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Preparation and Characterisation study of Nanochitosan (NCS) and polyvinyl alcohol (PVA) binary blends with glutraldehyde as a crosslinking agent

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ABSTRACT

The primary objective of this study is to provide comprehensive market intelligence on a global level of its one of the derivative chitosan, nanochitosan and its blend, the present study explore the synthesis of nanochitosan/polyvinyl alcohol a binary blend of different ratios (1:1), (1:2), (2:1) with glutraldehyde as a crosslinking agent. The prepared blends were characterized under advanced analytical aids such as Fourier transform infrared spectroscopy (FTIR), X-ray diffraction studies (XRD), Thermal analysis (TGA and DSC) for its physical and chemical properties studies.

Keywords: Nanochitosan, polyvinyl alcohol, binary blends, glutraldehyde, Characterization

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INTRODUCTION

The biopolymer chitosan a linear polysaccharide composed of randomly distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit, an organic strain of polymer) which is extracted naturally from the living things, such as the shells of shrimps, crabs and other crustaceans and some fungi by using alkali sodium hydroxide [1].

Pure chitosan is non-toxic, free of antigenic effects, biocompatible, biodegradable and polar [2-6]. Chitosan has a number of commercial and possible biomedical uses, is a well identified sorbent, effective in the adsorption of metal ions [7]. Nevertheless, the properties of chitosan, such as less mechanical stability, chemical degradation its poor solubility in water or in organic solvents, can limit its utilization for a specific application. An elegant way to improve or to modify the properties in chitosan is the chemical modification of the chain, generally by chemically modifying the functional groups, without modification of the initial skeleton in order to conserve the original properties and achieve nano form [8, 9]. The only feasible way is to reduce the particle volume, which, offers larger surface area and hence enhances the efficiency of chitosan. This is the source of today's most popular technology 'nano technology concept'; [10-12] the present work also concentrates on synthesis of one of its derivative nanochitosan which has been used for blend formation. Nanochitosan can be prepared by ionic crosslinking method of chitosan with sodium tripolyphosphate which has excellent physicochemical properties, making it a superior environmentally friendly material [13, 14].

The potential applications of nano-chitosan are well demonstrated in all the field such as adsorption of heavy metals, treatment of waste water and medical field, particularly in controlled drug delivery systems[15,16,].The nanoderivative of chitosan has high mechanical and thermal stability than chitosan hence this work is more concentrated on preparation of nanochitosan and its blends [17].

Polyvinyl alcohol is a biocompatible and nontoxic material which has hydrophilic film forming capacity and also increases the mechanical strength of the blend. PVA's resistance against organic solvents and aqueous solubility makes it adaptable for many applications [18]. PVA is normally used in the textile industries, for paper manufacturing, in the food packaging industry, and also as medical devices [19]. PVA is used as an industrial and commercial product due to its low environmental impact, which includes its high chemical resistance, aqueous solubility, and biodegradability [20, 21].Polymeric blending is able to provide materials with extended useful properties beyond the range that can be obtained from single polymer equivalents. It is a novel method of preparing new material with already available polymers which has been highlighted in this work [22].

The present study concentrates on preparation of binary blend of nanochitosan with polyvinyl alcohol of different ratio by weight such as (1:1, 1:2, 2:1) with glutraldehyde as the crosslinking agent to improve casting, swelling increasing the amorphous nature and water permissibility property of the blend (23,24). The prepared blends were studied by various analytical techniques.

MATERIALS AND METHODS

Materials

Chitosan (deacetylation 92% and MW 120,000) was procured from India Sea Foods, Cochin, Kerala, India. Sodium tripolyphosphate, polyvinyl alcohol, glutaraldehyde and acetic acid of AR grade were used without any further purification. Millipore water is prepared in the laboratory by double distillation of deionised water in quartz distillation plant.

Preparation of Nanochitosan by Ionotropic gelation

The nanochitosan was prepared by ionotropic gelation [25, 26] method using sodium tripolyphosphate. Due to non toxic nature of these components and ease of operation, we adopted the gel ionization technique for the synthesis of nano chitosan particles. About 1 g of chitosan was dissolved in 200 ml of 2% acetic acid solution which was prepared using the conductivity water. The above solution was stirred well for 15 minutes. Then to the above prepared chitosan solution, 0.8 g of sodium tripolyphosphate dissolved in 107 ml of conductivity water was added dropwise. A milky coloured emulsion like appearance was obtained. This solution was then allowed to settle as suspension by adding conductivity water in excess for 24 hours. After this process is over, the supersaturated solution was then decanted. Then the thick emulsion which was obtained above was then poured into the Petri plates [27].

Preparation of Nanochitosan – Polyvinylalcohol (NCS/PVA) (1:1, 1:2, 2:1)

A binary blend of nanochitosan - polyvinyl alcohol with glutaraldehyde of ratios (1:1, 1:2, 2:1) was prepared by weighing 1 g of nanochitosan dispersed in distilled water was taken and 1 gm of polyvinyl alcohol which was dissolved in minimum amount of distilled water was also taken separately. The above solutions were then mixed thoroughly by magnetic stirring with 7ml of glutraldehyde as a crosslink agent [27] and thereafter filtered and washed thrice with double distilled water. These biopolymer binary blends were stored at room temperature in double distilled water for few hours and then dried by pouring in a Petri dish and for 24 hrs in similar way other ratios were also prepared of different proportions. [25-27]

Characterization of Polymer blends

FT-IR spectroscopy:

Perkiln-Elmer spectrophotometer was used for FTIR study. The prepared nano chitosan-polyvinyl alcohol a binary blends of different ratio were analyzed by FTIR in the wavelength between 400cm^{-1} and 4000cm^{-1} and in solid state using KBr pellets.

