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## Physicochemical characterization of nylon fiber reinforced chitosan composites

<sup>1</sup>D. Saravanan, <sup>2</sup>K. Vijayalakshmi, <sup>2</sup>T. Gomathi and <sup>2</sup>P. N. Sudha

<sup>1</sup>Department of Chemistry, Manonmaniam Sundaranar University, Tirunelveli, Tamilnadu, India

<sup>2</sup>Department of Chemistry, DKM College for Women, Thiruvalluvar University, Vellore, Tamilnadu, India

### ABSTRACT

Chemical modification that lead to the formation of chitosan derivatives, the grafted chitosan and chitosan composites have gained much attention which was extensively studied and widely reported in the literature. Nowadays the development of natural fiber reinforced composites is the main attraction of research community because they are turning out to be an alternative solution to the ever depleting petroleum sources. In the present work nylon fiber is used as reinforcement. The ternary composites were prepared by mixing the chitosan, carboxy methyl starch and nylon fiber in 1:2:1 ratio with and without the cross linking agent like glutaraldehyde using solution casting method. The physicochemical characterization of prepared ternary composite samples have been studied by means of Fourier transform infra red spectroscopy (FT-IR), Thermo gravimetric analysis (TGA), Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) studies. The FT-IR results indicate the presence of cross linking between the chitosan, carboxy methyl starch and nylon fiber with the cross linking agent glutaraldehyde. The XRD studies were mainly carried out to find out the change in crystallinity of ternary composites of chitosan prepared with and without the cross linking agent glutaraldehyde. The enhancement in thermal properties of polymer composites prepared in the presence of cross linking agent glutaraldehyde was also identified by TGA experiment and the results were investigated

**Key words:** Polymer composites, carboxymethyl starch, chitosan, cross linking agent, glutaraldehyde.

### INTRODUCTION

Combination of two or more component materials generally leads to the formation of composites. An attempt to composite synthesis has been made to improve material properties such as stiffness, strength, toughness, etc. The resulting properties are largely dependent on the distribution, relative amounts and geometries of the constituents. One of the modified natural carbohydrate polymer derived from carapaces of crabs and shrimps which has received a great deal of attention for its applications in diverse fields was the chitosan owing to its biodegradability, biocompatibility, non-toxicity and anti-bacterial activity [1]. The deacetylated derivative of chitin is the chitosan, or (1,4)-2-amino-2-deoxy- $\beta$ -D-glucan [2, 3], which was obtained from crustaceans [4,5] such as shrimps, squids and crabs. This is generally obtained by alkaline deacetylation from chitin which composed of glucosamine and N-acetyl-glucosamine residues with a 1,4-  $\beta$  -linkage.

Due to its regenerative capacity and biodegradability, the starch has been taken seriously by researchers for various research works. This is the natural abundant polysaccharide produced as a storage polymer from many plants [6-9]. A very successful modification reaction for various starches is the carboxymethylation. The carboxymethyl starch (CMS) is a starch derivative in which the -OH groups of the starch molecule, are partially substituted by ether group (-O-CH<sub>2</sub>COOH) which exhibits varying degree of viscosity depending on its degree of substitution (DS) [10].

The considerable research and development have been expanded in natural fibers as reinforcement in thermoplastic resin matrix. Short fiber reinforced composites are relatively a new class of materials that find applications in most general purposes. Studies on the various properties of the short fiber composites have been done earlier[11-16]. Properties of short fiber elastomer composite critically depend upon the interfacial bonding between fiber and the matrix [17-20].

In the present work, effort has been made to prepare ternary composite by mixing carboxymethyl starch, chitosan and nylon fiber with the cross linking agent glutaraldehyde to improve the strength and thermal stability of polymer composite.

