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SYNTHESIS AND CHARACTERIZATION OF NANOCHITOSAN-POLYVINYL ALCOHOL-CARBOXYMETHYL STARCH TERNARY BLENDS OF VARIOUS COMPOSITIONS WITH GLUTARALDEHYDE AS CROSSLINKING AGENT

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ABSTRACT

The interest in biopolymers and its derivatives has increased in recent years due to its following properties such as biodegradability, biorenewability, biocompatibility, physiological inertness and hydrophilicity. The primary purpose of this study is to provide complete global level value of its one of the derivative chitosan in nanoform as nanochitosan mainly remediating tannery effluents. The nanochitosan has larger surface area as compared to chitosan. The present study explores the synthesis of nanochitosan/polyvinyl alcohol/ carboxymethylstarch a ternary blends of various ratio (1:1:1), (1:2:1), (1:1:2) and (2:1:1) with glutaraldehyde as a crosslinking agent. The prepared blends were characterized using sophisticated analytical tools such as Fourier transform infrared spectroscopy (FTIR), X-ray diffraction studies (XRD), Thermal analysis (TGA and DSC) and Scanning electron microscopic images (SEM)which confirms the formation of blends and its thermal stability.

KEYWORDS: Nanochitosan, polyvinyl alcohol, carboxymethyl starch, ternary blends, Characterization.

1. INTRODUCTION

The nanochitosan has more advantages than chitosan such as higher surface area, chemical and mechanical stability. It is a natural material with excellent physiochemical properties

environment friendly material, possesses bio activity and does not harm humans it also has high catalytic activity, anti bacterial and shrink –proofing properties, material having excellent physicochemical properties, this makes it a good applicant in drug and gene delivery, and also in removal of heavy metal.[1] The polyvinyl alcohol is nontoxic, good barrier for oxygen, aroma, oil and solvents, which is prepared by partial or complete hydrolysis of poly (vinyl acetate), Polyvinyl Alcohol is a synthetic resin with hydrophilic properties, it increases the persistence of the tear film and therefore used as a lubricant, forms a soluble plastic film upon drying.[2,3] The carboxymethyl starch is a natural starch derivative, which is a linear and branched starch polymer. The starch becomes more resistant to thermal degradation and bacterial attack because of it. Carboxymethylstarch is a derivative of starch. It has stability against freezing, excessive heat, and acids**.** Carboxymethyl starch is a renewable, nontoxic, and biodegradable polysaccharides with numerous applications such as removal of cations like calcium, iron, from dispersed phase.CMS has been extensively applied as wall paper adhesive, as textile printing thickener and also has applications in the pharmaceutical industry, cationic starch is used as wet end sizing agent in paper manufacturing.[4,5] The main aim of the present study was just to synthesize the nanochitosan/polyvinyl alcohol/ carboxymethylstarch blends of various ratios. The prepared blends were characterized and then the results were investigated.

2. MATERIALS AND METHODS

2.1 MATERIALS

Chitosan was gifted by India sea foods, Cochin, Kerala for our study. Carboxymethyl starch and Polyvinylalochol were of Sigma Aldrich, India, and Sodium tripolyphosphate were obtained from Central Drug House Pvt. Ltd. All other chemical used were of analytical grade. Millipore water was prepared in the laboratory by double distillation of deionised water in quartz distillation plant.

2.2 METHODS

2.2. A. Preparation of Nanochitosan by Ionotropic gelation

The nanochitosan was prepared by ionotropic gelation method using sodium tripolyphosphate. Ionotropic gelation is based on the ability of polyelectrolyte to cross link in the presence of counter ions to form hydrogels the faster ionic reactions between chitosan and TPP, non toxic nature of these components and easy process, we adopted the gel ionization technique for the synthesis of nanochitosan particles.[6]

2.2. B. Preparation of Nanochitosan (NCS) - Polyvinyl alcohol (PVA) and Carboxymethyl starch (CMS) a ternary blend (Ratio - 1:1:1, 1:2:1, 1:1:2, 2:1:1)

The ternary blend of nanochitosan - polyvinyl alcohol and carboxymethylstarch with glutraldehyde of above ratios were prepared. About 1 g of nanochitosan in dispersed form in distilled water was weighed and taken along with, 1 gm of polyvinyl alcohol which was dissolved in minimum quantity of distilled water separately and was dissolved with 1 gm weight of Carboxymethyl Starch dissolved in minimum amount of distilled water in a beaker separately. The above solutions were then thoroughly mixed under magnetic stirring with 7ml of glutraldehyde as a crosslinking agent and thereafter filtered, washed thrice with double distilled water. These biopolymeric ternary 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 of 1:1:1 ratio, in similar manner other ratios were also prepared of different proportions.[6,7,8]

3. Characterization of Polymer blends

FTIR study was carried by using Perkiln- Elmer spectrophotometer. The prepared nanochitosan-polyvinyl alcohol & carboxymethylstarch ternary blends were studied by FTIR in the wavelength range between 400cm^{-1} and 4000cm^{-}1. X–ray diffraction (XRD) patterns of nanochitosan-polyvinyl alcohol & carboxymethylstarch ternary blend composites were investigated using X-ray powder diffractometer (XRD – SHIMADZU XD – D1) using a Ni – filtered Cu KθX–ray radiation source. The comparative intensities were recorded within the range of $10^0 – 90^0$ (2θ) at a scanning rate of 50min^{-1}. Thermogravimetric analysis was studied to quantify the thermal weight loss of the nanochitosan-polyvinyl alcohol & carboxymethylstarch ternary blend on a SDT Q600 V8.0 build 95 instrument at a heating rate of 10^0C per minute in nitrogen atmosphere. The weight losses at different stages were analysed. The differential scanning calorimeter (DSC) was used to observe the thermal property of the nanochitosan-polyvinyl alcohol & carboxymethylstarch ternary blend composites. 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. The surface morphology and cross sectional morphology of the nanochitosan-polyvinyl alcohol & carboxymethylstarch ternary blend composites were observed with scanning electron microscopy to confirm the compatibility of the mixtures of nanochitosan-polyvinyl alcohol & carboxymethylstarch ternary blend. For the examination, the samples were cut into pieces of various sizes and wiped with a thin gold – palladium layer by a sputter

coater unit (VG – microtech, UCK field, UK) and the cross section topography was analysed with a Cambridge stereoscan 440 scanning electron microscope (SEM, Leica, Cambridge.).