X – Ray Diffraction Studies

X–ray diffraction (XRD) patterns of nano chitosan-polyvinyl alcohol binary blends composites of different ratio were studied using X-ray powder diffractometer (XRD – SHIMADZU XD – D1) using a Ni – filtered Cu KθX–ray radiation source. The relative intensities were recorded within the range of 10^0 – 90^0 (2θ) at a scanning rate of 5^{0}min^{-1}.

Thermo Gravimetric Analysis

Thermogravimetric analysis was conducted to measure the thermal weight loss of the nano chitosan-polyvinyl alcohol a binary blend on a SDT Q600 V8.0 Build 95 instrument at a heating rate of 10^{0}C per minute in nitrogen atmosphere. The weight losses at different stages were recorded and analysed.

Differential Scanning Calorimetry

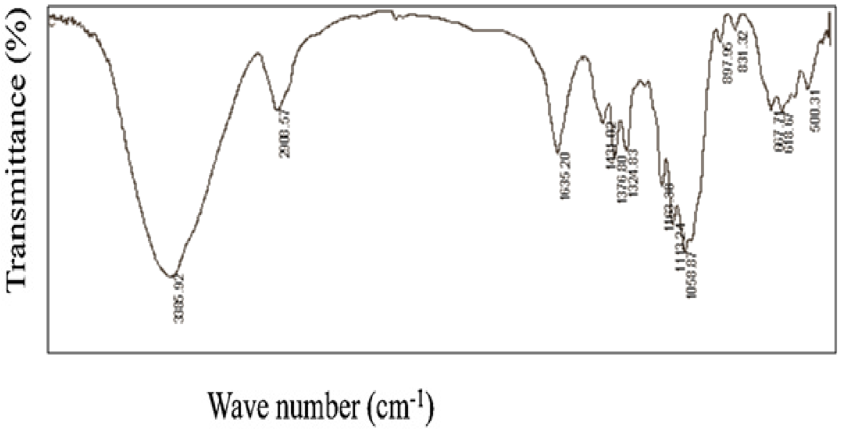
The differential scanning calorimeter (DSC) was used to examine the thermal stability of the nanochitosan-polyvinyl alcohol a binary blends. The measurements were performed with NETZSCH DSC 200 PC in a pan Al, pierced lid in the N_2 atmosphere at a heating rate of 10^0 K /min. The results were recorded and analysed.

RESULT AND DISCUSSION

FT-IR spectra of nanochitosan and binary blend with crosslinking agent glutaraldehyde

FTIR spectroscopy is one of the most powerful techniques for investigation of multicomponent systems because it provides information on the blends composition and also polymer - polymer interactions. The following section describes the FT-IR spectral details of nanochitosan (Figure 1), PVA and PVA crosslinked with glutaraldehyde (Figure 2a and 2b), NCS: PVA composites with crosslinker glutaraldehyde in different weight ratio of (1:1, 1:2, 2:1) in (Figures 3, 4, 5).

Fig (1): FT-IR spectrum of nanochitosan



The IR spectra of nanochitosan showed a prominent peak at 3385.92cm^{-1} corresponds to -OH stretching of axial OH group, and -NH stretching. A peak at 2908.57cm^{-1} was due to aliphatic –CH asymmetric stretching. Strong peaks obtained at 1635.20cm^{-1}, 1163.38 cm^{-1}, 897 cm^{-1} indicate the presence of –NH bending, C-O- C stretching of glycosidic linkage and C-C stretching. Appearance of new peaks at 1219.00 cm^{-1} and 1058.87 cm^{-1}corresponds to P=O stretching, P-O stretching respectively was due to the interaction of sodium tripolyphospate with chitosan and confirms the conversion of chitosan to nanochitosan [29,30,31]. The shift of the peaks observed at 3385.92cm^{-1} to lower wavenumber in nanochitosan indicate crosslinking had taken place effectively between sodium tripolyphosphate and chitosan.

Fig (2): FTIR spectrum a. Pure PVA b. PVA crosslinked with GA [Ref. 32, 33]

