Physico-chemical characterization of cross linked chitosan-polyacrylonitrile polymer blends

S. Raghunadh Acharyulu, T. Gomathi and P. N. Sudha

Department of Chemistry, Sri Chandrasekharendra Saraswathi Viswamahavidyalaya, Kanchipuram, India
Department of Chemistry, D. K. M. College for Women, Vellore, Tamilnadu, India

ABSTRACT

Chitin a natural polymer extracted commercially from the shells of crustaceans such as prawns, crabs, krill, insects and shrimps. Chitosan is prepared from chitin by partially decaying its acetamido groups with a strong alkaline solution. Chitin and chitosan have a wide variety of applications such as wastewater treatment which decreases the Chemical Oxygen Demand [COD] and used in preventing infections of wounds and also as a food supplement, which lower plasma cholesterol and improves the HDL cholesterol. Besides these applications chitosan has a few drawbacks like acidic solubility, low thermal and mechanical stability. To rectify these drawbacks of chitosan can be modified physically and chemically. In this present study, the biopolymer chitosan was cross linked with glutaraldehyde and blended with the copolymer polyacrylonitrile in different ratios and the prepared blend was characterized by FTIR, DSC, TGA and XRD studies. The prepared cross linked Chitosan-Poly acrylonitrile blend has good thermal stability and better adsorption capacity.

Keywords: Chitosan, Polyacrylonitrile, glutaraldehyde, thermal stability

INTRODUCTION

Chitin is a white, hard, inelastic, nitrogenous polysaccharide, biodegradable, bio-compatible, non-toxic material was called as Poly [β-(1-4)-2-acetamido-2-deoxy-D-glucopyranose] also called as N-acetyl-D-glucosamine [1]. It was extracted commercially from the shells of crustaceans such as prawns, crabs, krill insects and shrimps. It is a highly insoluble material resembling cellulose with low chemical reactivity. The structure is related to cellulose with hydroxyl at position C-2 is replaced by an acetamido group. Chitosan is prepared from chitin by partially decaying its acetamido groups with a strong alkaline solution.

Chitosan is an excellent adsorbent for metal removal in near-neutral solutions because of the large number of NH₂ groups. Excellent adsorption characteristics of chitosan for heavy metals can be attributed to high hydrophilicity, presence of a large number of functional groups (acetamido, primary amino and/or hydroxyl groups) and flexible structure [2]. Chitin-Chitosan has a wide variety of applications such as wastewater treatment which decreases the Chemical Oxygen Demand [COD] and microbial population. The reactive amino group selectively binds to virtually all group III transition metal ions but does not bind to groups I and II (alkali and alkaline earth metal ions) [3]. Also, due to its cationic behavior, in acidic media, the protonation of amine groups leads to adsorption of metal anions by ion exchange [4-7]. These are also used in preventing infections of wounds and as a food supplement, which lower plasma cholesterol and improves the HDL cholesterol. Besides these applications, Chitosan has few drawbacks like acidic solubility, low thermal and mechanical stability. To rectify these drawbacks Chitosan can be modified
physically and chemically. In recent days Chitosan has chemically modified in different forms by different scientists. Thus, modified Chitosan rectify all the drawbacks, which have come with Chitosan alone.

Chitosan beads which are prepared from Chitosan flakes have good adsorption capacity towards the heavy metal ions from aqueous solutions. Graft polymerization of acrylamide on Chitosan using ammonium per sulphate as an initiator was prepared [8] which have also the good results in removal of heavy metals from industrial effluent. Veno et al demonstrated that Chitosan in the form of Chitosan-Cotton was an accelerator of wound healing. VinaChitin membranes prepared by decrystallizing ricefield crabs shells are used for deep burns and orthopedic trauma and ulcer conditions. Chitosan films prepared by Martinez-Camacho et al [9], which are biodegradable, biocompatible, flexible, durable, strong, tough and have moderate values of water and oxygen permeability, decrease the respiratory rate of food and also inhibit the microbial growth.

Wan Ngah et al [10] be proven that Chitosan composites have better adsorption capacity when compared with Chitosan alone. Wang and Wang [11] reported that N, O – carboxymethyl – chitosan have better adsorption capacity in removal of Cango Red. Apart from all the above chemical modifications, in the present study cross linked Chitosan was blended with the copolymer polyacrylonitrile in different ratios and thus prepared copolymer blend was characterized by FTIR, DSC, TGA and XRD studies.

MATERIALS AND METHODS

Chitosan was a kind gift from Indian Sea food, Cochin, Kerala, India. Polyacrylonitrile was purchased from Sigma Aldrich, Bangalore, India. All chemicals used in the study are of analytical grade.

2.1 Preparation of cross linked chitosan
2g of Chitosan was dissolved in 50 mL of 2% aq. acetic acid solution with constant stirring to form a homogeneous solution. About 15 ml of cross linking agent glutaraldehyde was added to the above prepared Chitosan solution (50 ml) which was then stirred for 20 minutes using magnetic stirrer.