4. RESULTS AND DISCUSSION

4.1 FT-IR spectroscopy

FTIR spectroscopy provides information on the blend and composite composition and also polymer - polymer interactions. The following section describes the FT-IR spectral details of nanochitosan (Figure 1), and NCS/PVA/CMS composites of various composition is described in the (Figure 1 a,b,c,d) weight ratio in the presence of the cross linking agent glutaraldehyde.

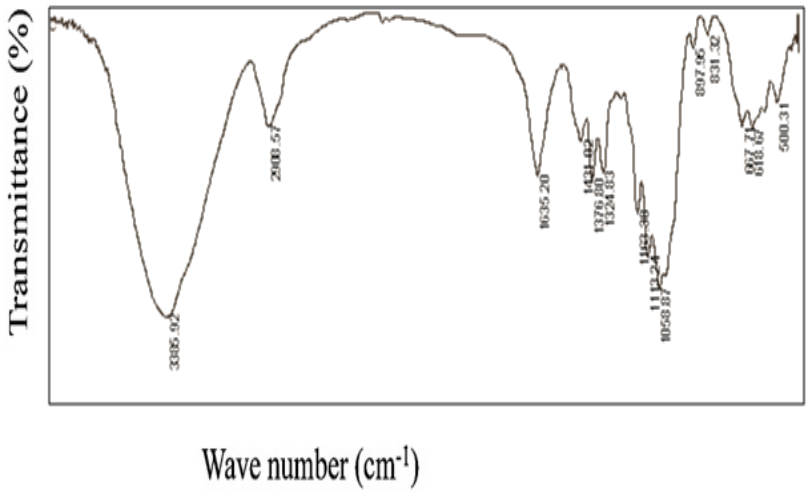


Fig: 1. The FT- IR spectrum of nanochitosan.

The spectra shows major peak at 3386.92cm^{-1} corresponds to –OH stretching of axial OH group, -NH stretching. The peak obtained at 2908.57cm^{-1} corresponds to the aliphatic –CH asymmetric stretching. Certain peaks observed at 1635.20cm^{-1}, 897 cm^{-1} corresponds to –NH bending and C-C stretching. P=O Stretching 1219.00 cm^{-1}, P-O stretching 1058.87 cm^{-1} are the additional peak seen in nanochitosan which was not present in chitosan. C-O- C stretch 1163.38 cm^{-1} also observed.[6,7,8]

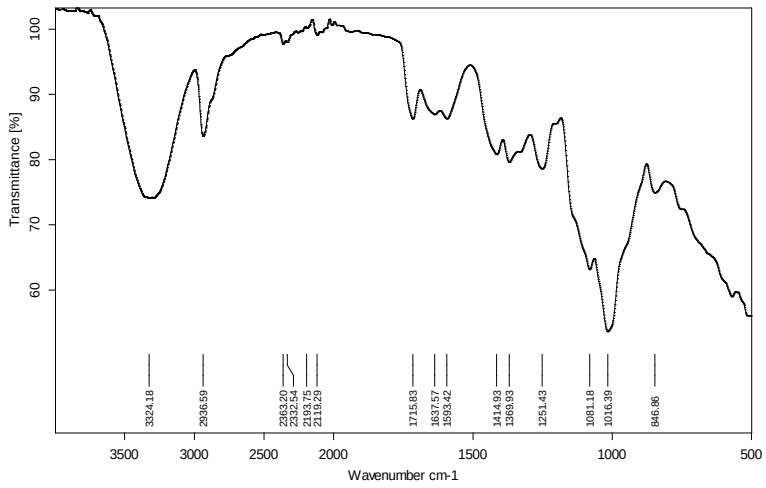


Fig.1.a. FTIR Spectra of NCS/PVA/CMS (1:1:1) with GLU.

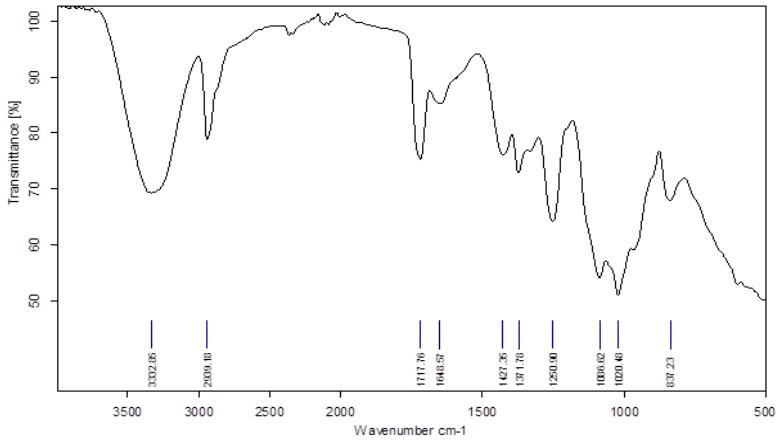


Fig.1.b. FTIR Spectra of NCS/PVA/CMS [1:2:1] with GLU.

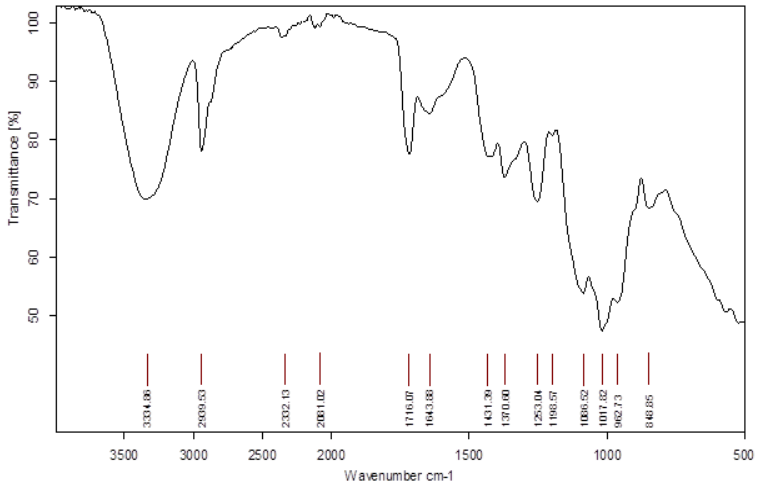


Fig. 1. c. FTIR Spectra of NCS/PVA/CMS [1:1:2] with GLU.