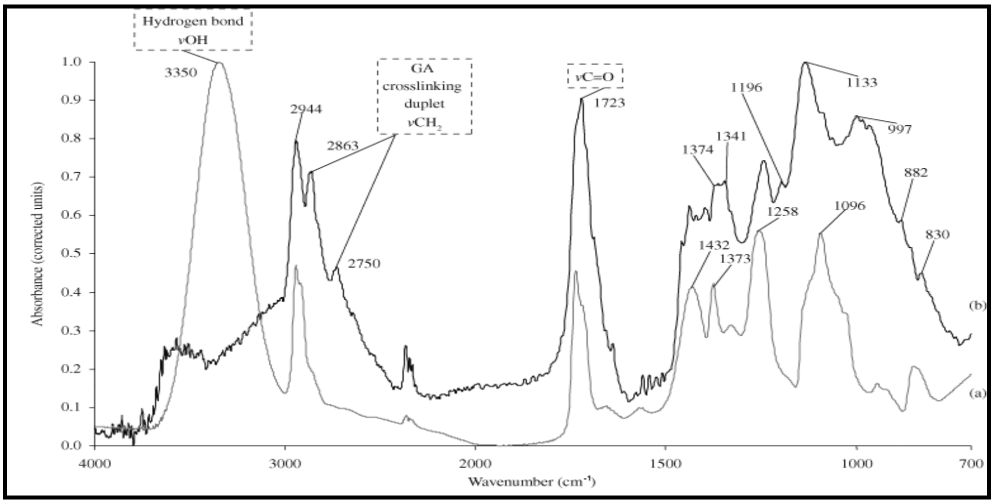


Figure 2a, shows the FTIR spectrum of pure PVA, where all major peaks related to hydroxyl and acetate groups were observed. More specifically the broad band observed between 3550 and 3200 cm^{-1} was associated with the stretching O-H from the intermolecular and intra- molecular hydrogen bond. The vibrational band observed between 2840 and 3000 cm^{-1} refers to the stretching C=H from alkyl groups and the peaks between 1750 and 1735 cm^{-1} are due to the stretching C=O and C-O from acetate group remaining from PVA (saponification reaction of polyvinyl acetate) [34, 35, and 36].

Figure 2b, shows the FTIR spectrum of PVA crosslinked by glutaraldehyde (PVA/GA), two prominent peaks are observed at 2860 and 2730 cm^{-1} corresponds to C–H stretching are related to aldehydes, duplet absorption with peaks contributes to the alkyl chain [35-39]. The PVA reaction with GA resulted in significant alterations in the bands regarding to hydroxyls (O-H) at 3330-3350 cm^{-1}, normally associated with the acetal bridge formation. Therefore, it was assume that glutaraldehyde was acted as chemical crosslinker among PVA polymer chains.

Fig (3): FTIR spectrum of NCS: PVA [1:1] ratio with crosslinking agent glutaraldehyde.

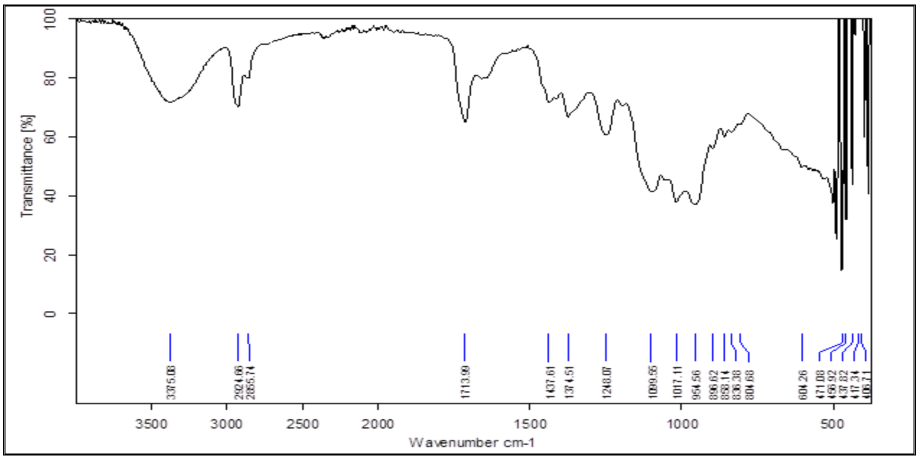


Fig (4): FTIR spectrum of NCS: PVA [1:2] ratio with crosslinking agent glutaraldehyde.

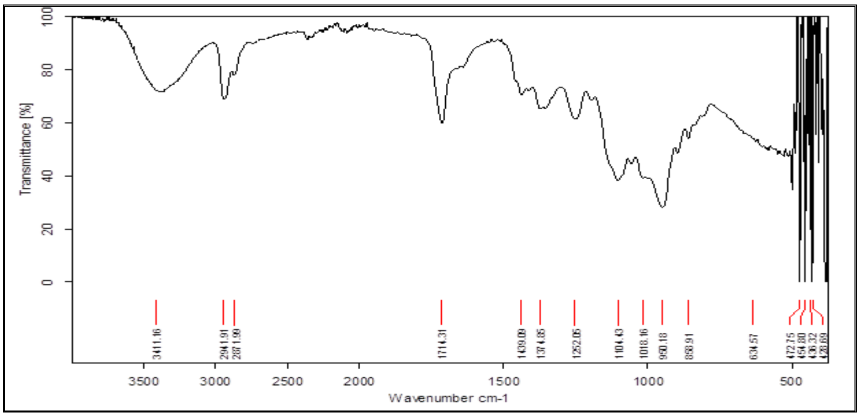
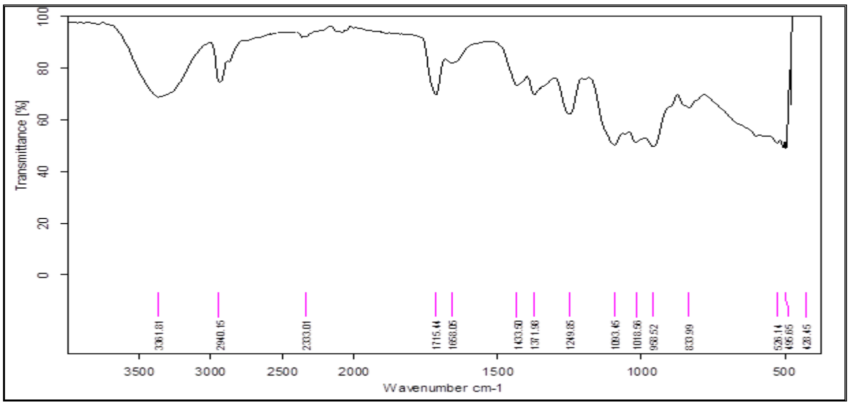


Fig (5): FTIR spectrum of NCS: PVA [2:1] with crosslinking agent glutraldehyde.