## MATERIALS AND METHODS

### MATERIALS

Chitosan was kind gift from India Sea Foods, Cochin, Kerala which is 92% deacetylated. Nylon fiber was purchased from Placon Agencies, Chennai. Carboxymethyl starch, glacial acetic acid and the cross linking agent glutaraldehyde was obtained from Sisco Research Laboratories Pvt, Ltd, SD fine-chem Ltd, India. All the chemicals used in the present work were of analytical grade

### PREPARATION OF CHITOSAN / CARBOXYMETHYL STARCH /NYLON FIBER (1:2:1) TERNARY COMPOSITE

A known weight of the carboxy methyl starch (2g) and chitosan (1g) were dissolved in water and glacial acetic acid separately. It was then mixed well and stirred for 30 minutes. About 1g of nylon fiber was cut into very small pieces of approximately 0.25 cm length to be used as dust fibers. The above prepared nylon dust fibers were then added to the mixture of chitosan and carboxy methyl starch solution. This chitosan/carboxymethyl starch/nylon fiber mixture (1:2:1) was then stirred well at room temperature with moderate agitation for one hour. After the agitation process is over the prepared ternary composite was then poured into a petri dish and allowed to dry in vacuum for 10 hours to remove the solvent completely. A similar procedure was carried out to prepare the ternary composite (1:2:1) in the presence of glutaraldehyde (10ml) as a cross linking agent.

### CHARACTERIZATION

#### FT-IR Spectroscopy

FTIR measurements of the prepared nylon fiber reinforced ternary composite samples was recorded by Fourier transform infra-red spectrophotometer (FT-IR) using the Perkin Elmer 200 FTIR spectrophotometer, in the range of 500-4000 $\text{cm}^{-1}$  at 25°C with a resolution of 4  $\text{cm}^{-1}$ .

#### XRD diffraction studies

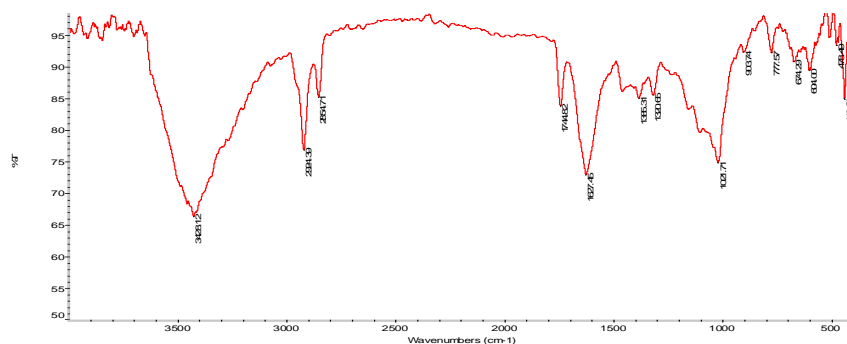
X-ray diffraction (XRD) studies of nylon fiber reinforced ternary composites was performed with the X-ray powder diffractometer (XRD – SHIMADZU XD – D1) using a Ni – filtered Cu K $\alpha$  X-ray radiation source.

#### TGA analysis

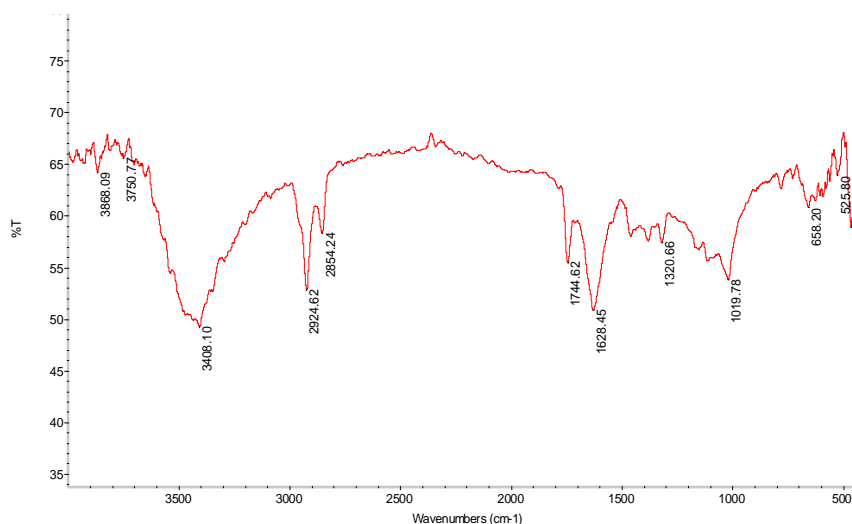
The thermo gravimetric analysis of the chitosan / carboxymethyl starch /nylon fiber (1:2:1) ternary composite prepared with and without the crossing linking agent glutaraldehyde was carried out on a Perkin Elmer thermal analysis instrument.