2.2 Preparation of cross linked chitosan polyacrylonitrile blends
A binary polymer solution consisting of 2 g PAN (Aldrich 18131-5) in 50 mL of dimethylformamide (DMF) and 2 gms of Chitosan in 50 mL of 2% aq. acetic acid solution mixed previously with 15 ml of cross linking agent glutaraldehyde was stirred for 30 min on a magnetic stirrer to form a homogenous solution. The resultant mixture was kept for 30 min and the solution was cast in polystyrene plates and air dried. Similar procedure was adopted for the preparation of (cross linked chitosan: poly acrylonitrile) blends (1:1), (1:2), (1:3), (2:1) and (3:1) ratios.

2.3 Characterization of Polymer blends
The prepared cross linked Chitosan copolymer blend was analyzed by FTIR in the wavelength between 400 cm\(^{-1}\) and 4000 cm\(^{-1}\) and in solid state using KBr pellets. Perkin-Elmer spectrophotometer was used for FTIR study and DSC thermogram was obtained by NETZ-SCH-Geratebau GmbH thermal analyser. This copolymer blend was also analyzed using TGA and XRD studies.

RESULTS AND DISCUSSION

3.1 FTIR studies
The cross linked chitosan was confirmed by FTIR spectroscopy and the spectra of chitosan and cross linked chitosan are depicted in Figure 1 and 2 respectively.

The IR spectrum of the chitosan (Figure 1) has strong peaks observed at 3454 cm\(^{-1}\) due to OH group and the bands at 2923.08 cm\(^{-1}\) and 1021.37 cm\(^{-1}\) may be due to C-H stretching vibration and C-O-C stretching vibrations respectively. In the case of cross linked chitosan some changes can be observed, the peaks are sharper than that of pure chitosan. The peak at 1628 cm\(^{-1}\) shifts to the lower wavenumber 1604 cm\(^{-1}\). This band is most probably composed of amide I band of chitosan and C=N stretching band of shiff’s base [12]. Moreover, it is not observed any band at ~1715 cm\(^{-1}\), related to the free aldehyde group [13]. Two main crosslinking mechanisms, involving formation of Schiff’s base structures or Michael-type adducts, have been proposed for the reaction of chitosan and glutaraldehyde [14]. The FTIR spectra of cross linked chitosan (Figure 2) showed a broad absorption bands at 3415.9 cm\(^{-1}\) due to OH-stretching in chitosan. The characteristic absorptions at 2387.199 cm\(^{-1}\) and 2352.7 cm\(^{-1}\) are due to NH\(_3\) stretching and
the absorption at 1409 cm$^{-1}$ represents the –C-H- bending of –CH$_2$ in glutaraldehyde. The absorption at 1604 cm$^{-1}$ is due to (CH$_2$)$_3$HC=N- stretching which is a characteristic absorption due to glutaraldehyde crosslinking with chitosan.

![FTIR spectra of chitosan](image1)

![FTIR spectra of cross linked chitosan with glutaraldehyde](image2)

![1:1 ratio FTIR spectra of cross linked chitosan with polyacrylonitrile](image4)
The FTIR of the blends of ratios 1:1, 1:2, 1:3, 2:1 and 3:1 (Figures 3 – 7) shows the characteristic absorption peak at around 2140 cm\(^{-1}\) represents the presence of CN group in poly acrylonitrile. Apart from these absorptions band at 3415.9 cm\(^{-1}\) is due to OH stretching in chitosan and the absorptions at 2352.7 cm\(^{-1}\) and 2328 cm\(^{-1}\) represents the protonated NH\(_3^+\) group. The -CH\(_2\)OH- stretching frequency became less intense, C-O-C stretching frequency is going to higher absorption frequencies and the -NH\(_2\)- bending frequency (Amide (II) band) is also disappear, these characteristics have proven that the cross linked chitosan was blended with poly acrylonitrile. When the percentage of polyacrylonitrile increases then peaks in FTIR spectra becomes very broad.
3.2 Differential Scanning Calorimetric analysis:
Differential scanning calorimetry (DSC) is the best analytical technique to find the polymer crystallinity, which measures the physical nature of the sample, i.e. Whether it is heated, cooled or under isothermal conditions. In this technique a sample would heat or cool at linear intervals of temperature and measure the particular temperature and energy accompanied with any one of the range of thermal events [16]. The following figures 8 and 9 shows the DSC curves of pure chitosan and the chitosan cross linked with glutaraldehyde. The glass transition temperature of pure chitosan is observed at 200°C, when it is cross linked with glutaraldehyde the glass transition temperature is observed at 168°C. Figures 10 - 14 shows the DSC curves of different ratios of cross linked chitosan blended with polyacrylonitrile (1:1, 1:2, 1:3, 2:1 and 3:1). But the glass transition temperature went to higher values 201°C, 204°C, 204.5°C, 205°C and 206°C respectively when the cross linked chitosan blended with the copolymer polyacrylonitrile. Above results conforms that cross linked chitosan –polyacrylonitrile copolymer blend is having more thermal stability when compared with chitosan alone.

