transition temperature (T_g) of the blend was observed at 220°C and the exothermic peak (T_c) at 362.20°C. The single T_g of both the Schiff base derivatives represents good miscibility and compatability.

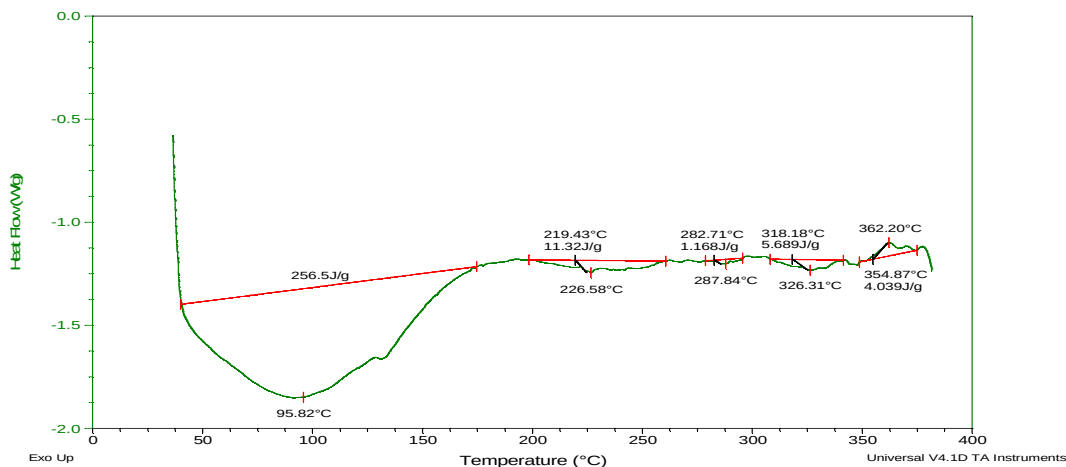


Figure – 6: DSC Thermogram of chitosan/vanillin Schiff base

X – Ray Diffraction Studies

The X-ray diffraction (XRD) analysis is a useful tool in determining the structure and crystallization of polymer matrices [18]. Powder X-ray diffraction patterns of various samples were measured to investigate the change of crystalline nature of chitin after blending. This has been proved to be a useful tool to study crystal lattice arrangements and yields very useful information on degree of sample crystallinity.

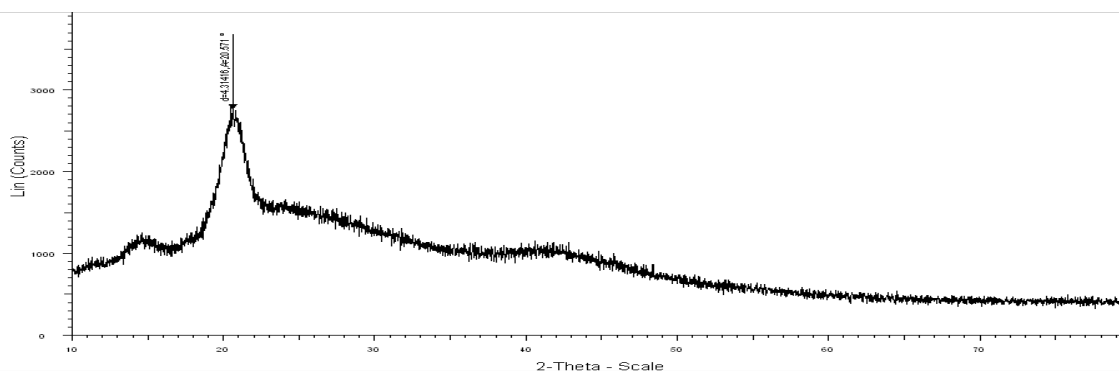


Figure- 7: XRD of chitosan/o-vanillin Schiff base

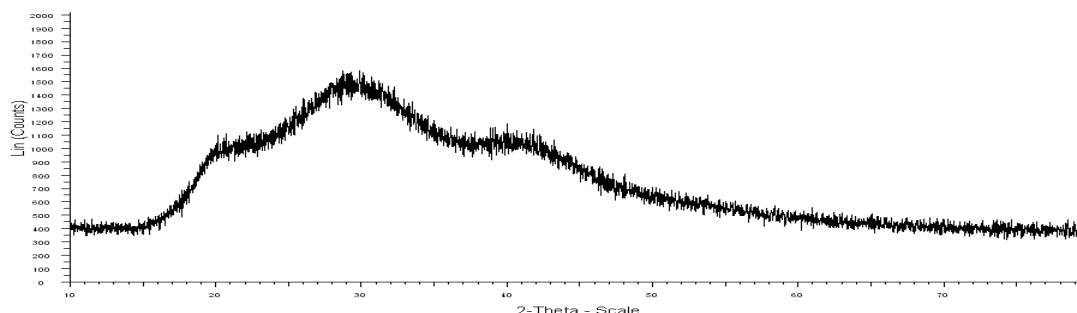


Figure- 8: XRD of chitosan/vanillin Schiff base

X-ray diffractogram of chitosan had a semi crystalline state with two main diffraction peaks at 10° and 20° . The weak diffraction peak centered at diffraction angle 2θ - 10° and sharp diffraction peak at 20° are indicative of high degree of crystalline morphology of chitosan [19, 20]. The X-ray diffractogram of chitosan/O-vanillin and chitosan/vanillin Schiff bases showed that the crystallographic peaks around 2θ - 10° , 20° of chitosan was shifted to higher value 20° and 30° (Figures – 7 and 8) conclude the strong interaction occurred between chitosan and aldehyde.