Fig. 1. d. FTIR Spectra of NCS/PVA/CMS [2:1:1] with GLU.

Thus the shift in the peak confirms the perfect formation of blend.

Table: 1. FTIR Spectral details of Nanochitosan, Polyvinyl alcohol, Carboxymethyl starch ternary blend of various compositions.

Responsible group	Wave number cm^{-1}			
	(1:1:1) with GLU	(1:2:1) with GLU	(1:1:2) with GLU	(2:1:1) with GLU
N-H stretching and O-H stretching	3324.18	3332.85	3334.86	3332.86
C-H asymmetric modes	2936.59	2939.18	2939.53	2938.40
C=O stretching	1715.83	1717.76	1716.07	1716.78
Carbonyl stretching (amide I) and C=N stretching	1637.57	1648.57	1643.88	1641.18
$-CH_2$ scissoring	1414.93	1427.35	1431.39	1416.02
O-H bending	1369.93	1371.78	1370.60	1326.88
P=O stretching	1251.43	1250.90	1253.04	1252.56
C-O-C stretching of polysaccharide structure.	1081.18, 1016.39	1086.62, 1020.48	1098.57, 1017.82	1081.86, 1017.94
CH_2 rocking	846.86	837.23	848.85	845.64

The FTIR spectrum of Nanochitosan, Polyvinyl alcohol, Carboxymethylstarch (1:1:1) with GLU ternary blend compared to other ratio. The broad band at 3324.18cm^{-1} upon blending is due to the intermolecular hydrogen bonding N-H and O-H stretching vibration. On comparing with pure nanochitosan the above mentioned peak has been shifted to lower wave number during blending. The absorption bands present at 1715.83 cm^{-1} and 1637.57cm^{-1} is assigned to the C=O and C=N stretching vibrations.

4.2. XRD STUDIES

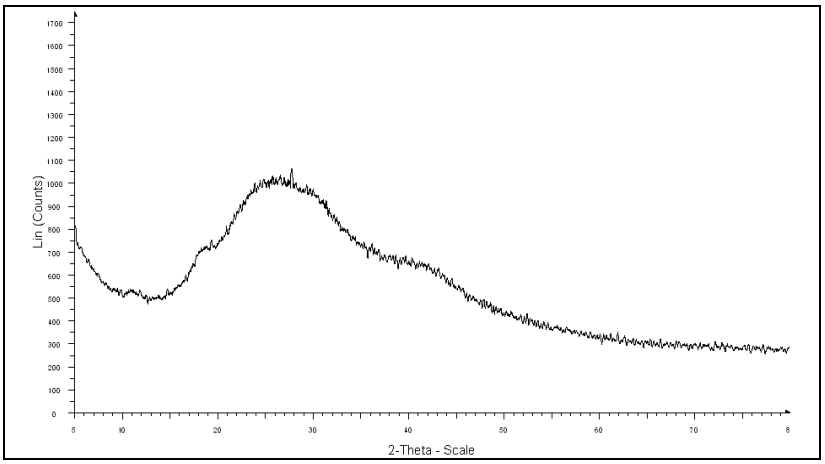


Fig: 2. XRD pattern of the nanochitosan.

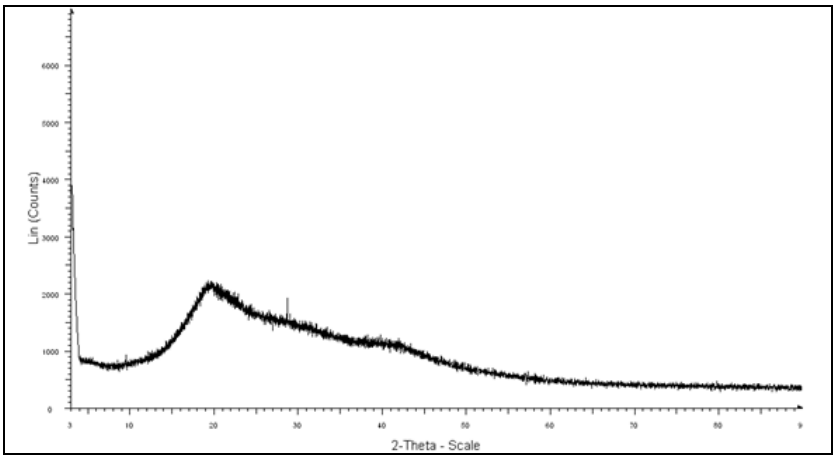


Fig: 2. a. XRD pattern of NCS/PVA/CMS (1:1:1) with GLU.

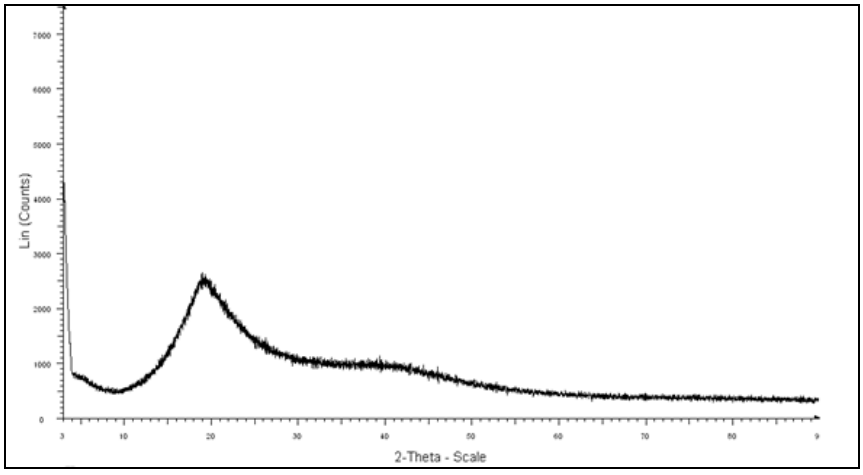


Fig: 2. b. XRD pattern of NCS/PVA/CMS (1:2:1) with GLU.

