

SYNTHESIS AND CHARACTERISATION OF TERNARY BLENDS OF CHITOSAN

RAMASUBRAMANIAN S.², NASREEN K.¹, VIJAYALAKSHMI K.¹, GOVINDARAJAN C.*² AND SUDHA P.N.¹

¹PG and Research Department of Chemistry, D.K.M. College for Women, Vellore, Tamilnadu, India

²Bharathiar University, Coimbatore, Tamilnadu, India

*Corresponding Author: Email- parsu8@yahoo.com, gvrajan2003@yahoo.com, ram_ss_99@yahoo.com

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Abstract- Polymer blends were prepared in the presence and absence of cross linking agent like glutaraldehyde. Ternary blends were prepared by mixing of carboxymethyl cellulose, chitosan and starch, in the various ratios in presence and absence of the cross linking agent like glutaraldehyde. The characterization of various polymeric blends were carried out by advanced analytical techniques such as Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and Thermo gravimetric analysis (TGA). The obtained results of IR studies reveal the presence of cross linking between the polymers and cross linking agents. From the results of DSC and TGA it was concluded that the blend prepared with glutaraldehyde as a cross linking agent was found to be highly thermally stable. The present study reveals that the polymer blends are very strong in the presence of cross linking agent than in the absence of cross linking agent. The results are discussed.

Key words: Carboxymethyl cellulose, starch, chitosan blends, cross linking agent, Thermal stability.

Introduction

Polymers have played an important role from the beginning of life [1]. The chemical modification of polysaccharides is the most important route to modify the properties of the naturally occurring biopolymers and to use this renewable resource in the content of sustainable development [2]. Blending of two or more polymers to obtain materials with new and unique properties has become one of the most important research topics in the field of polymers [3]. The main purpose of blending the polymers is to obtain materials with additional properties and minimum sacrifice of their original properties [4].

Mixing of two or more polymers to produce ternary and ternary is a well established route to achieve a certain amount of physical polymer systems [5, 6]. Well known examples of blends are the impact modified, (rubber) toughened polymers, where polymers with different glass transition temperature are blended and improved the strength of polymer blends by cross linking agents [7-9].

Blends of synthesis and natural polymers represent a new class of materials which have attracted much attention especially in bio application as biomaterial. The successes of synthetic polymers as biomaterial relies mainly on their wide range of mechanical properties [5]. Blending can usually be implemented more rapidly and economically than the development of new materials [5, 6].

Blends are able to improve many properties such as mechanical and thermal properties [10]. In the present work effort has been made to prepare ternary blends by mixing starch and chitosan with cross linking agent to improve the strength and thermal stability of polymer blend.

Experimental procedure

Materials

Chitosan was received from India Sea Foods, Cochin, Kerala which is 92% deacetylated. Glacial acid was obtained from SISCO Research Laboratories PVT, LTD, India. Carboxymethyl cellulose is provided by THERMO FISHER SCIENTIFIC PVT LTD India. Starch was obtained from HI-PURE FINE CHEM PVT LTD, India. Glutaraldehyde was obtained from SDFINE-CHEM LTD, India.

Ternary Blend Preparation

A known weight of the solutions of Carboxymethyl cellulose, starch and chitosan were prepared by dissolving in water and glacial acetic acid separately. These solutions were mixed at different weight ratios in the presence and absence of glutaraldehyde (10ml) as a cross linking agent at room temperature with moderate agitation for one hour. Then the above prepared mixture were poured into a Petri dish and dried under vacuum for 10hrs to remove the solvent.

Characterization

FTIR measurements were done using KBr pelleted samples with a Perkin Elmer 200 FTIR spectrophotometer, in the range of 4000-400 cm⁻¹. DSC analysis of the polymeric blend samples were carried out with the Perkin Elmer thermal analyzer with pierced lid in the nitrogen atmosphere at a heating rate of 10 °C/min. The thermo gravimetric analysis of the carboxymethyl cellulose /starch /chitosan blends with and without the cross linking agent glutaraldehyde was carried out on a Perkin Elmer thermal analysis instrument. In this technique the mass of the substance is measured as a function of temperature.