Also the higher semi crystalline nature of the blend which was indicated by broad amorphous peak indicating that there was a molecular miscibility and an interaction between chitosan, O-vanillin and vanillin.

Scanning Electron Microscopy

The surface morphology and cross sectional morphology of chitosan Schiff bases of O-vanillin and vanillin (Figure 9 and 10) are characterized by SEM. The SEM images showed a microporous and fibrous structure. The expected interactions between chitosan matrix and aldehyde was well exposed through hydrogen bonding and the formation of imine linkage which make the Schiff base derivatives stable with many hydrophilic sites at the surface. The cross sectional morphology of the same showed the fine interaction with pores and microvoids. The pores are effective in increasing the functional surface in the Schiff bases which enabled the same to be used promising material.

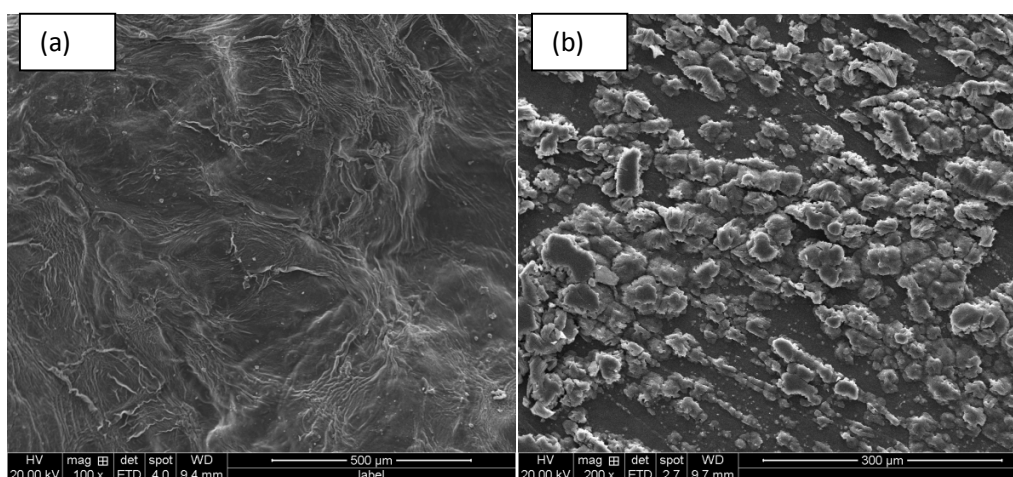


Figure 9: SEM images of chitosan/O-vanillin Schiff base a) Surface morphology b) Crosssectional morphology

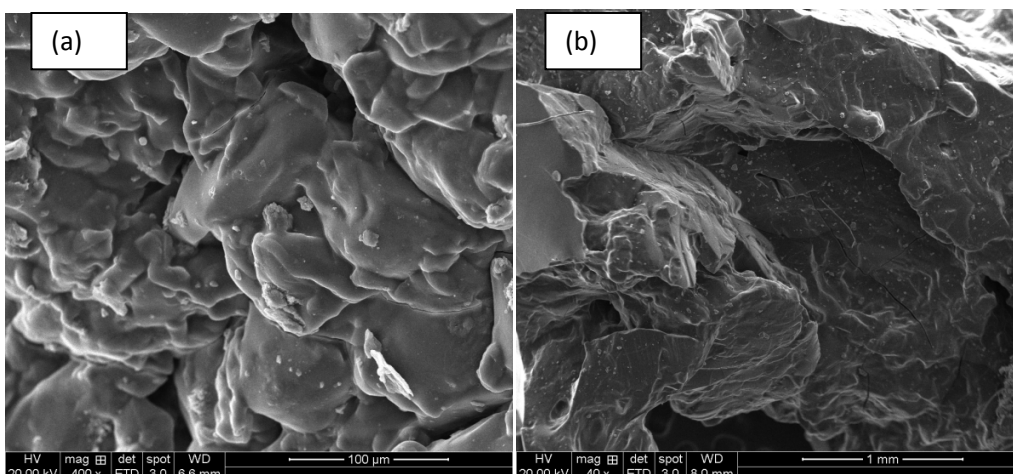


Figure 10: SEM images of chitosan/vanillin Schiff base a) Surface morphology b) Crosssectional morphology

CONCLUSION

The biopolymer chitosan with its wide range of application was used as a promising material in the biomedical field. By modifying its properties by forming Schiff base derivatives with o-vanillin and vanillin, it plays a vital role. The characterization of the chitosan Schiff bases was carried out. Some of the characterization procedures include FTIR, TGA, DSC, XRD and SEM analyses. From the above analyses, it was found that chitosan Schiff bases have been formed well with modified thermal and crystalline properties.

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