



# Enhancement of thermal stability in the presence of crosslinking using natural biopolymer

D.Saravanan<sup>1</sup> and P.N.Sudha<sup>2\*</sup>

<sup>1</sup>Department of Chemistry, Sathyabama University, Chennai, Tamil nadu, India.

<sup>2</sup>Department of Chemistry, DKM College, Thiruvalluvar University, Vellore, Tamil Nadu, India.

## ARTICLE INFO

### Article history:

Received: 26 December 2011;

Received in revised form:

5 March 2012;

Accepted: 17 March 2012;

### Keywords

Chitin, Cross linking Agent,  
Thermal stability,  
Polymer blend.

## ABSTRACT

The present study evaluated the properties of polymeric blend films obtained from chitin and bentonite by the casting/solvent evaporation method. Polymer blend films of chitin and bentonite were prepared from homogeneous solutions in trichloroacetic acid at various proportions of chitin and bentonite. The cross linking agent like formaldehyde were incorporated into the polymer blends to improve the properties such as mechanical strength, tensile strength, surface hardness, stiffness, resistance to temperature and solvent attack. The structure and physical properties of the blend films were analyzed by Fourier transform spectroscopy (FTIR), thermo gravimetric analysis (TGA), differential scanning calorimetry (DSC) and wide angle XRD analysis. FTIR analyses confirmed that interactions were present between the hydroxyl groups of bentonite and amide group of chitin (lone pair of electrons available on nitrogen atom) in the blend films. Thermo gravimetric analyses showed that in the blend films, the thermal stability increased with increasing bentonite content. The differential scanning calorimetry (DSC) studies revealed an endothermic peak corresponding to water evaporation around 100°C in the films and an exothermal peak corresponding to the decomposition in the chitin side chain and blend films. The chitin-bentonite blend films exhibited a higher thermal stability in the presence of cross linking agents (formaldehyde) was found out.

© 2012 Elixir All rights reserved.

## Introduction

Chitin has been reported to be the second most abundant natural polysaccharide in nature (Gregorio, 2006) and is commonly found in crab and shrimp shells containing 10-15% of chitin (Austin and Brine, 1977). It consists mainly of  $\beta$  - (1 $\rightarrow$ 4)-2- acetamido- 2- deoxy-D-glucopyranose units (Gonzalez-Davila et al, 1990). It carries one acetamido group (lone pair of electrons available on nitrogen atom) and hydroxyl group per glucose ring, thus allowing excellent complexation capacity with metal ions (Lerivrey et al).

Chitin possesses many beneficially biological properties such as biocompatibility, biodegradability, non-toxicity, adsorption properties. They have been broadly applied in waste water treatment (Peter,1995). Nowadays natural polymeric materials have become increasingly important due to their natural abundance and low costs (Deans and Dixon, 1992). However, due to its low mechanical strength and flexible behavior, chitin has limited in application water treatment, while addition of synthetic polymers increased its properties tremendously. The mechanical properties of chitin film can be improved by blending with other natural (Bianchi, et al.1995) or synthetic polymers (Lee, et al.1996).

Chitin exhibits a strong tendency to form intra- and inter-molecular hydrogen bonding between the polymer chain and is water insoluble due to its rigid crystalline structure (Minke and Blackwell, 1978; Sugimoto et al 1998) with a network of organized fibers, this structure confers rigidity and resistance to organisms that contain it. (Roberts 1992). Chitin is known as

potential useful biomedical materials for wound healing, artificial skin, suture and drug carrier (Lee et al.1996).

Different kinds of substances have been used to form composite (blend) with chitin and chitosan such as montmorillonite (Wang et al, 2007), polyurethane (Won et al, 2009), activated clay (Chang et al, 2004), bentonite (WanNgah et al, 2010), poly vinyl alcohol, poly vinyl chloride, kaolinite (Zhu et al, 2010), oil palm ash (Hameed et al, 2008) and perlite (Kalyani, et al, 2005). Chitin composites have been proven to have better adsorption capacity and resistance to acidic environment (Veera et al, 2008). Bentonite contains a high proportion of swelling clays. It mainly composed of montmorillonite with a composition of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, MgO, Fe<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, and K<sub>2</sub>O (Holzer, et al, 2010 and Li, Q., Yue, 2010). Bentonite is a 2:1 type aluminosilicate, the unit layer which consists of one Al<sup>3+</sup> octahedral sheet between two Si<sup>4+</sup> sheets (Wei et al 2009).

In this paper, the main objective was to prepare the polymer blend whose chemical structure and physical properties of blend were characterized by FTIR analysis. The thermal analysis (TGA and DSC analysis) showed that the blending compound had higher thermal stability than the pure chitin.