FTIR Analysis

Figure: 1 shows the FT-IR spectral details of carboxymethyl cellulose / chitosan/ starch (2:1:1) blend. The FT-IR spectra of ternary polymer blend of chitosan (2:1:1) shows the prominent peaks at 3432.23cm⁻¹ confirms the intermolecular hydrogen bonding [11], N-H stretching, O-H stretching and strong polymerization. Peaks observed at wave numbers such as 2926.64,2856.27,1718.11,1383.72cm⁻¹ corresponds to asymmetrical and symmetrical C-H stretching in CH₂ and CH₃ [12], carbonyl stretching in secondary amides and O-H inplane bending.

Figure: 2 shows the FT-IR spectral details of carboxymethyl cellulose / chitosan/ starch (2:1:1) blend in the presence of cross-linking agent glutaraldehyde. From the above FT-IR spectral details of carboxymethyl cellulose / chitosan/ starch (2:1:1) blend in the presence of cross-linking agent glutaraldehyde, we can see the prominent peaks at 3426.97,2863.61,1715.52,1383.36cm⁻¹corresponding to intermolecular hydrogen bonding X ray diffraction studies, N-H stretching, aliphatic C-H stretching in methyl group O-H in plane bending in alcohols.

Thermal analysis

Thermogravimetric analysis

The thermo gravimetric analysis of carboxymethyl cellulose, starch and chitosan blends IN presence and absence of cross linking agent glutaraldehyde was carried out on a Perkin Elmer thermal analysis. Figure: 3 shows the TGA thermo gram of carboxymethyl cellulose / chitosan/ starch (2:1:1) blend. The TGA thermogram details of carboxymethyl cellulose / chitosan/ starch (2:1:1) shows that around 70% of the sample gets disintegrated within 850°C. At the end of the experiment around 74% of the blend gets disintegrated leaving behind 26.7821% of the blend is remained as a residue. Figure: 4 shows the TGA thermo gram of carboxymethyl cellulose / chitosan/ starch (2:1:1) blend in the presence of glutaraldehyde. The residual temperature was found to be 800°C. Around 78% of the sample is disintegrated within 750°C.Maximum weight loss occurs at the temperature range of 250°C -550°C. At the end of the

experiment i.e., at 850°C only 24.2442% of the blend remained as a residue. From the results it is evident that crosslinking had increased thermal stability of the blend.

Differential Scanning Calorimetry

Figures 5 and 6 show the DSC curve of carboxymethyl cellulose / chitosan/ starch (2:1:1) blend with and without glutaraldehyde at the cross linking agent respectively. The figure (5) shows that the glass transition temperature of the carboxymethyl cellulose / chitosan/ starch blend is observed at 190°C. Fig (6) shows that glass transition temperature of the blend carboxymethyl cellulose / chitosan/ starch (2:1:1) in the presence of cross linking agent glutaraldehyde is found to be 280°C. On comparing the DSC curves of carboxymethyl cellulose / chitosan/ starch (2:1:1) with and without the cross linking agent glutaraldehyde, it was found that glass transition temperature is shifted to higher values. Above results conforms that, the blend in the presence of cross linking agent has higher thermal stability.

X-Ray Diffraction Studies

Figures 7 and 8 show the X Ray diffraction patterns The XRD pattern of carboxymethyl cellulose / chitosan/ starch (2:1:1) blend shows the peaks at 2θ=22° and 2θ=42° from the broad nature of peaks conclude that the sample has semi crystalline nature. Whereas, XRD pattern of carboxymethyl cellulose / chitosan/ starch (2:1:1) of the presence of cross linking agent shows two broad peaks at around 20° and 42° which it indicates that, the sample has amorphous structure.

Conclusion

The results suggest that there is strong interaction between the molecular chains of carboxymethyl cellulose, chitosan and starch, which may lead to the miscibility at specific ratios of the two components blended. From the FTIR results, it was found that the C=N type of linkage were observed in the cross linked polymer showing the binding between the polymer and the cross linking agents. From the results of DSC and TGA it was observed that the cross linking agents enhanced the thermal stability of the polymer blend. The blend prepared with glutaraldehyde showed better miscibility than that without the cross linking agent.