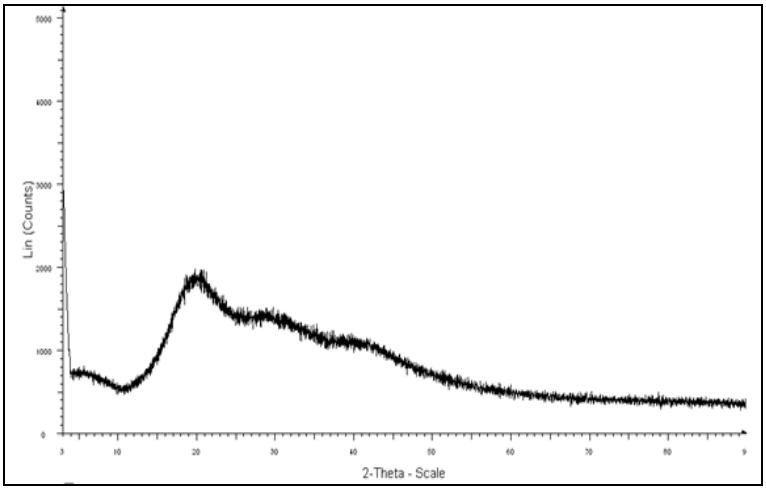


Fig: 2. c. XRD pattern of NCS/PVA/CMS (1:1:2) with GLU.

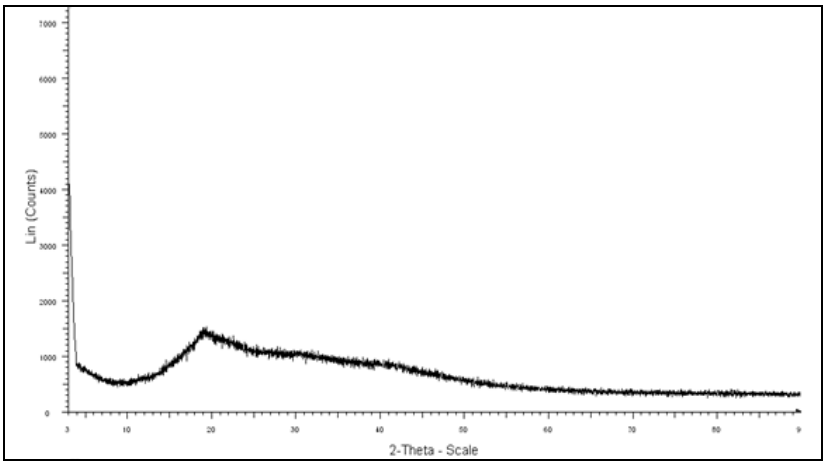


Fig: 2. d. XRD pattern of NCS/PVA/CMS (2:1:1) with GLU.

Table – 2: XRD details of Nanochitosan and NC/PVA/CMS blends.

Samples	2 θ Values		Xc%
Nanochitosan	27º	-	16.2
NC/PVA/CMS (1:1:1)+ GLU	19°	-	19.8
NC/PVA/CMS (1:2:1) + GLU	19°	-	21.3
NC/PVA/CMS (1:1:2) + GLU	20°	30°	27.10
NC/PVA/CMS (2:1:1) + GLU	20°	-	28.72

From the XRD pattern of NC/PVA/CMS ternary blends with GLU a broad distorted humplike diffraction peak at around $2\theta = 19^0$ was obtained for all the ratios, thus indicating amorphous morphology of the blend.

From the degree of cystallinity values as given in the Table - 2 it was concluded that when the concentration of PVA increases the morphology of blend changes to semi crystalline form whereas increase in concentration of NC and CMS makes the blend more amorphous.

4.3 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a thermal analysis techniques used to characterize a wide variety of materials it gives a relation between losses in weight of material with temperature. Thermal details of ternary blends of NC/PVA/CMS of various ratios in presence and of glutaraldehyde are discussed below.[8]

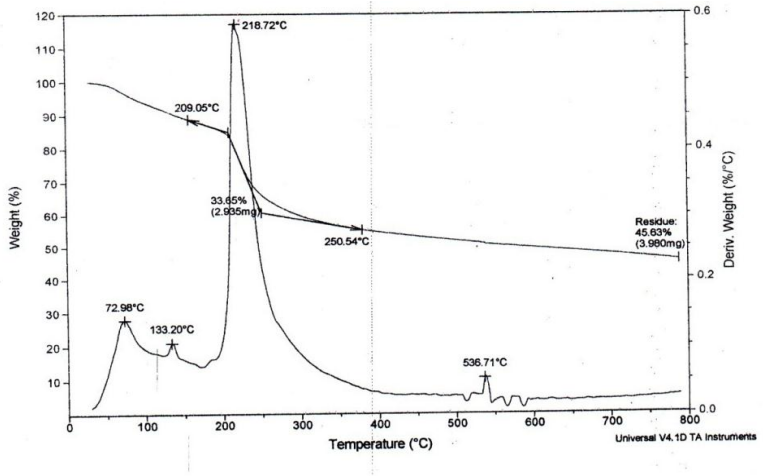


Fig.3. Thermogram of Nanochitosan.