## Experimental Details

### Materials

Chitin was obtained from India sea foods, Cochin which is 99% pure. All other materials such as formaldehyde and powdered bentonite are of analytical grade.

### Blend Preparation

A known weight of chitin and bentonite were dissolved in trichloro acetic acid separately. The chitin and bentonite solutions were mixed at various ratios with moderate agitation for 30 minutes.

The blend films were prepared by casting the mixed solutions onto polystyrene plated and allowing the solvent to evaporate at room temperature. Similar experiments were performed in the presence of formaldehyde.

### FTIR analysis

The films were dried at 60 °C overnight before measurement. Chemical structure of pure and the blend films were investigated by FTIR measurement, FTIR measurements were performed using KBr pelleted samples with a Perkins Elmer 200 FTIR spectrophotometer with a resolution of 4 $\text{cm}^{-1}$  in the range of 400 – 4000  $\text{cm}^{-1}$ .

### Thermal gravimetric analysis

The thermo gravimetric analysis of the bentonite/chitin blends without and with cross linking agents such as formaldehyde were carried out on TGA Q500 V20.10 Build 36 instrument. In this technique the mass of the substance and thermal decomposition of polymer blend are measured as a function of temperature.

### Differential scanning calorimetry

The glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ) of these blend were carried out with the NETZSCH DSC 200 PC in a pan Al, pierced lid in the nitrogen atmosphere at a heating rate of 10 degree Kelvin per minute.

## Results and discussions

### FTIR

As shown in Fig. 1, the spectrum of pure chitin film shows a broad band at 3434  $\text{cm}^{-1}$  which is due to the OH stretching. The band at 1561  $\text{cm}^{-1}$  is assigned for the NH bending (amide II) ( $\text{NH}_2$ ) (Kurita et al.1993) while the small peak at 1654  $\text{cm}^{-1}$  is attributed to the C=O stretching (amide I)  $\text{O}=\text{C}-\text{NHCH}_3$ . The bands at 2926, 1414, 1317 and 1262  $\text{cm}^{-1}$  are assigned to  $\text{CH}_2$  bending due to pyranose ring.

The band at 1378  $\text{cm}^{-1}$  is due to  $\text{CH}_3$  wagging. The characteristic features of chitin spectrum in this study are similar to that of previous reports (Chunhua xiong, 2010). Fig. 2 represents the FTIR spectrum of chitin/bentonite (1:1) blend in the presence of cross linking agent.

The peak at 3434  $\text{cm}^{-1}$  corresponding to OH group of chitin is significantly shifted to lower wave number at 3402  $\text{cm}^{-1}$  in the chitin/bentonite blend, which indicates that both the chitin and bentonite have good interaction through intermolecular hydrogen bonding.

Two peaks in the range of 3650-3400 were observed due to OH group of bentonite and OH group of chitin. As can be seen, the presence of bentonite in the chitin caused remarkable shift for the C=O stretching peak at 1654  $\text{cm}^{-1}$  of chitin to a higher wave number at 1658  $\text{cm}^{-1}$ .

In addition, the bands at 2926 and 1317  $\text{cm}^{-1}$  of chitin disappeared in the spectrum of chitin/bentonite blend. These observations indicate the existence of good miscibility between chitin and bentonite in the presence of cross linking agent.

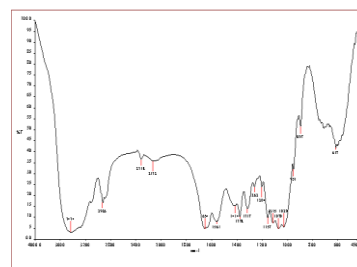


Fig 1: FTIR spectrum of pure chitin

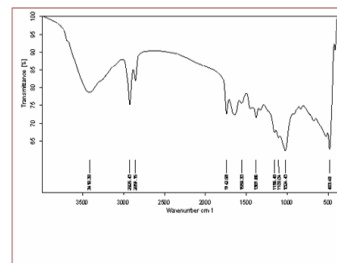


Figure 2: FTIR spectra of CT/BE (1:1) with cross linking agent (Formaldehyde)

### Thermo gravimetric analysis

TGA has been used to investigate the thermal degradation, phase transition and crystallization of the polymers. In order to ascertain the thermal stability, the prepared films were subjected to TGA analysis (Stephen et al; 2002).

The TGA thermo grams of chitin, CT/BE (1:1) blend and CT/BE (1:1) blend in the presence of cross linking agents are presented in Figures 3 –5. Chitin has two degradation temperatures which the temperatures lower than 100 °C indicating the loss of water. The temperature above 100 °C indicates the decomposition of pyranose ring structure. The TGA of blended polymer shows different decomposition temperatures. Maximum decomposition was observed around from 370 °C in CT/BE (1:1) blend in the presence of cross linking agent, which may be due to the decomposition of side chains. Maximum weight loss occurs at temperature range of 150-400° C. Hence compared to chitin, blended film in the presence of cross linking agent is found to be thermally more stable.