## RESULTS AND DISCUSSION

FTIR spectroscopy was used to characterize the interactions between chitosan, carboxy methyl starch and nylon fibre. Figure- 1 shows the FTIR spectra of chitosan /carboxy methyl starch/nylon fiber (1:2:1) ternary composite. The prominent peak observed at 3428.12  $\text{cm}^{-1}$  corresponds to the intermolecular hydrogen bonded OH stretching and NH stretching [21]. The presence of methylenic CH stretching was identified from the sharp peak obtained at around 2924.39  $\text{cm}^{-1}$ . Also certain absorption peaks which were obtained at 1744.82  $\text{cm}^{-1}$ , 1627.45  $\text{cm}^{-1}$ , 1385.31 $\text{cm}^{-1}$  and 1021.71  $\text{cm}^{-1}$  was attributed to C=O stretching, N-H deformation, C-H stretching vibration , OH bending and C-N Stretching respectively.



**Figure 1: FTIR spectra of chitosan/carboxymethyl starch/nylon fiber (1:2:1) ternary composite**



**Figure 2: FTIR spectra of chitosan/carboxymethyl starch/nylon fiber (1:2:1) ternary composite – glutaraldehyde**

Figure-2 shows the FT-IR spectral details of chitosan/carboxy methyl starch/nylon fibre (1:2:1) ternary composite prepared in the presence of cross linking agent glutaraldehyde. The absorption peak obtained at  $3408.10\text{ cm}^{-1}$  and  $2924\text{ cm}^{-1}$  confirm the presence of NH stretching in secondary amides and CH stretching  $\text{CH}_2$  group. Certain absorption bands which were obtained at  $1744.62\text{ cm}^{-1}$ ,  $1628.45\text{ cm}^{-1}$ ,  $1320.66\text{ cm}^{-1}$ ,  $1019.78\text{ cm}^{-1}$ , correspond to C=O stretching, C=N stretching, O-H bending, C-N Stretching vibration respectively.

The chemical interactions are reflected by changes in the peaks of characteristic spectra after physical mixing of two or more substances with the cross linking agent [22]. On comparing the FT-IR results of Figure-2 with Figure-1, it was observed that an additional peak was obtained in Figure (2) at  $1628.45\text{ cm}^{-1}$  corresponding to the presence of C=N stretching. This observed peak confirms the strong blending of carboxymethyl starch, chitosan and nylon fiber with the cross linking agent glutaraldehyde respectively. The chemical interactions are reflected by changes in the peaks of characteristic spectra after physical mixing of two or more substances [22].

### X-RAY DIFFRACTION STUDIES

Figures (3) and (4) shows the X-ray diffraction patterns of chitosan/carboxymethyl starch/nylon fiber (1:2:1) ternary composite prepared with and without the cross linking agent glutaraldehyde. In the XRD patterns of the chitosan/carboxymethyl starch/nylon fiber (1:2:1) ternary composite peaks were obtained at various  $2\theta$  values such as  $18^\circ$ ,  $22^\circ$ ,  $27^\circ$ ,  $28^\circ$ ,  $31^\circ$ ,  $33^\circ$ ,  $44^\circ$ ,  $48^\circ$ ,  $52^\circ$ ,  $53^\circ$ . These peaks indicate the presence of crystalline forms. The XRD patterns of the chitosan/carboxymethyl starch/nylon fiber (1:2:1) ternary composite prepared in the presence of cross-linking agent glutaraldehyde also shows peaks at various  $2\theta$  values such as  $11^\circ$ ,  $12^\circ$ ,  $17^\circ$ ,  $18^\circ$ ,  $25^\circ$ ,  $28^\circ$ ,  $29^\circ$ ,  $32^\circ$ ,  $34^\circ$ ,  $36^\circ$ ,  $38^\circ$ ,  $40^\circ$ ,  $41^\circ$ ,  $43^\circ$ ,  $45^\circ$ ,  $57^\circ$ ,  $65^\circ$ .