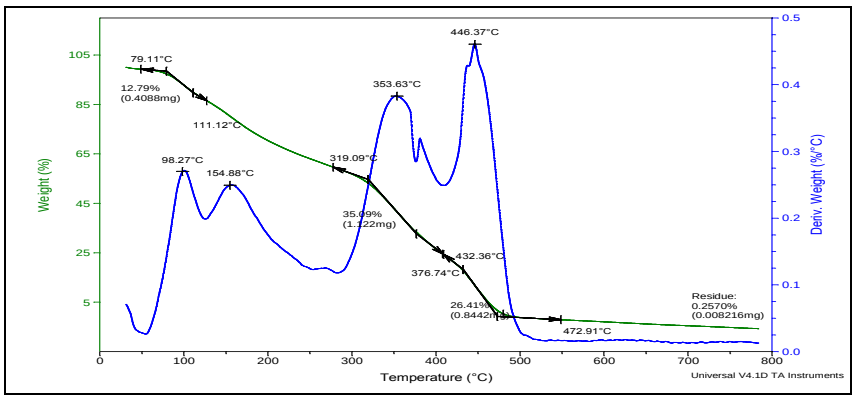


Fig: 3. a. Thermogram of NCS/PVA/CMS (1:1:1) with GLU.

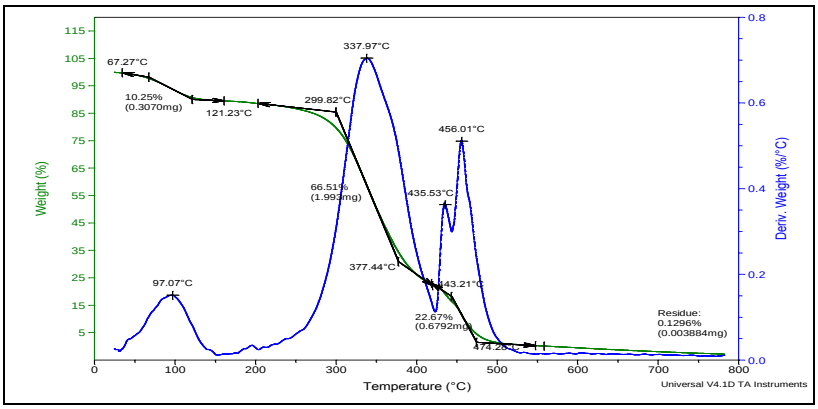


Fig: 3. b. Thermogram of NCS/PVA/CMS (1:2:1) with GLU.

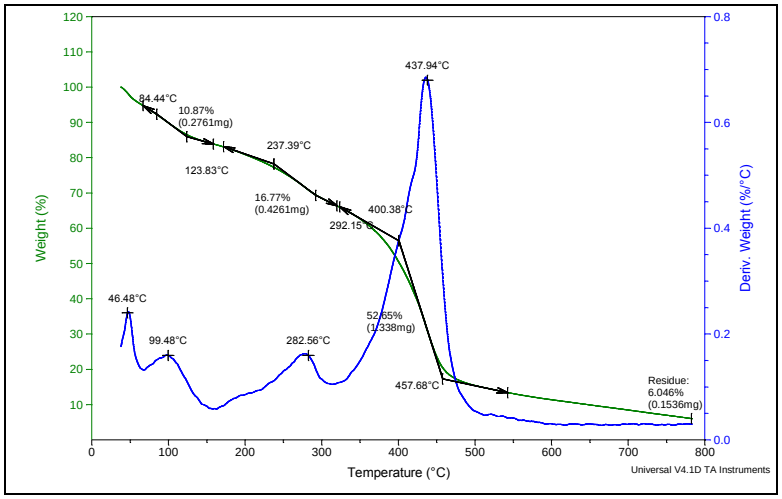


Fig: 3. c. Thermogram of NCS/PVA/CMS (1:1:2) with GLU.

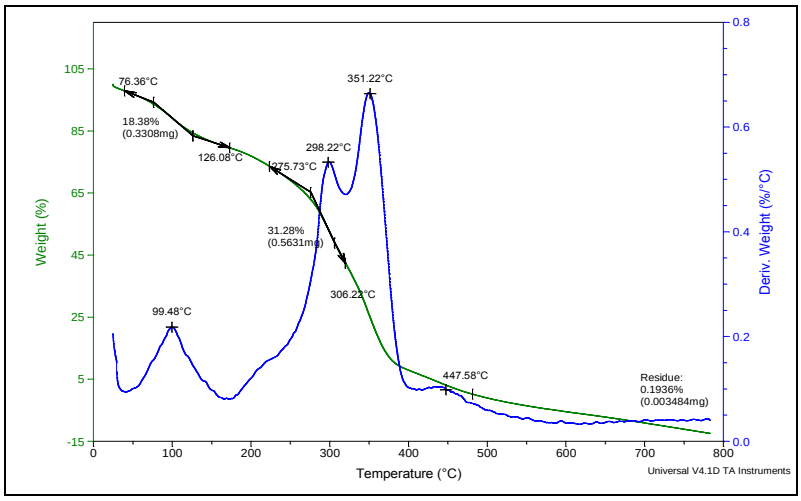


Fig: 3. d. Thermogram of NCS/PVA/CMS (2:1:1) with GLU.

Table 3: TGA Thermal details of Nanochitosan and Nanochitosan, Polyvinyl alcohol, Carboxymethyl starch ternary blends with GLU.

Percentage Decomposition %	Decomposition Temperature ° C			
	(1:1:1) with GLU	(1:2:1) with GLU	(1:1:2) with GLU	(2:1:1) with GLU
10	110	140	110	100
20	160	270	180	140
30	180	320	270	270
40	250	340	350	290
50	350	350	390	300
60	370	360	430	310
70	400	377.44	450	360
80	430	443.21	457.68	370
90	460	468	-	447.58

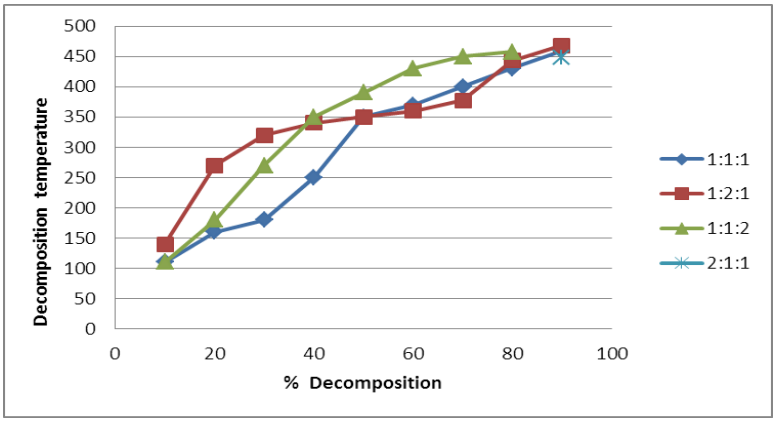


Fig. 3.e TGA Thermal details of NCS/PVA/CMS ternary blends with GLU.