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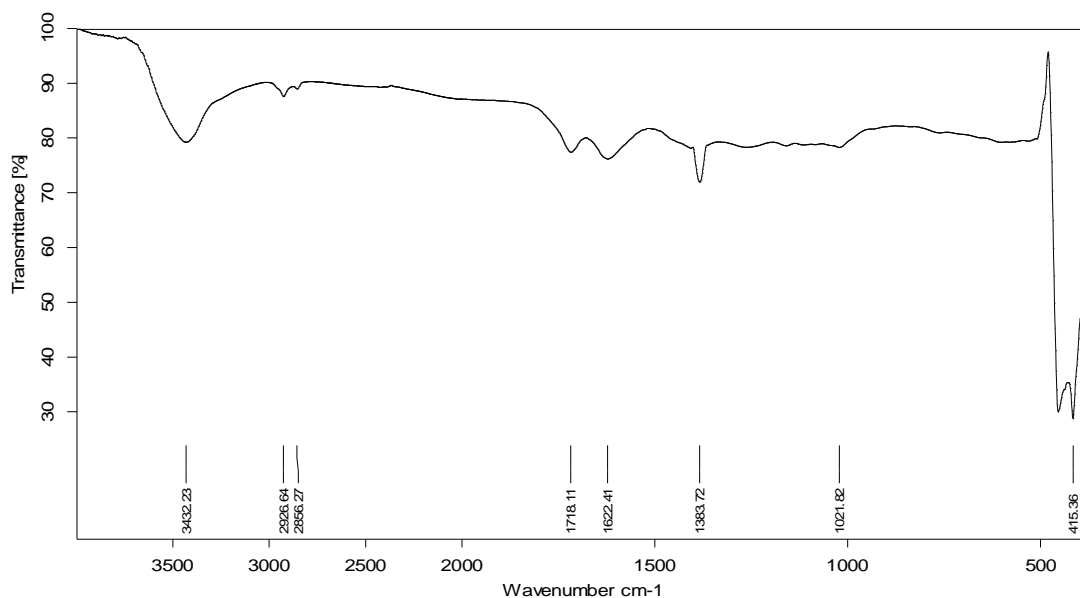


Fig. 1- ft-ir spectral details of carboxymethyl cellulose / chitosan/ starch (2:1:1)

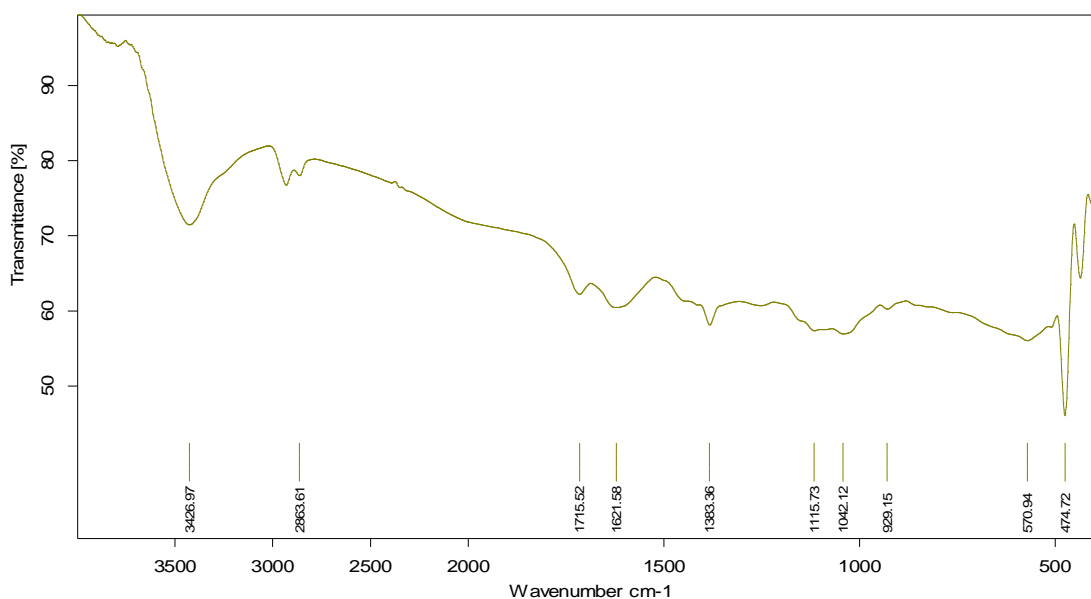


Fig. 2- ft-ir spectral details of carboxymethyl cellulose / chitosan/ starch(2:1:1)-glutaraldehyde