The above observed sharp peaks indicate that the chitosan/carboxymethyl starch/nylon fiber (1:2:1) ternary composite prepared with glutaraldehyde as cross linking agent has more number of crystalline forms. On comparing the XRD patterns of chitosan/carboxymethyl starch/nylon fiber (1:2:1) ternary composite prepared with and without the cross linking agent, it was found that the degree of crystallinity was found to be increased. These peaks confirms that the chitosan/carboxymethyl starch/nylon fiber (1:2:1) ternary composite prepared in the presence of the cross

linking agent has higher thermal stability with the formation of different crystalline forms. The significant shift in the diffraction peaks and the diffraction pattern with a sharp peak indicated that there was a molecular miscibility and interaction between the components [23].

Interestingly, the intensities of the peak at around  $2\theta = 10^\circ$  were enhanced in chitosan/carboxymethyl starch/nylon fiber (1:2:1) ternary composite while incorporating 10 ml of glutaraldehyde. This suggests that there was a slight phase separation between chitosan, carboxymethyl starch, nylon fiber and also it was observed that certain interaction takes place among these three components with the cross linking agent glutaraldehyde [22].

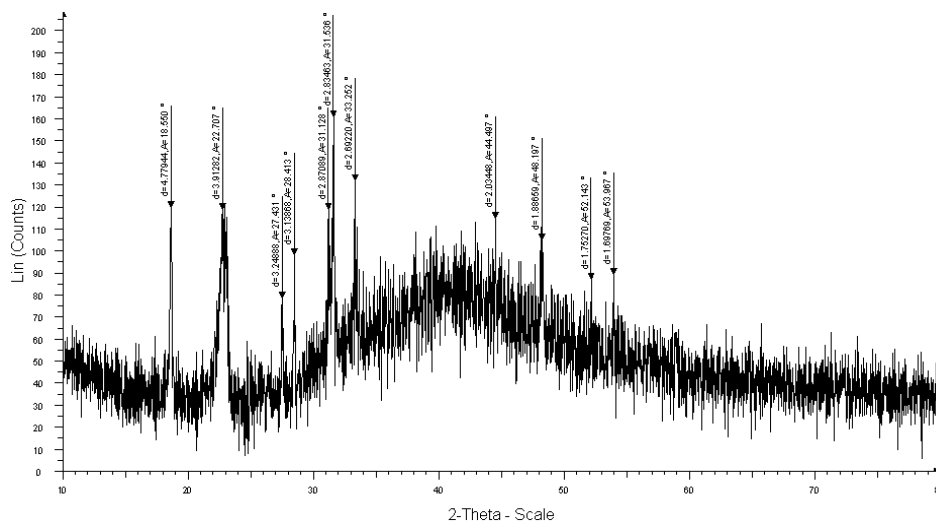


Figure 3: Chitosan/carboxymethyl starch/nylon fiber (1:2:1) ternary composite

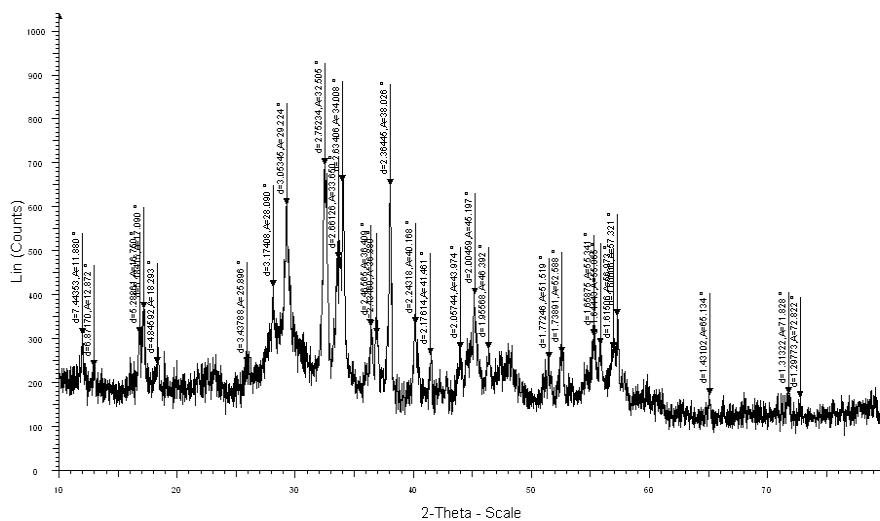


Figure 4: Chitosan/carboxymethyl starch/nylon fiber (1:2:1) ternary composite – glutaraldehyde