The thermal detail also shows two significant weight losses, one weight loss at 50-100°C is due to the moisture vaporization, the other at 300-400°C is due to the maximum thermal degradation between PVA and CMS and above 450 °C due to the thermal degradation of crosslinkages in nanochitosan. The sample of various ratio compared was found that they disintegrate at high temperature and residues were observed even at 700°C. The highest weight loss occurs at a temperature range 266.46 – 477.17°C.

4.4 Differential Scanning Calorimetry (DSC)

The differential scanning calorimeter (DSC) is a basic tool in thermal study. It can be used in many industries from Pharmaceuticals and polymers, to nanomaterials and food products.[9,10] The DSC thermal data of nanochitosan, ternary blends of NC: PVA: CMS of various ratios in presence glutaraldehyde were discussed below:

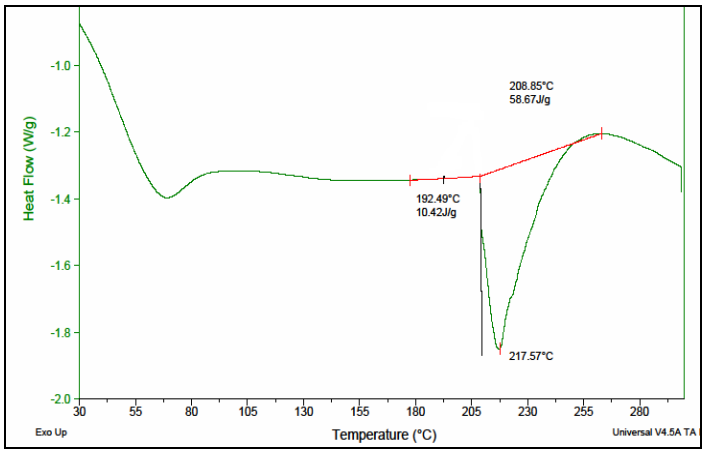


Fig: 4. DSC curves of the nanochitosan.

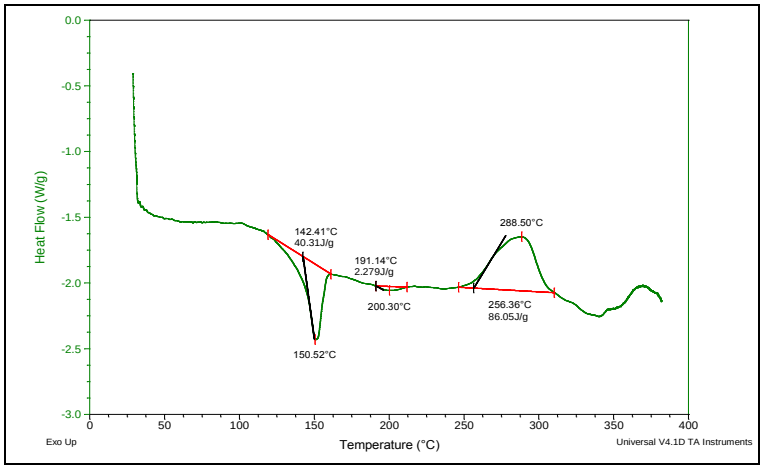


Fig: 4.a. DSC curves of NCS/PVA/CMS (1:1:1) with GLU.

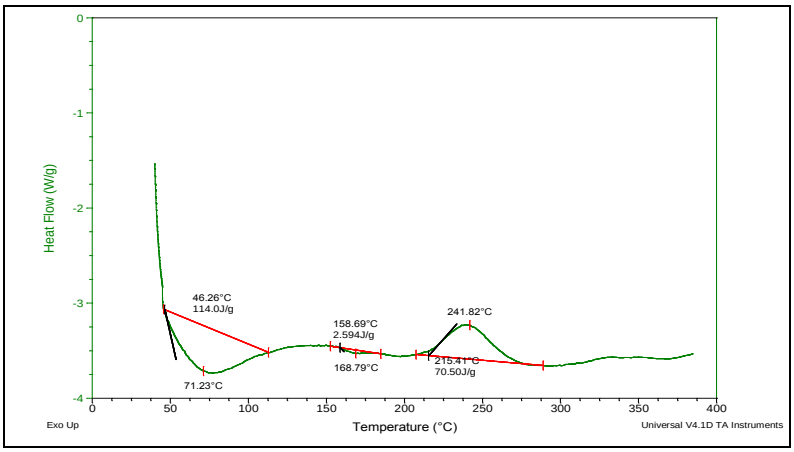


Fig: 4.b. DSC curves of NCS/PVA/CMS (1:2:1) with GLU.

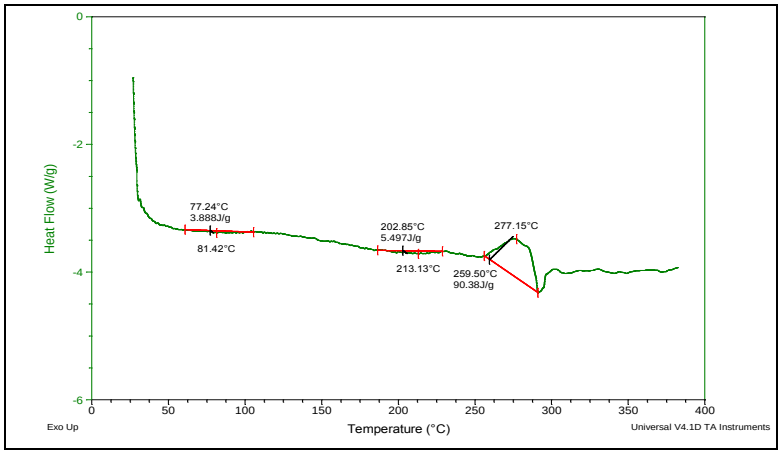


Fig: 4.c. DSC curves of NCS/PVA/CMS (1:1:2) with GLU.