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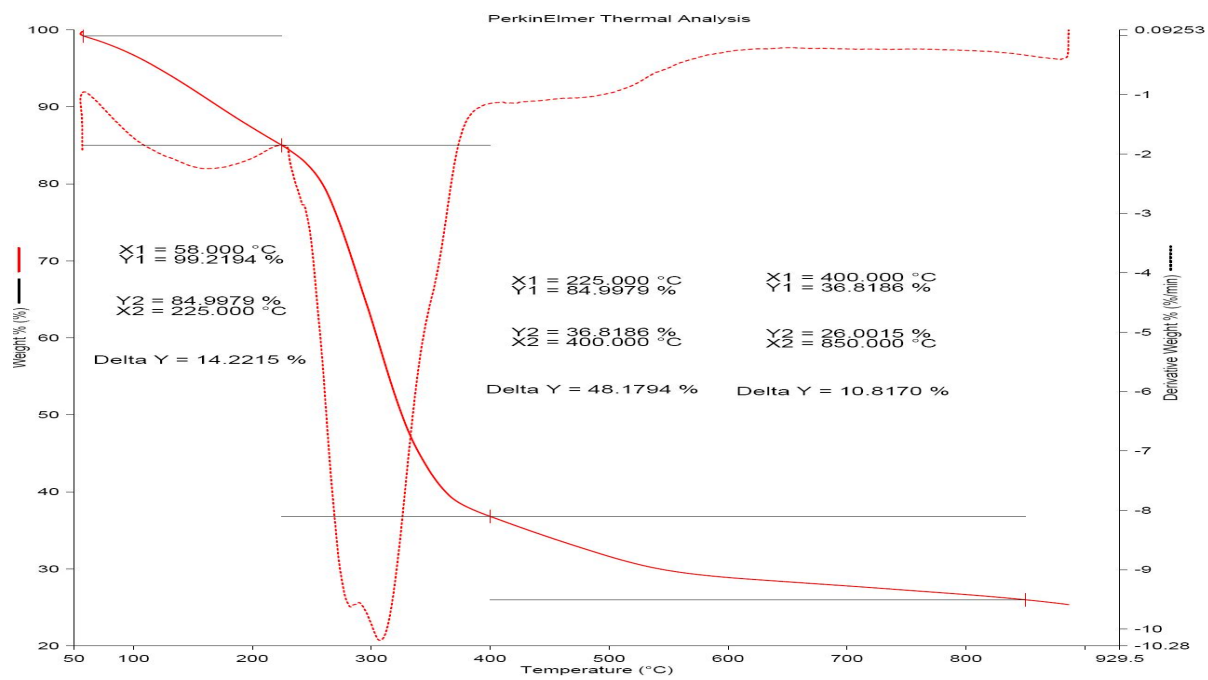


Fig. 3 - tga thermogram of carboxymethyl cellulose / chitosan/ starch (2:1:1)