### THERMOGRAVIMETRIC ANALYSIS

The thermal decomposition details were given in Table-1. Figure-5, represents the percentage decomposition of the sample at different temperatures. The TGA thermo gram details of (Figure-5) chitosan/carboxy methyl starch/nylon fiber (1:2:1) ternary composite shows that around 72% of the sample was disintegrated within  $350^\circ\text{C}$ . The weight loss was observed to maximum in the temperature range of  $219^\circ\text{C}$ - $400^\circ\text{C}$  which may be to the breaking of hydrogen bonds between polymers. The residual temperature of the composite was found to be  $750^\circ\text{C}$ . At the end of the experiment above  $750^\circ\text{C}$ , 6.905% of the sample remained as a residue. The gradual weight loss was observed from  $350^\circ\text{C}$ .

**Table-1 : TGA thermogram details of chitosan/carboxymethyl starch/nylon 6 (1:2:1) in the presence and absence of glutaraldehyde crosslinker**

Percentage decomposition	Decomposition Temperature(°C)	
	CS/CMS/NY 6 (1:2:1)	CS/CMS/NY 6 (1:2:1) - GLU
10	80	100
20	150	150
30	230	300
40	250	420
50	260	430
60	320	440
70	360	450
80	495	460
90	750	510

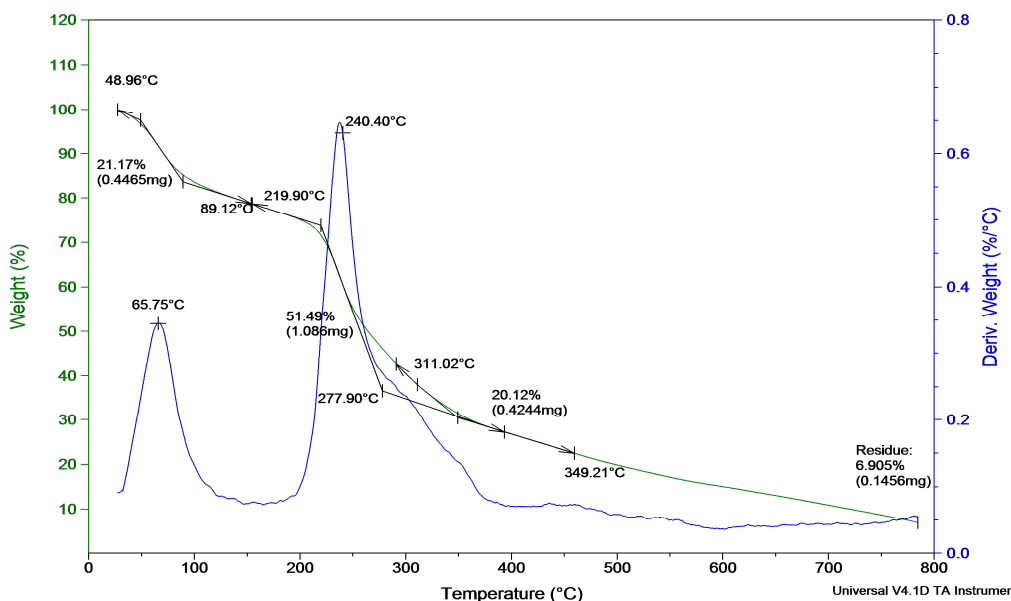
**Figure-5: TGA thermogram details of chitosan/carboxy methyl starch/nylon fiber (1:2:1) ternary composite**

Table-1 and Figure- 6 represents the TGA thermogram details of chitosan/carboxy methyl starch/nylon fiber (1:2:1) ternary composite prepared in the presence of cross linking agent glutaraldehyde. From the above figure it was evident that the maximum weight loss was observed in the temperature range of 415°C– 460°C and in addition to this it was also observed that around 2.516% weight of the composite was left as residue at the end of the experiment.