The FT-IR spectrum of NCS: PVA blends with glutaraldehyde in different ratio (1:1,1:2, 2:1) was shown in figure 3,4 and 5 respectively. A peak for -OH stretching and -NH stretching for NCS is observed at 3385.92cm^{-1} which has been found to be shifted to lower wavelength at 3375.08 cm^{-1}, 3368.3 cm^{-1} and 3376.7 cm^{-1} for ratios 1:1, 1:2 and 2:1 respectively.

Peaks at 1219.00 cm^{-1} for P=O stretching and 1058.87 cm^{-1} for P-O stretching in NCS was observed to have a shift in the IR spectrum for various ratios of the blends prepared and their peaks obtained are 1248.07 cm^{-1} and 1017.11cm^{-1} for 1:1 ratio [40], 1252.06 cm^{-1} and 1018.16cm^{-1} for 1:2 ratio [41], 1252.06 cm^{-1} and 1018.16cm^{-1} for 2:1 ratio respectively. Moreover, the P-O band and P=O band for NCS has undergone a significant shift in the prepared blend of 1: 1 ratio suggest that this blend is better for metal adsorption.

X-Ray diffractogram of nanochitosan and binary blend with crosslinking agent glutaraldehyde

Fig (6): XRD pattern of NCS

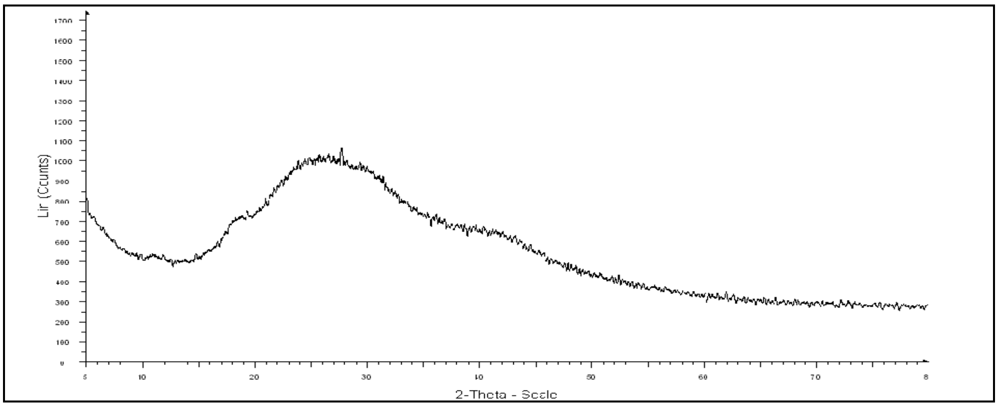


Fig (7): XRD pattern of the blend NCS: PVA [1:1] with crosslinking agent glutraldehyde

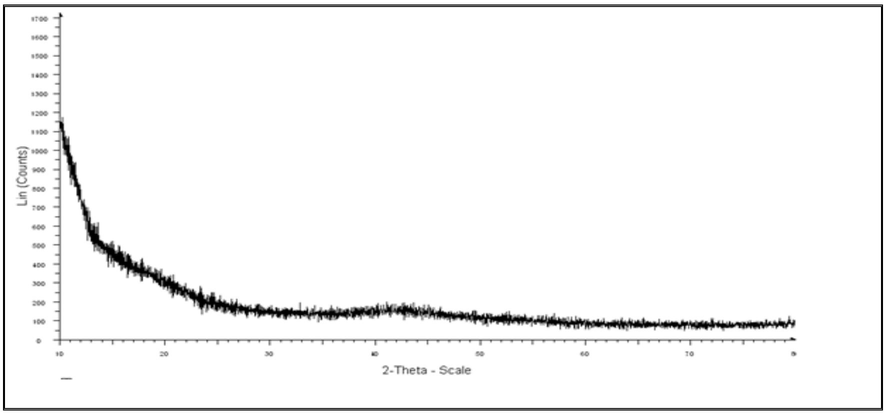


Fig (8): XRD pattern of the blend NCS: PVA [1:2] with crosslinking agent glutraldehyde

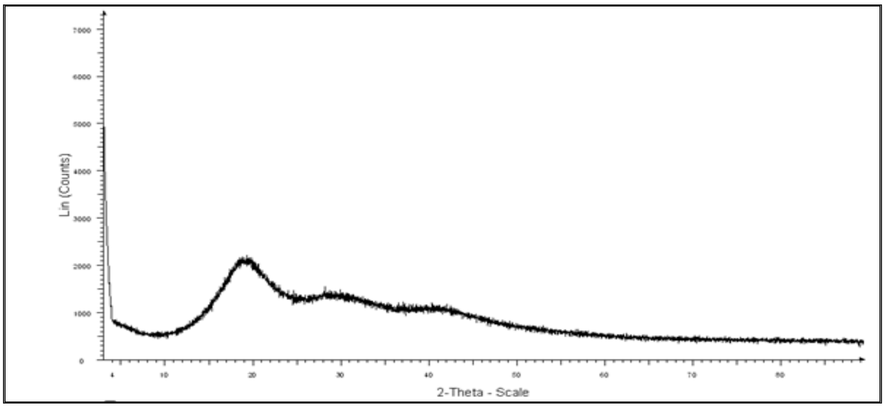
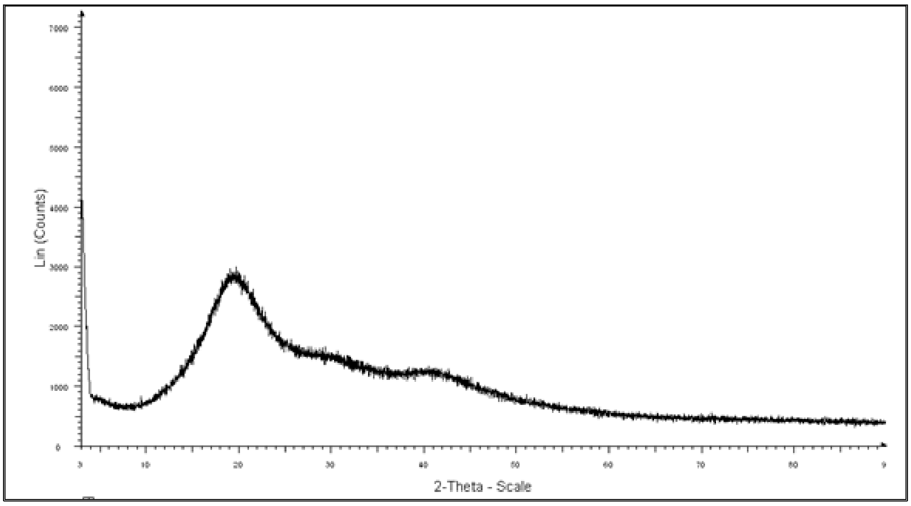