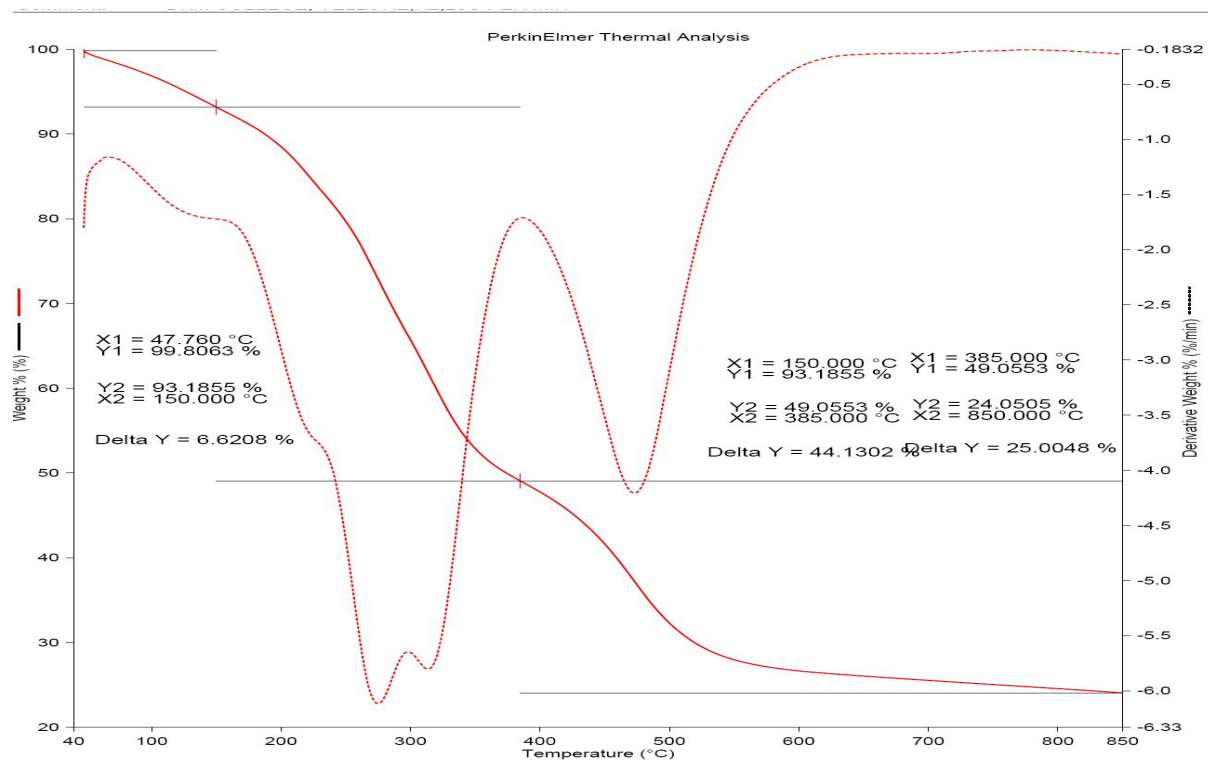


Fig. 4 - tga thermogram of carboxymethyl cellulose / chitosan/ starch (2:1:1) - glutaraldehyde

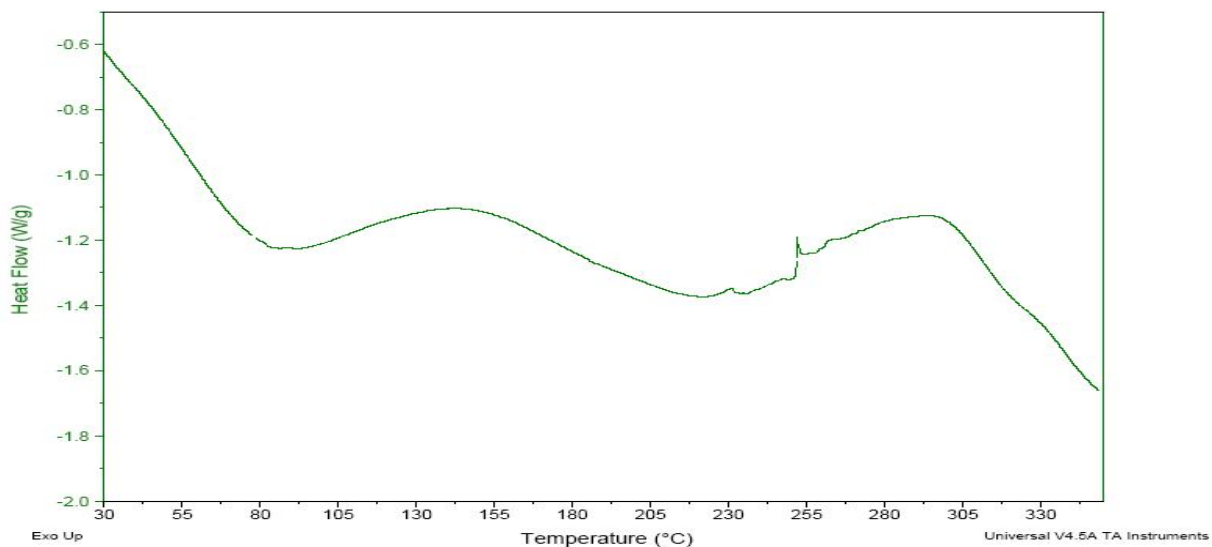


Fig. 5 - dsc thermogram of carboxymethyl cellulose / chitosan/ starch (2:1:1)