The initial weight loss for all the samples starts around 62 °C with loss of weight. This may corresponds to the loss of bound water and acetic acid from the composite. The second weight loss was mainly due to the melting temperature,  $T_m$ , during which there was 50% weight loss. The third weight loss was observed in the certain temperature range which may be correspondent to the structural decomposition of the composite [24].

On comparing Figures -5 and 6 it was concluded that the chitosan/carboxy methyl starch/nylon fiber (1:2:1) ternary composite prepared with the cross linking agent glutaraldehyde was found to be highly thermally stable. This was confirmed from the increased value of initial decomposition temperatures (100°C) in case of chitosan/carboxy methyl starch/nylon fiber (1:2:1) ternary composite prepared in the presence of cross linking agent glutaraldehyde when compared to initial decomposition temperatures (80°C) in case of chitosan/carboxy methyl starch/nylon fiber (1:2:1) ternary composite prepared in the absence of cross linking agent glutaraldehyde.

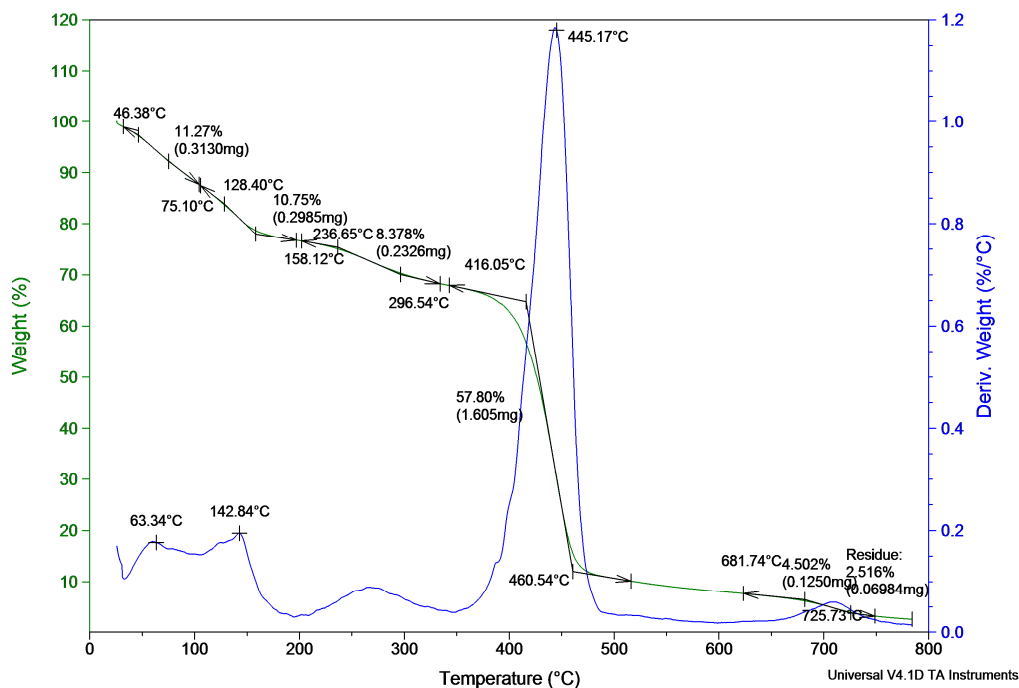


Figure-6 -TGA thermogram details of chitosan/carboxy methyl starch/nylon fiber (1:2:1) ternary composite-glutaraldehyde

#### DIFFERENTIAL SCANNING CALORIMETRY

Figure-7 represents the DSC curve of chitosan /carboxy methyl starch/nylon fiber (1:2:1) ternary composite respectively. One endothermic and one exothermic peak were observed at 59.10°C and 271.85°C. The DSC curve of chitosan /carboxy methyl starch/nylon fiber (1:2:1) ternary composite shows that the glass transition temperature was observed at 155°C. The DSC curve details of chitosan/carboxy methyl starch/nylon fiber (1:2:1) ternary composite prepared in the presence of cross linking agent glutaraldehyde was represented in Figure-8. Broad endothermic peaks are observed at various temperatures 67°C and 200.55°C. These observed peaks indicates the crystallization behavior of prepared ternary composite. The glass transition temperature of the ternary composite prepared in the presence of cross linking agent glutaraldehyde was found to be 165°C