Fig (9): XRD pattern of the blend NCS: PVA [2:1] with cross linking agent glutraldehyde



The XRD spectra patterns of nanochitosan particles obtained using ionic gelation technique is shown in Figure 6. The spectra shows well defined distinctive peak for nanochitosan particles at 2θ value of 20. The broadening of the peak was due to the amorphous nature of the nanochitosan polymer by the ionic crosslinking of TPP with chitosan which can deform the crystalline structure of chitosan [42, 43].

The XRD spectra patterns of NCS: PVA blends with glutaraldehyde in different ratio (1:1,1:2, 2:1) was shown in figure 7, 8 and 9 respectively. From the figures it was seen that for all the blends the diffraction peaks are observed at 2θ values around 20. The peaks are relatively low intense confirming the increase in the amorphous nature of the formed blend [41-43].

TGA of nanochitosan and binary blend with crosslinking agent glutaraldehyde

Fig (10): TGA pattern of NCS

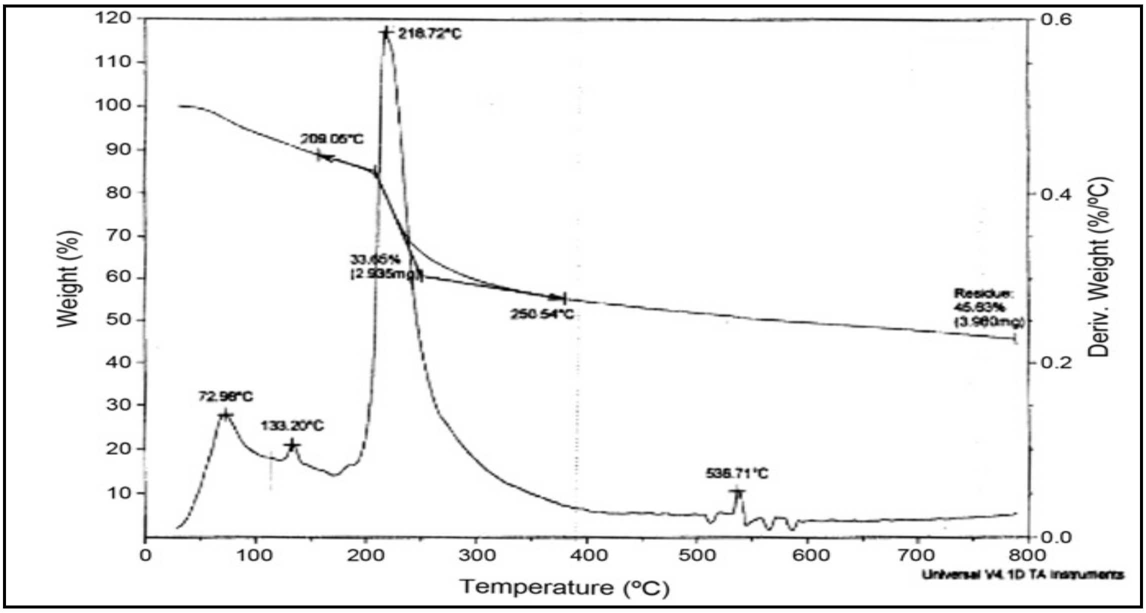


Fig (11): TGA pattern of the blend NCS: PVA [1:1] with crosslinking agent glutraldehyde