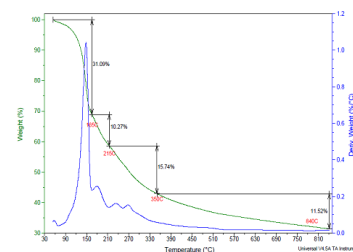


Figure 3: TGA spectra of pure chitin

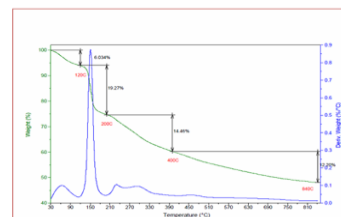
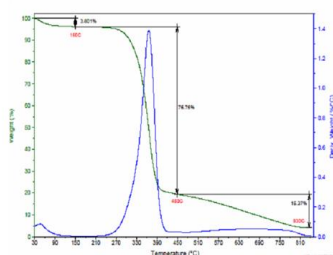


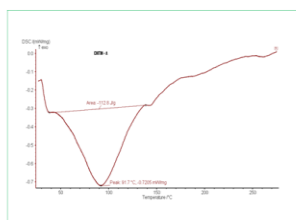
Figure 4: TGA spectra of CT/BE (1:1) blend



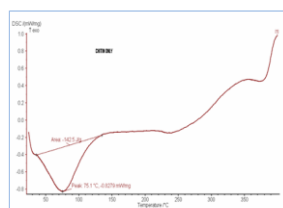
**Figure 5: TGA spectra of CT/BE (1:1) with cross linking agent (Formaldehyde)**

#### DSC analysis

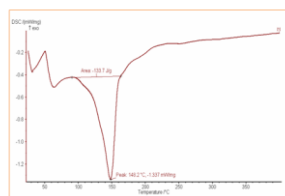
The Fig.16-19 shows the DSC curves of CT/BE (1:1), CT/BE (1:1) blend in the presence of cross linking and pure chitin. Broad endothermic peaks are observed at various temperatures indicating the crystallization of the blended polymers as well as evaporation of water in the films, and appeared in all the film samples, as has been reported earlier (Zhuang et al ;2002, and Mucha et al; 2005) and decomposition of side chain. The glass transition temperature of pure chitin is 75.1 °C, whereas the glass transition temperature of CT/BE blend (1:1) is 91.7° C and CT/BE (1:1) blend in the presence of cross linking agent is 148.2 °C. On comparing the DSC curves of chitin, it was found that the endothermic peaks and the glass transition temperatures of chitin/bentonite blends in the presence of cross linking agents are shifted to higher values. It confirms that the blended polymer has higher thermal stability than the original chitin.



**Figure 6: DSC spectra of pure chitin**



**Figure 7: DSC spectra of CT/BE (1:1) blend**



**Figure 8: DSC spectra of CT/BE (1:1) with cross linking agent (Formaldehyde)**

#### Conclusion

The various physico-chemical analyses indicated that the interaction between chitin and bentonite molecules. The FTIR results suggest that there is strong interaction between the molecular chains of chitin and bentonite, which may lead to the miscibility at specific ratios of the two polymer components blended. From the results of DSC and TGA analyses, it was

observed that the blended polymers have higher thermal stability in the presence of cross linking agent.