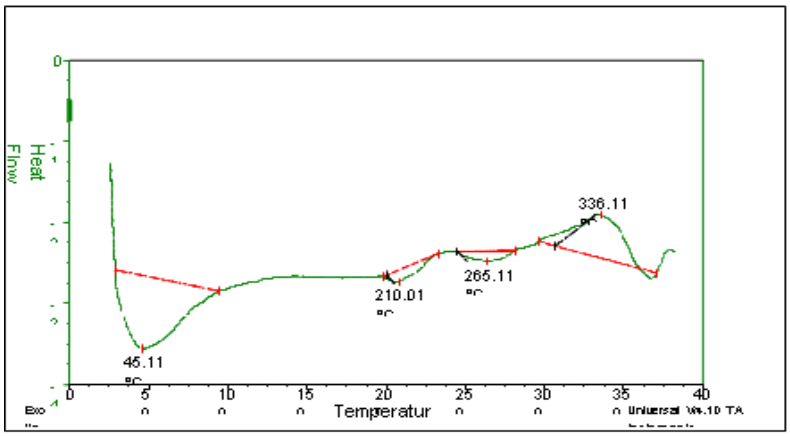


Fig: 4.d. DSC curves of NCS/PVA/CMS (2:1:1) with GLU.

Table – 4: DSC Thermogram of the NC/PVA/CMS blends of various ratios prepared in the presence of glutaraldehyde.

Sample	Tg °C	Tc °C		Tm°C
Nanochitosan	142.5	68	217.57	>300
NC/PVA/CMS 1:1:1 + Glu	175	150.52	200.30	256.36
NC/PVA/CMS 1:2:1 + Glu	215	71.23	158.69	241.82
NC/PVA/CMS 1:1:2 + Glu	240	81.42	213.13	277.15
NC/PVA/CMS 2:1:1 + Glu	285	45.11	265.11	336.11

For the blends in presence of crosslinking agent glutaraldehyde the Tg value of NC/PVA/CMS (**1:1:1,1:2:1, 1;1:2, 2:1:1)** was found to be 175°C, 215°C, 240°C, and 285 °C respectively which was greater than nanochitosan. Also the single Tg value expressing polymer- polymer miscibility.

4.5. SEM ANALYSIS

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline or amorphous form and orientation of materials making up the sample.[11,12]

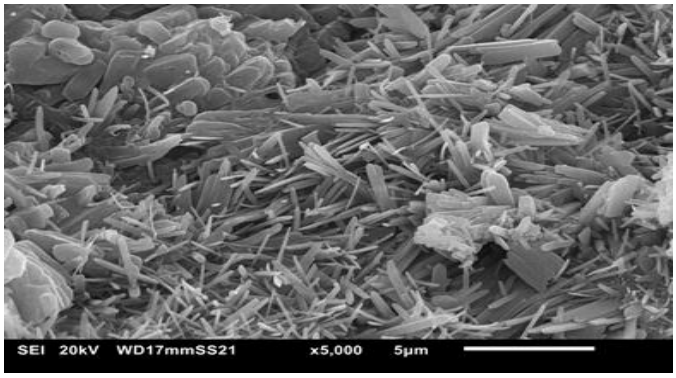


Fig: 3. SEM image of Nanochitosan.

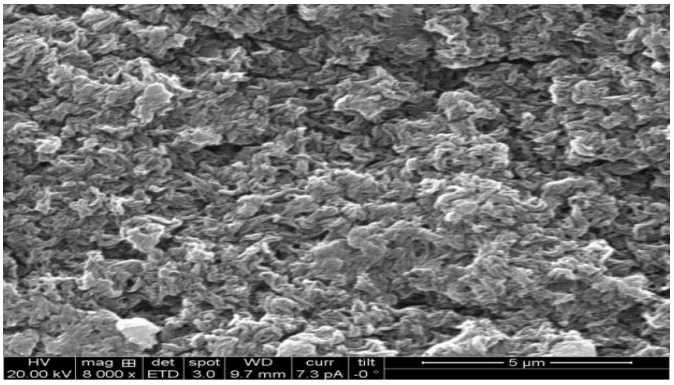


Fig: 3. a. SEM image of NCS: PVA: CMS (1:1:1) with GLU.

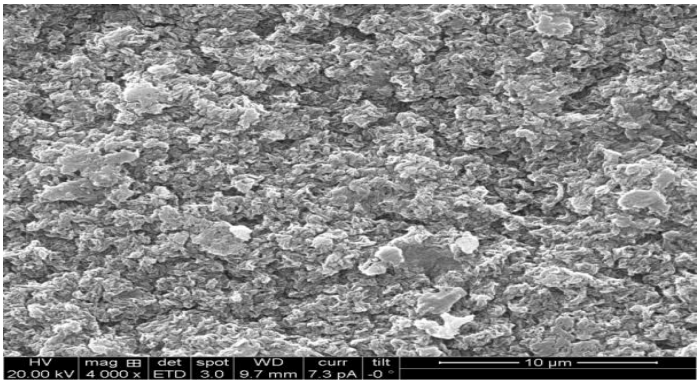


Fig: 3.b.SEM image of NCS: PVA: CMS (1:2:1) with GLU.