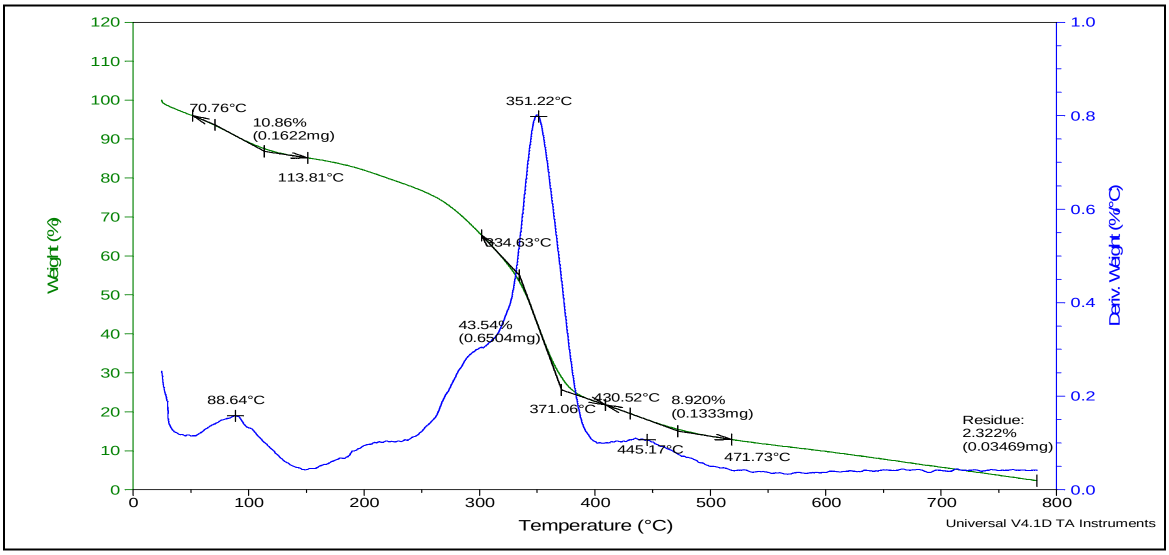


Fig (12): TGA pattern of the blend NCS: PVA [1:2] with crosslinking agent glutraldehyde

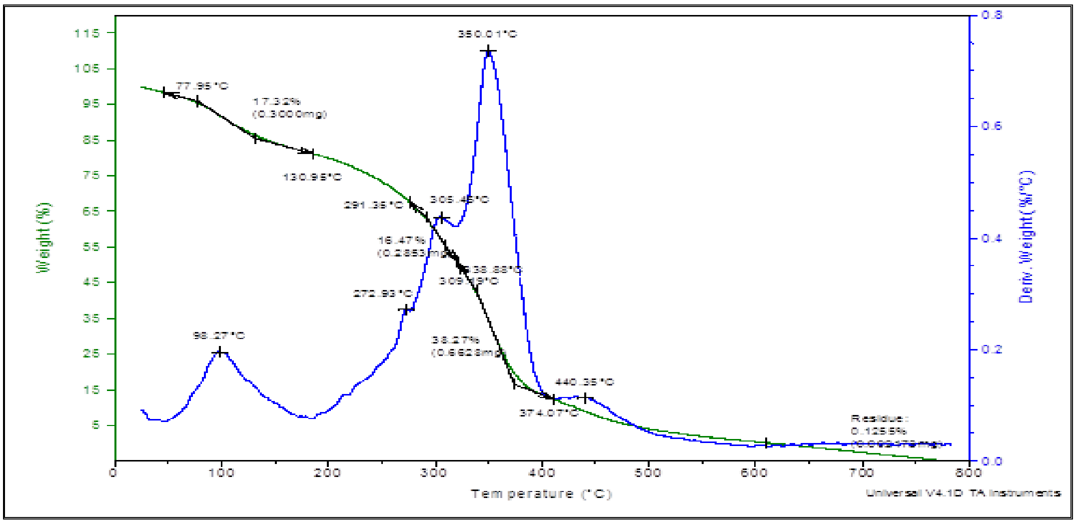
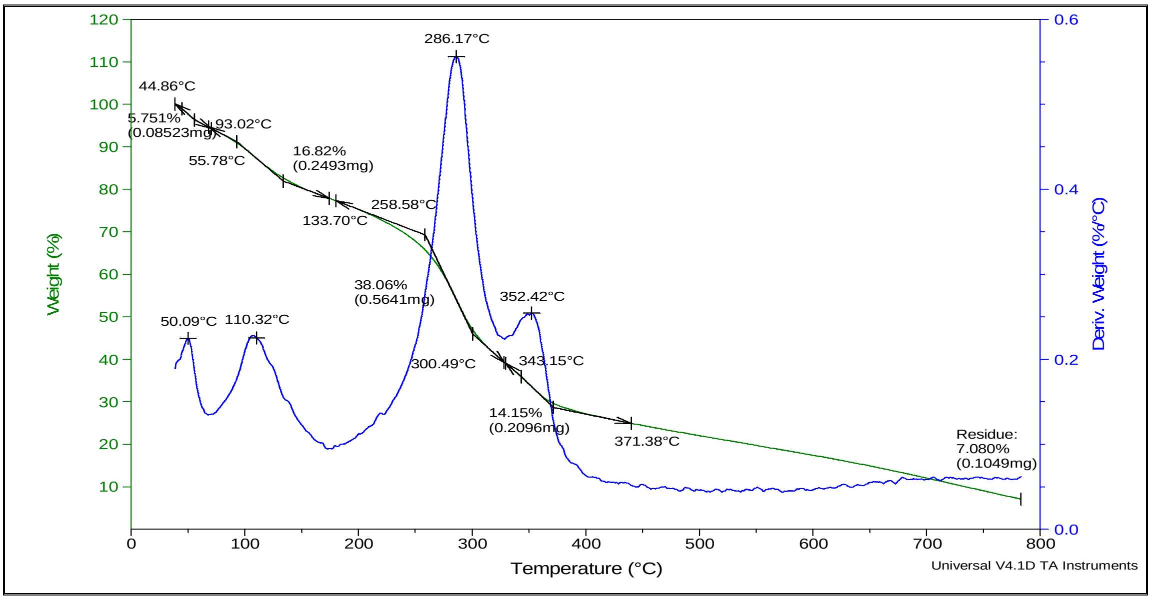


Fig (13): TGA pattern of the blend NCS: PVA [2:1] with crosslinking agent glutraldehyde



TGA thermogram of nanochitosan (figure- 10) indicate that the first thermal event occurs at temperature range 50 - 150 °C with a weight loss of 8% to 10 % which may be due to the loss of residual water present in the sample. According to literature data pyrolysis of nanochitosan starts by a random splitting of the glycosidic bonds, followed by a further decomposition to acetic, butyric and lower fatty acids [44, 45]. The thermal degradation of nanochitosan, up to 800^{0}C shows that around 45.63 % of the sample remained as residue at the end of the experiment.