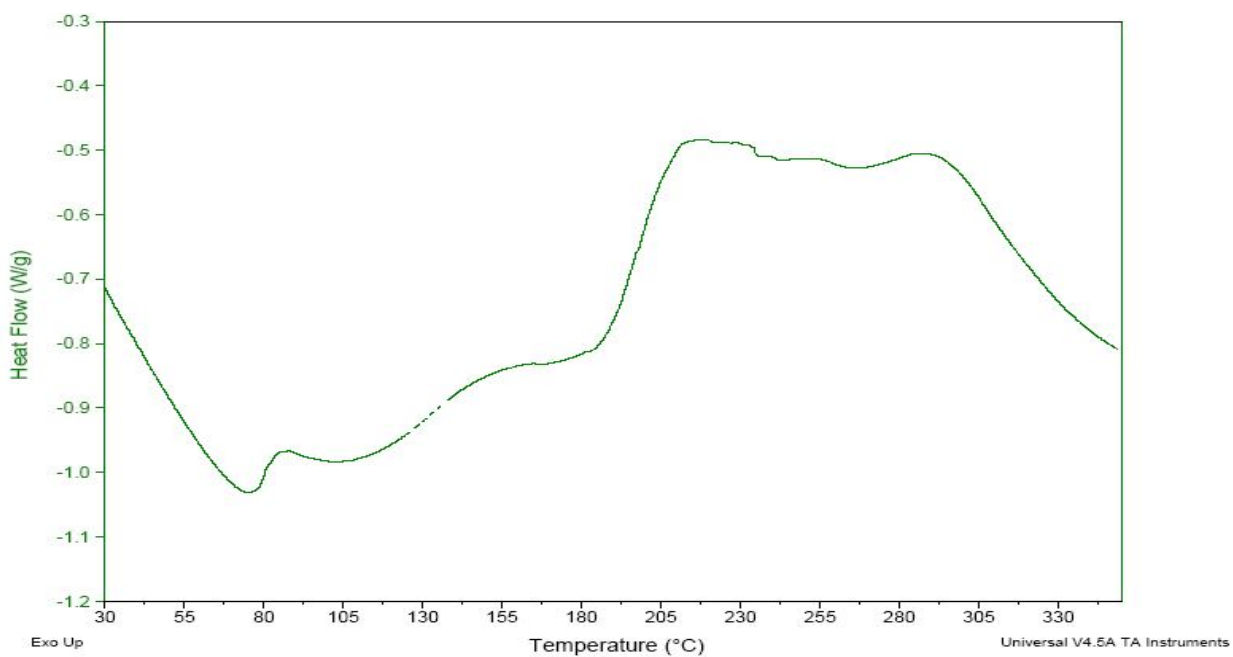


Fig. 7 - tga thermogram of carboxymethyl cellulose / chitosan/ starch (2:1:1) - glutaraldehyde