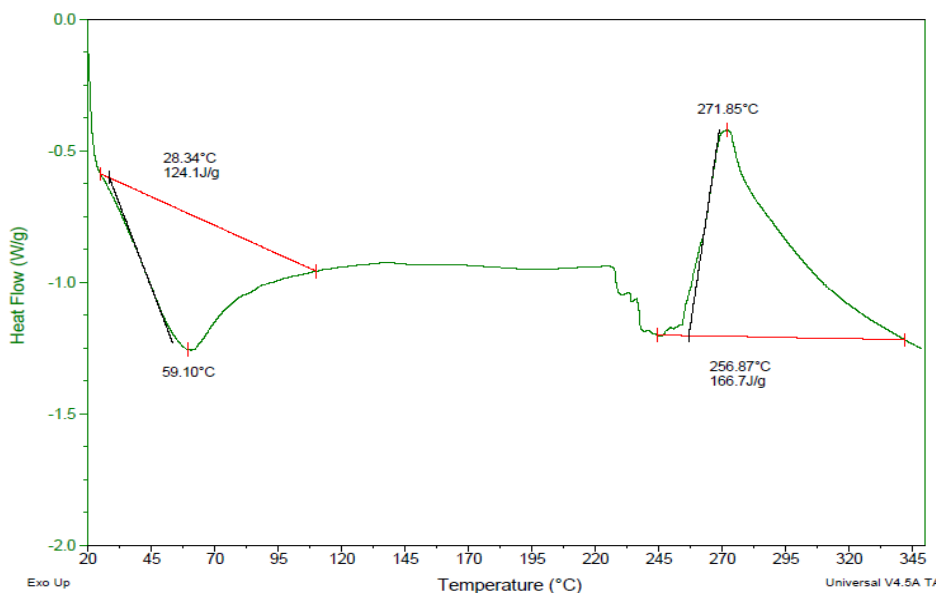


Figure-7 –DSC curve of chitosan/carboxy methyl starch/nylon fiber (1:2:1) ternary composite

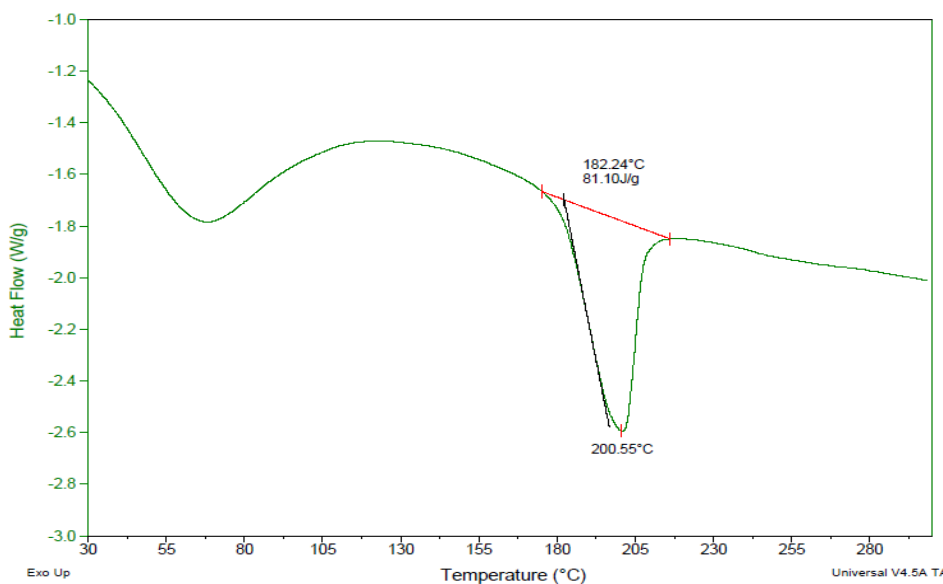


Figure-8 –DSC curve of chitosan/carboxy methyl starch/nylon fiber (1:2:1) ternary composite-glutaraldehyde