TGA thermograms of NCS: PVA blends with glutaraldehyde in different ratio (1:1, 1:2, 2:1) are presented in Figures (11 – 13). For all the blends the maximum decomposition occurs in the range of 350-400°C temperature which was mainly due to the pyrolysis of the polymer. From the thermogram values it was concluded that the blend with the ratio 1:1 is thermally stable up to 750°C leaving behind 2.322% as residue at the end of the experiment whereas for the blends with the ratio 1:2 and 2:1, they decomposed at 690.09°C leaving behind 0.125 % residue and at 699°C leaving behind 7.080% of residue respectively. The above data confirms the blend 1:1 is thermally more stable and suitable for carrying out further study of adsorption process.

DSC studies of nanochitosan and binary blend with crosslinking agent glutaraldehyde

Fig (14): DSC pattern of NCS

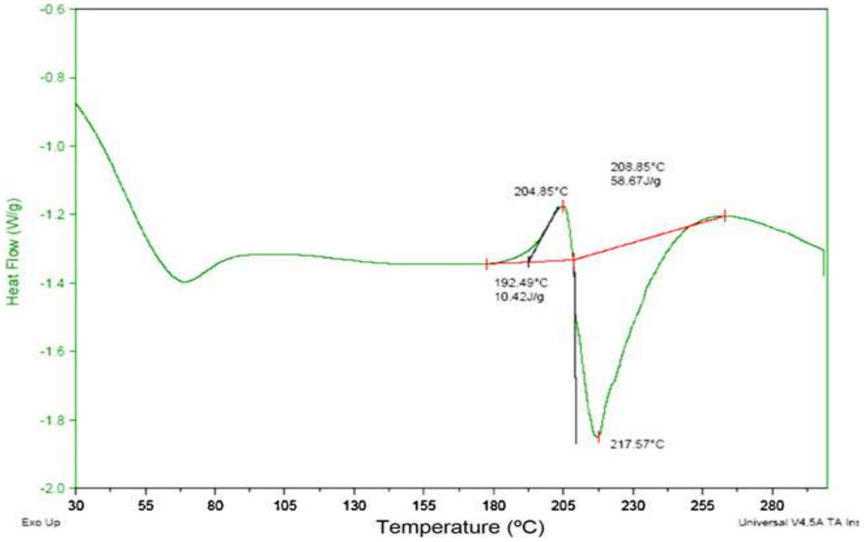


Fig (15): DSC pattern of blend NCS: PVA [1:1] with crosslinking agent glutaraldehyde

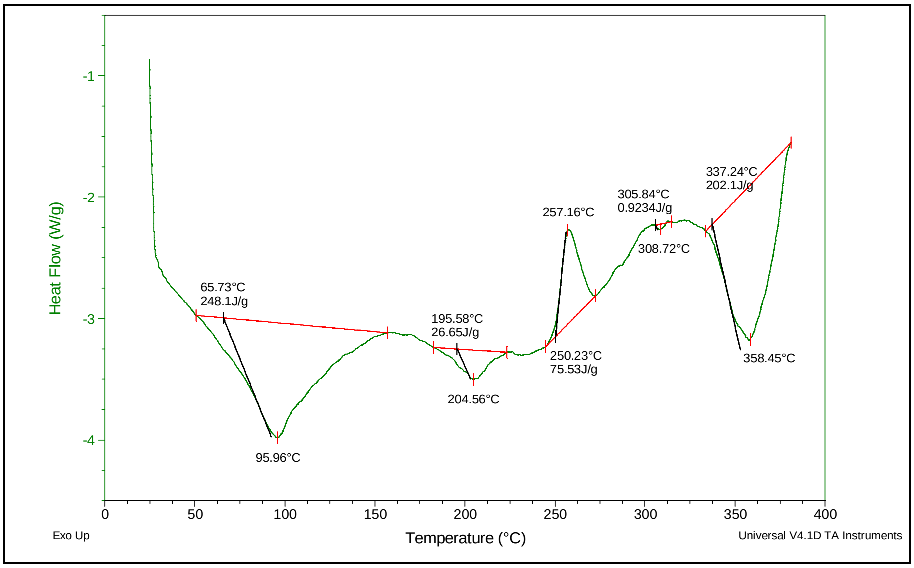


Fig (16): DSC pattern of blend NCS: PVA [1:2] with crosslinking agent glutaraldehyde