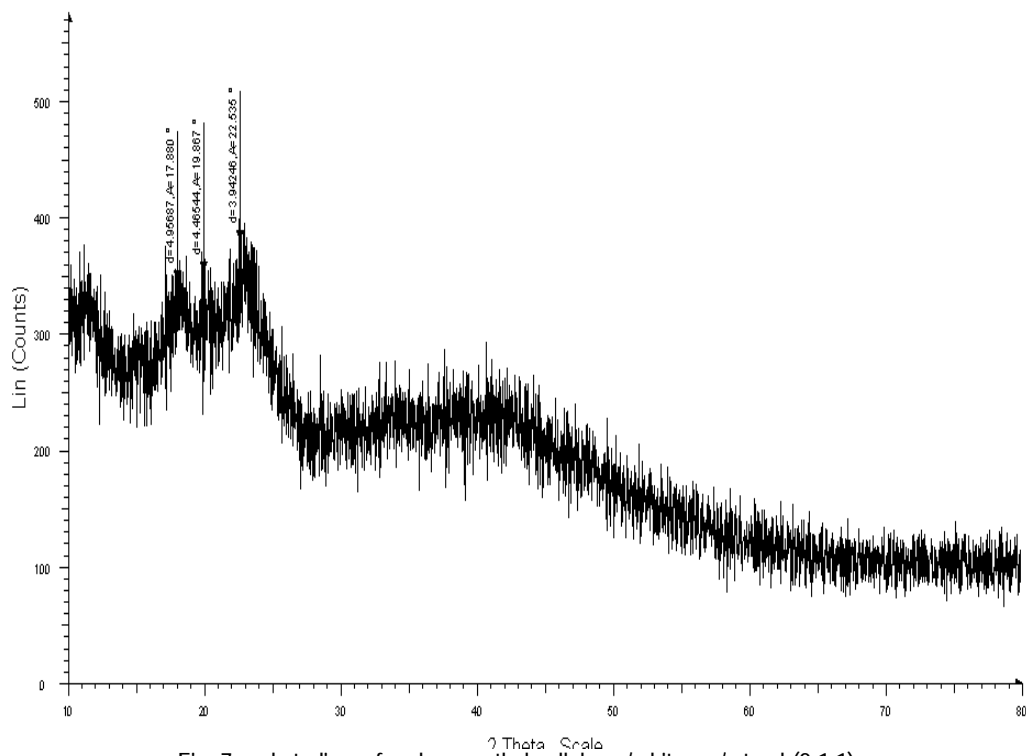


Fig. 7- xrd studies of carboxymethyl cellulose / chitosan/ starch(2:1:1)

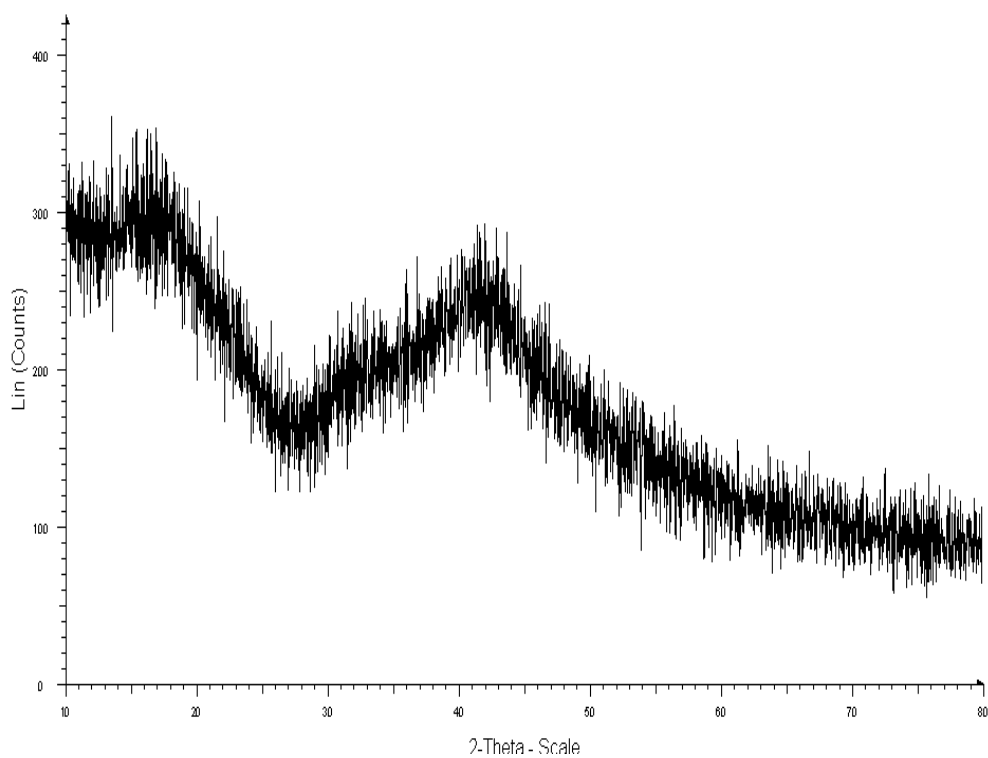


Fig. 8- xrd studies of carboxymethyl cellulose / chitosan/ starch(1:1:2) -glutaraldehyde