### CONCLUSION

The above observed results suggest that there is strong interaction between the molecular chains of chitosan, carboxy methyl starch and nylon fiber which may lead to the miscibility at specific ratios. From the FTIR results, it was found that the C=N type of linkage were observed in the cross linked polymer. This obtained peak confirms the cross linking between the chitosan, carboxy methyl starch and nylon fiber with the cross linking agent glutaraldehyde. The XRD results indicate the increase in crystallinity of ternary composites of chitosan prepared with the cross linking agent glutaraldehyde. From the results of TGA and DSC it was observed that the cross linking agent glutaraldehyde enhanced the thermal stability of the polymer composite. The ternary composite prepared with glutaraldehyde showed better thermal stability than that without cross linking agent.

### REFERENCES

- [1] A. Esam . El-hefian and H.Abdul.Yahaya, *Maejo Int. J. Sci. Technol.*, **2010**, 4(02), 210-220
- [2] R.A.A. Muzzarelli, *Natural Chelating Polymers*, Pergamon Press, Oxford, **1973**.
- [3] H.I. Bolker, *Natural and Synthetic Polymer: An Introduction*, Marcel Dekker, New York, **1974**.
- [4] T.C Yang and R.R Zull, *Ind. Eng. Chem. Prod. Res. Dev.*, **1984**, 23, 168-172.
- [5] T.A .Khan, K.K Peh and H.S Ch'ng, *J. Pharm. Sci.*, **2002**, 5, 205-512.
- [6] P. Aggarwal, *Thermochimica Acta*, **1999**, 340-341, 195-203.
- [7] S.H Iman, S.H.Gordon, L. Mao and L. Chen. *Polymer Degradation and Stability*, **2001**, 73: 245-533.
- [8] J. Lörcks, *Polymer Degradation and Stability*, **1998**, 59: 245-249.
- [9] J.J.G. Van Soest, and J.F.G. Vliegenthart, *Trends in Biotechnology*, **1997**, 15(6): 208-213.
- [10] Z. Stojanovic, K.Jeremic and S.Jovanovic, *Starch/Starke*, **2000**, 52 (11): 413-419.
- [11] W. Guo and M.Ashida, *J. Appl. Polym. Sci.* **1993**, 49, 1081.
- [12] V.G. Geethamma, Joseph Reethamma, and Sabu, Thomas, *J. Appl. Polym. Sci.* **1995**, 55,583.
- [13] F. Suhara, S.K.N. Kutty and G.B. Nando, *Polym. Plast. Technol. Eng.* **1998**, 37, 241.
- [14] T.D. Sreeja and S.K.N. Kutty, *Prog In. Rubber Plast. & Recycling Technol.* **2002**,18, 1.
- [15] T.D. Sreeja and S.K.N. Kutty, *J. Elastomers and Plastics*, **2002**, 34, 157.
- [16] R.S. Rajeev, E.S.K. Bhowmick, K.D. Anil and S. Bandyopadhyay, *J. Appl. Polym. Sci.* **2003**, 90, 544.
- [17] H. Ismail, N. Rosnah, H.D, Rozman. *Eur. Polym. J.*, **1997**, 33, 1231.
- [18] S.Varghese, B. Kuriakose, S. Thomas A.T. Koshy, *J. Adhesion sci. Technol*, **1994**, 8, 235.
- [19] A. Ward, A.M Ghoneim, A.F, Younan, A.M, Bishai A.M. *Inter.J.Polym. Mater.* **2001**, 48,355.
- [20] A.M Ismail, A.M. Ghoneim, *Polym.Plast. Technol.Engg.* **1999**, 38, 71
- [21] H. Du, Y. M. Yu, J. H. Zheng, R. H. Huang, and L. N. Zhang, *Journal of Applied Polymer Science*, **2001**, 80(13), 2558–2565.
- [22] Qiu-Ping Zhong and Wen-Shui Xia, *Food Technol. Biotechnol.* **2008**, 46 (3) 262–269.
- [23] Q.P. Zhang, and W.S Xia, *Food. Technol. Biotechno* **2008**, 46(3): 262-269
- [24] B.S Mudigoudra, S.P.Masti, R.B.Chougale, *Research Journal of Recent Sciences*, **2012**, Vol. 1(9), 83-86.