#### References

- Gregorio, c., 2006. Non-conventional low cost adsorbent for dye removal: a review *Bioresource Technology* 97, 1061-1085.
- Austin, P.R. and Brine, C.J. 1977. Chitin films and fiber. U.S. patent 4, 029, and 727.
- Gonzalez-Davila M, Santana-Casiano M J and Millero F J 1990 *J.Colloidal .inter. Sci.* 137,102.
- Peter, M.G. 1995. "Applications and environmental aspects of chitin and chitosan" *Journal of Macromolecular Science, Pure and applied chemistry*. Vol. 32, pp.629-640
- Deans JR , Dixon BG ,(1992) Uptake of Pb<sup>2+</sup> and Cu<sup>2+</sup> by novel Biopolymers. *Water Res.* 26(4) : 469-472 .
- Binachi, E., Marsona, E., & Tacchino, A. (1997). Thermo reversible gels of chitin. *Carbohydrate Polymers*, 32, 23-26.
- Lee, Y.M., Kim, S.H. and Kim, S.J. 1996. Preparation and characterization of β- chitin and poly (vinyl alcohol) blend. *Polymer*. 37(26), 5897.
- Lerivrey J, Dubois B, Decock P, Micera J, and Kozlowski H (1986) Formation of D-glucosamine complexes with Cu (II) , Ni(II) and Co(II) ions. *Inorg.Chem.Acta.* 125, 187-190.
- Minke, R., & Blackwell, J. (1978). The structure of α-chitin. *Journal of Molecular Biodegradation*, 120, 67–81.
- Sugimoto M, Morimoto M, Sashiwa H, Saimoto H, Shigemasa Y. Preparation and characterization of water-soluble chitin and chitosan derivatives. *Carbohydr Polymer* 1998; 36: 49-59.
- Roberts, G. A. F., 1992. Preparation of chitin and chitosan. *Chitin chemistry*, MacMillan Press, London, 54-83.
- Wang, L., & Wang, A. (2007). Adsorption characteristics of Congo Red onto theChitosan / montmorillonite nanocomposite. *Journal of Hazardous Materials*, 147, P: 979–985.
- Won, S. L., Lee, H. C., Jeong, Y. G., Min, B. G., & Lee, S. C. (2009). Preparation and acid dye adsorption behavior of polyurethane/chitosan composite foams. *Fibers and Polymers*, 10, P: 636–642.
- Chang, M. Y., & Juang, R. S. (2004). Adsorption of tannic acid, humic acid and dyes From water using the composite of chitosan and activated clay. *Journal of Colloid and Interface Science*, 278, P: 18–25.
- WanNgah, W. S., Ariff, N. F. M., & Hanafiah, M. A. K. M. (2010). Preparation,Characterization and environmental application of cross linked chitosan-coated bentonite for tartrazine adsorption from aqueous solutions. *Water, Air and Soil Pollution*, 206, P: 225–236.
- Zhu, H. Y., Jiang, R., & Xiao, L. (2010). Adsorption of an anionic dye by Chitosan/ kaolin/-Fe<sub>2</sub>O<sub>3</sub> composites. *Applied Clay Science*, 48, P: 522–526.
- Hameed, B. H., Hasan, M., & Ahmad, A. L. (2008). Adsorption of reactive dye onto Cross-linked chitosan/oil palm ash composite beads. *Chemical Engineering Journal*, 136, P: 164–172.
- Kalyani, S., Ajitha, P. J., Srinivasa, R. P.,&Krishnaiah, A. (2005). Removal of Copper and Nickel from aqueous solutions using chitosan coated on perlite as biosorbent.*Separation Science and Technology*, 40, P : 1483–1495.
- Veera, M. B., Krishnaiah, A., Jonathan, L. T., Edgar, D. S., & Richard, H. (2008). Removal of arsenic (III) and arsenic (V) from aqueous medium using chitosan-coated biosorbent. *Water Research*, 42, P: 633–642.

20. Holzer, L., Munch, B., Rizzi, M., Wepf, R., Marschall, P., & Graule, T. (2010). 3-D microstructure analysis of hydrated bentonite with cryo-stabilized pore water. *Applied Clay Science*, 47, P: 330–342.
21. Li, Q., Yue, Q. Y., Sun, H. J., Su, Y., & Gao, B. Y. (2010). A comparative study on the Properties, mechanism and process designs for the adsorption of non-ionic or anionic Dyes onto cationic-polymer/bentonite. *Journal of Environmental Management*, 91, P: 1601–1611.
22. Wei, J. M., Zhu, R. L., Zhu, J. X., Ge, F., Yuan, P., He, H. P., et al. (2009). Simultaneous Sorption of crystal violet and 2-naphthol to bentonite with different CECs. *Journal of Hazardous Materials*, 166, P: 195–199.
23. Kurita, K., Tomita, K., Tada, T., Ishii, S., Nishimura, S., and Shimoda, K. 1993. Squid chitin as a potential alternative chitin source: Deacetylation behavior and characteristic properties. *Journal of Polymer Science. Part A: Polymer Chemistry*. 31: 485-491.
24. Stephan A M , Saito Y , Muniyandi N , Renganathan N G , Kalyanasundram S , Elizabeth R N 2002; Preparation and characterization of PVC/PMMA blend polymer Electrolytes complexed with LiN (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>. *Solid State Ionics* 148: P: 467-473.
25. Zong, Z., Kimura, Y., Takahashi, M., Yamane, H (2000). *Polymer*, 41, P: 899.
26. Chunhua Xiong, *J.Chem.Soc.Pak*, Vol.32, No.4, 2010.
27. Li, Z. Zhuang, X.P; Fei Liu, X; Guan , Y.L; Yao, K.D. *Polymer* 2002, 43, 1541-1547.
28. Mucha, M; Pawlak, A. *Thermochim Acta* 2005, 427, 69-76.