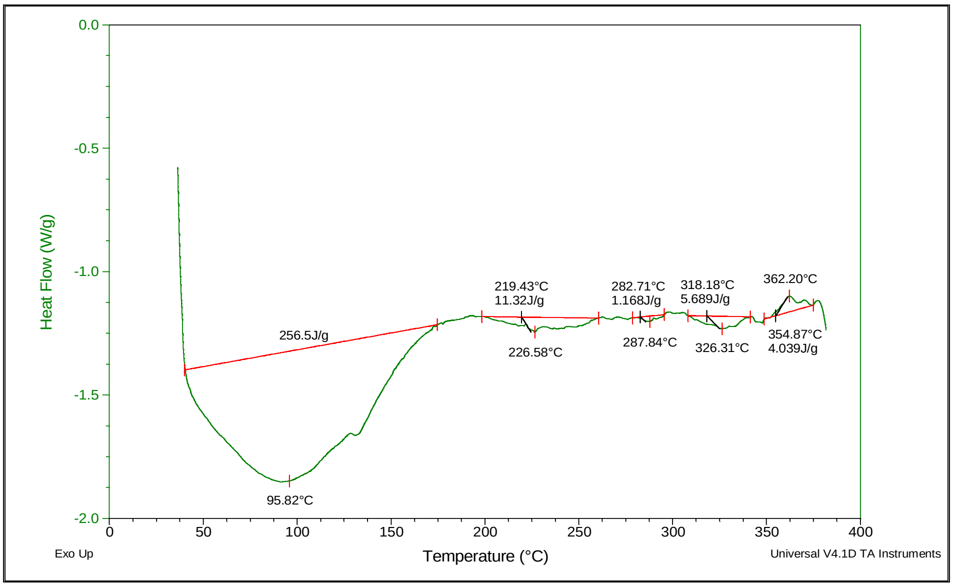
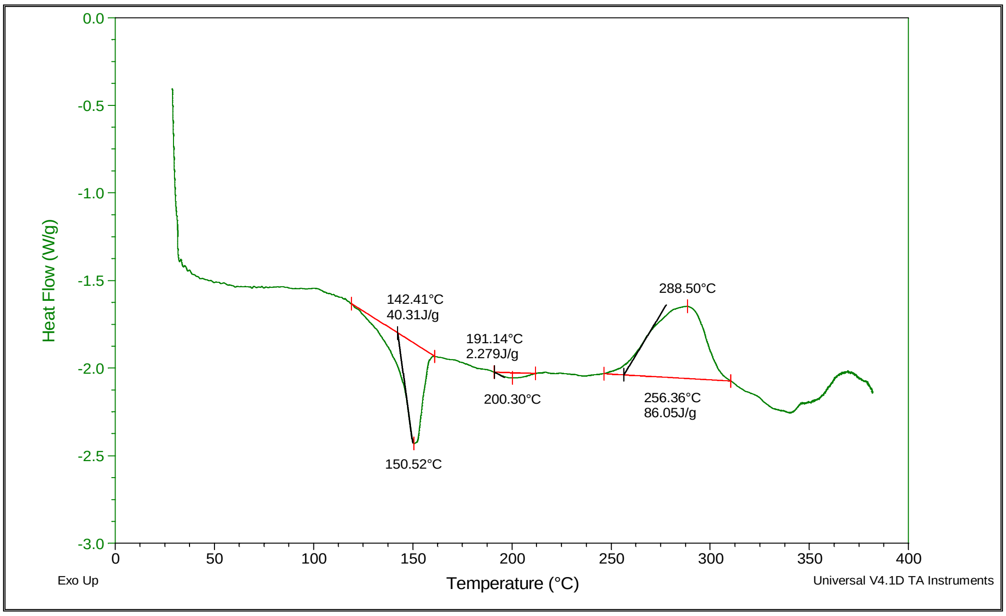


Fig (17): DSC pattern of blend NCS: PVA [2:1] with crosslinking agent glutaraldehyde



The DSC curve of nanochitosan in figure 14 has a wide endothermic peak below 80 ^{0}C which is due to the removal of absorbed water and a sharp endothermic peak at 217 ^{0}C associated with the breakage of chitosan phosphoric acid cross linkage. The decomposition of chitosan nanoparticles is expected to happen well above 300 ^{0}C as evidenced from TGA studies. The Tg of nanochitosan was observed at 210^{0}C and the amorphous nature of nanochitosan was confirmed from TGA result [42-46].

Figure.15-17 shows the DSC curves of NCS: PVA blends with glutaraldehyde in different ratio (1:1, 1:2, 2:1). Broad endothermic peaks are observed at various temperatures indicating the crystallization of the polymer blend as well as evaporation of water and decomposition of side chain [45-48]. The Tg of NCS: PVA blends with glutaraldehyde in different ratio (1:1, 1:2, 2:1) was observed at 340^{0}C, 335^{0}C and 235^{0}C respectively.

On comparing the DSC curves of nanochitosan, and the polymer blends NCS:PVA with different ratios the blend (1:1) has higher glass transition temperature of 340^{0}C. Hence, it was found that the endothermic peaks and the glass transition temperatures of NCS: PVA blend shifted to higher values. It confirms that the blended polymer 1:1 has higher thermal stability than nanochitosan with the formation of different crystalline forms.

CONCLUSION

In this study, the NCS: PVA binary blend were prepared at various ratios (1:1, 1:2, 2:1) with crosslinking agent glutarldehyde. The blends were characterized using analytical techniques such as FTIR, XRD, TGA and DSC. From the FTIR results, it was found that the the peaks were shifted to higher wave number during blend formation which confirms the nanochitosan were effectively bound with polyvinyl alcohol. XRD studies elucidate that the prepared blend was highly amorphous and suitable for adsorption process. TGA and DSC results indicate that the addition of glutaraldehyde enhances the thermal stability and compatibility of the prepared binary blends. It was concluded from the above results that the binary blends were highly suitable for heavy metal removal and this type of work could promote the synthesis of some functionalised new polymer blend from the existing polymer for achieving specific property and can be utilized for several applications.

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