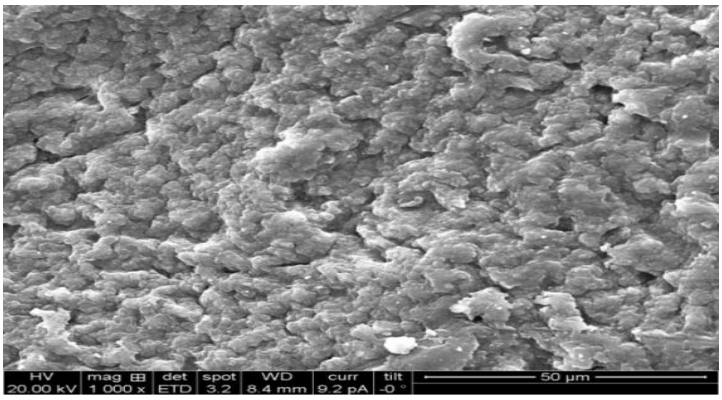


Fig: 3.c. SEM image of NCS:PVA:CMS(1:1:2) with GLU.

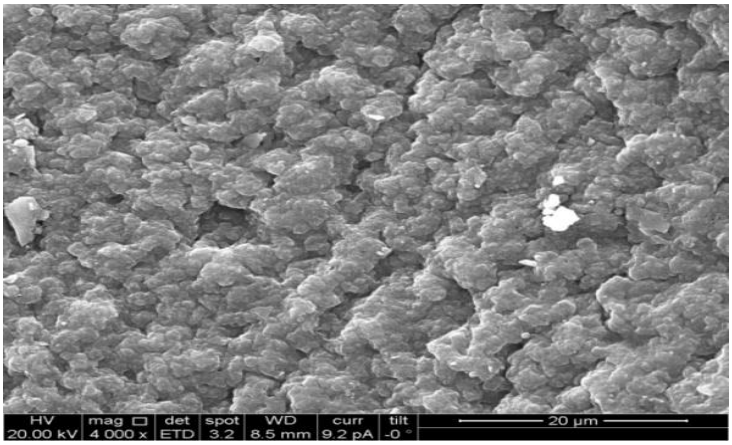


Fig: 3.d. SEM image of NCS: PVA: CMS (2:1:1) with GLU.

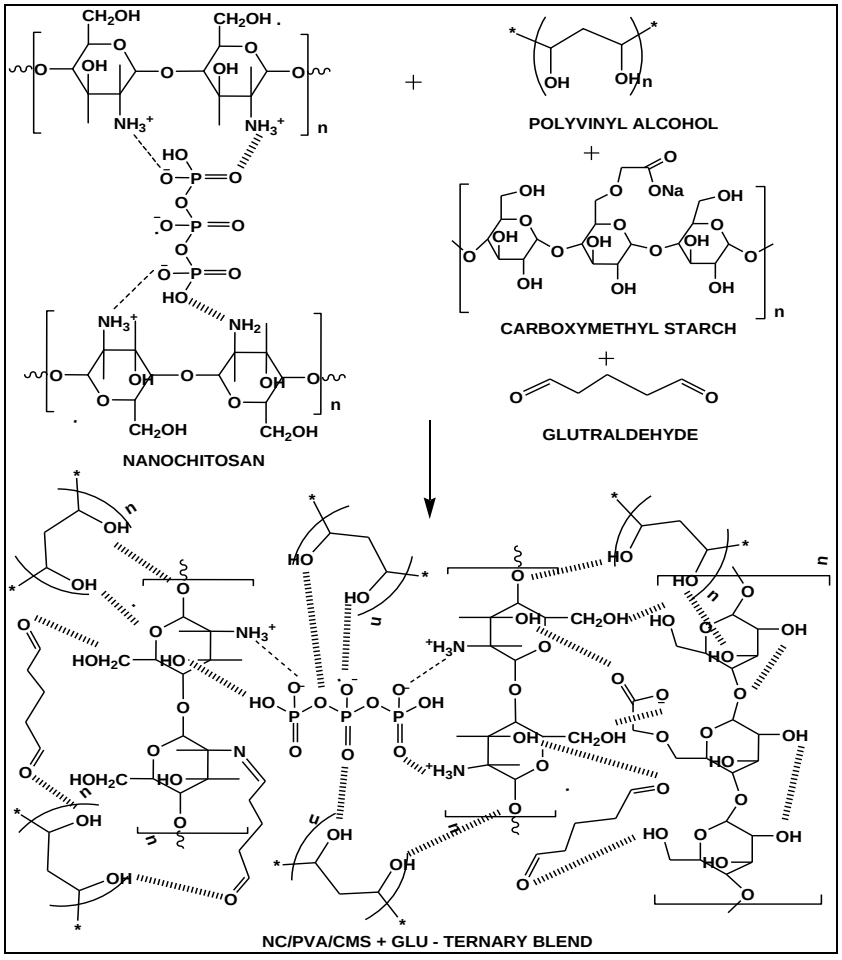
Thus suggesting that the blend has high coarse and porous area. When samples with crosslinking agent glutaraldehyde **(Figure: 3.a, b, c, d.)** compared with the nanochitosan. The surface smoothens on addition of crosslinking agent as shown in the figure.

The observed results indicate that a very good interfacial adhesion between the ternary blend. The prepared ternary blend of ratio **1:1:1** ratio was found to be highly suitable for the adsorption process and this may be due to the rough surface nature of blends.

CONCLUSION

The present study was mainly aimed to synthesize and the characterization was carried out for the prepared blends to confirm its formation and suitability for adsorption. The result of FTIR confirms the nanochitosan were effectively bound with polyvinyl alcohol and carboxymethylstarch. TGA and DSC show the thermal stability and compatibility of the blends. The FTIR results exhibits the formation of the ternary blend prepared in the presence of glutaraldehyde by studying its various functional group. The, appearance and disappearance of peaks and the shift in peak position during formation of blend was very well revealed in the FTIR results. The convalent interaction such as imine formation and the non-covalent interactions were seen in the ternary blends in the presence of glutaraldehyde. Further analysis such as XRD results confirm these interactions which were supported by the change in crystallinity value after blending. The amorphous nature of the blends increases comparatively. Especially to NC/PVA/CMS (1:1:1) ternary blend prepared in the presence of glutaraldehyde and it can be further applied for the removal of heavy metal studies due to its increased amorphous nature. This type of work could encourage the synthesis of new polymers, where some functionality is required, for specific purposes.

4.6. Proposed mechanism for the synthesis of nanochitosan ternary blend (NC/PVA/CMS) with glutaraldehyde.



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