The polymer–polymer miscibility can be estimated by determining the glass transition temperature (Tg) of the blend and its comparison with the Tg of component polymers, if one of the components is crystalline, then depression in the melting temperature Tm can also be used to study the blend the compatibility [17]. By estimating the depression in the melting temperature (Tm) of the blend, we can estimate the blend miscibility of one of the components is crystalline in nature.
3.3 TGA Analysis:
TGA is commonly used in research to determine characteristics of materials such as polymers. TGA technique is very helpful to understand the degradation temperatures, moisture content and percentage of inorganic and organic components in material. It is also often used to determine the corrosion kinetics at high temperature oxidations. The thermal gravimetric analysis was carried out on a Perkin-Elmer agent thermal analysis. Figure 15 shows the TGA spectrum of pure chitosan, which indicates that around 65% of the chitosan gets disintegrated within 840°C. At the end of the experiment around 65% of the chitosan gets disintegrated and leaving 35.07% of the chitosan remained as residue. Figure 16 shows the TGA spectrum of cross linked chitosan with glutaraldehyde. According to the spectra around 88.39% of the cross linked chitosan gets disintegrated within 830°C. Maximum weight loss occurs at the temperature range of 225°C-530°C. At the end of the experiment ie at 830°C only 11.61% of the cross linked...
chitosan remains as residue. From the above results it is evident that chitosan cross linked with glutaraldehyde had more thermal stability when compared with chitosan.

Figures 17 - 21 shows the TGA spectras of cross linked chitosan-polyacrylonitrile blend in different ratios (1:1, 1:2, 1:3, 2:1 and 3:1). Figure 17 shows the TGA spectra of cross linked chitosan with polyacrylonitrile in 1:1 ratio, which indicates that around 85% of the polymer blend gets disintegrated at 850°C. Maximum weight loss occurs at the temperature range of 250°C to 550°C. At the end of the experiment around 85% of the blend gets disintegrated and leaving behind 15.1467% of the blend as residue.

When the percentage ratio of copolymer polyacrylonitrile increases then the percentage disintegration is decreasing and the percentage of residue remains is increasing as shown in figures 18 - 21. From the above results it is evident that blending of copolymer polyacrylonitrile with cross linked chitosan had more thermal stability when compared with the chitosan alone.
3.4 XRD Analysis:

X-ray diffraction (XRD) is an advanced technique to understand the skeleton structures in semi crystalline polymers like thermoplastics, thermoplastic elastomers and liquid crystalline polymers. Now a day’s many well established methods were introduced for the determination of molecular structure, crystallinity and analysis of texture to enhance the speed and precision of these measurements. In these XRD technique is the best and accurate analytical method. Figure 22 shows the X-ray diffraction pattern of pure Chitosan. The XRD analysis was used to study the crystallinity of the prepared samples. The peaks at 2θ=10° and 20.09° for pure chitosan confirms the semicrystalline nature. Figure 23 shows XRD spectra of cross linked Chitosan with glutaraldehyde which has two broad peaks at 2θ=22° and 2θ=42°, indicates that the sample is going from crystalline to amorphous nature [17]. Also the shift in the 2θ values confirms the effective crosslinking would have taken place. It is well known that the rigid crystalline structure of pure Chitosan is stabilized mainly by intra and intermolecular Hydrogen bonds [18]. When glucosamine units in Chitosan membranes are protonated hydrogen bonding involving the NH2 groups is disrupted, so the rigid crystalline structure weakens. Further, ionic crosslinking, which increases packing of the Chitosan chains, can deform the crystalline regions [19]. Thus the interaction detected in this work decreases the membrane crystallinity, and changes in crystallinity can be used to monitor the progress of the cross-linking reaction.

The XRD of the prepared blends (Figure 24, 25, 26, 27 & 28) shows shift in 2θ value also the nature of the peak is different compared with the XRD of pure chitosan and crosslinked chitosan, confirms blending. The broad single peak was seen at 2θ = 42°, which has proved that the crystallinity disappearing gradually and the amorphous character of the blends increasing. If the percentage ratio of copolymer polyacrylonitrile will increase in the blend then the amorphous nature of cross linked Chitosan-polyacrylonitrile blend is increasing rapidly.
Figure 22: XRD details of Chitosan

Figure 23: XRD details of crosslinked Chitosan

Figure 24: XRD details of CCS-PAN (1:1) blend

Figure 25: XRD details of CCS-PAN (1:2) blend

Figure 26: XRD details of CCS-PAN (1:3) blend

Figure 27: XRD details of CCS-PAN (2:1) blend
CONCLUSION

Modified chitosan blends were prepared using glutaraldehyde and polyacrylonitrile. Fourier transform infrared spectroscopy of unmodified and modified chitosan membranes confirmed the formation of covalent and ionic crosslinking between chitosan and gluteraldehyde and polyacrylonitrile. Thus chemically modified Chitosan blends was characterized by FTIR and XRD studies, TGA and DSC analysis. The thermal analysis of these Chitosan blends showed improved thermal stability when compared with Chitosan alone. These Chitosan blends have good adsorption capacity.

REFERENCES