Available online at www.scholarsresearchlibrary.com

Scholars research library

Archives of Applied Science Research, 2011, 3 (6):342-350
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-508X
CODEN (USA) AASRC9

Comparative Study of Thermal Stability Using Natural Polymer Blend by Cross Linking

[1]D. Saravanan, [2]T. Gomathi and P. N. Sudha[2*]

[1]Department of Chemistry, Sathyabama University, Chennai, Tamilnadu, India
[2]Department of Chemistry, DKM College, Thiruvalluvar University, Vellore, Tamilnadu, India

---

ABSTRACT

Chitin has wide range of applications as a biomaterial, but barriers still exist to its broader use due to its physical and chemical limitations. The present study evaluated the properties of polymeric blend films obtained from chitin and bentonite (Zeolite mineral) by the casting/solvent evaporation method. The cross linking agents formaldehyde and glutaraldehyde 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 analysed by Fourier transform infra red spectroscopy (FTIR), thermogravimetric analysis (TGA), diferential 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, while XRD studies shows that the films to exhibit an amorphous character. Thermogravimetric analyses showed that in the blend films, the thermal stability increased in the presence of crosslinking agent. The differential scanning calorimetry (DSC) studies revealed an endotherm corresponding to water evaporation around 100°C in all the films and an exothermal, 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 was found out.

Keywords: Chitin, Crosslinking Agent, Thermal stability, Polymer blend.

INTRODUCTION

The chitin ($C_8H_{13}O_5N$), a polymer composed of N-acetyl-d-glucosamine residues [1], is a natural polysaccharide of major importance, first identified in 1884. Meanwhile, chitin is an inexpensive biological material and can be obtained from seafood such as the shells of crab, shrimp and lobster [2]. It is the second most abundant organic resource next to cellulose on earth [3]. Chitin can be prepared in various forms such as powder [4], gel [5, 6], fiber and film [7]. Because chitin possesses many beneficially biological properties such as biocompatibility, biodegradability [8], non toxicity, adsorption properties, hemostatic activity, etc.

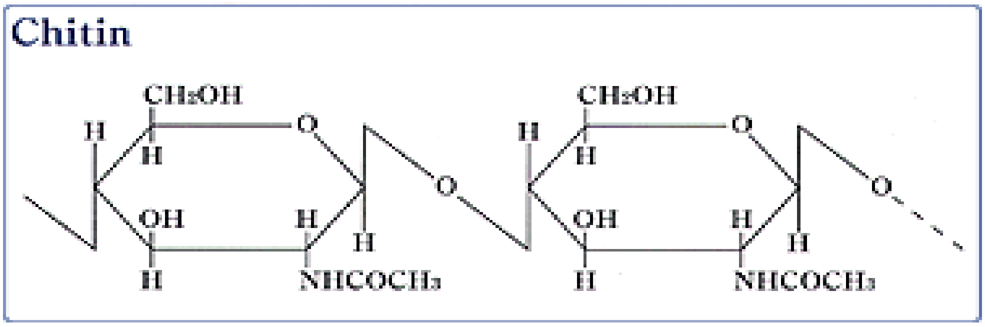

Figure-1: Structure of chitin

Chitin exhibits a strong tendency to form intra- and inter-molecular hydrogen bonding between the polymer chains and is water insoluble due to its rigid crystalline structure [9-11] with a network of organized fibres, this structure confers rigidity and resistance to organisms that contain it. Chitin is known as potential useful biomedical materials for wound healing, artificial skin, suture and drug carrier [12].

Additionally, it is worth remembering that chitin extraction does not cause any disturbance to the ecosystem. Chitin exhibits numerous interesting physico-chemical, biological and mechanical properties with great potential applications. It carries one -NHCO- group and one –OH- group per glucose ring (Figure 1), thus allowing excellent complexation capacity with metal ions, [13] particularly transition and post transition metals. Chitin has strong inter- and intra-molecular hydrogen bonding between the polymer chains and is water-insoluble due to its rigid crystalline structure [9, 10].

Polymer blending is an attractive method for producing new polymeric materials with tailored properties [14]. Other advantages of polymer blending are versatility, simplicity and inexpensiveness [15, 16]. In this present study, the natural polymer blend was prepared with and without the presence of glutaraldehyde as crosslinking agent and characterized using the following analytical tools Fourier transform spectroscopy (FTIR), thermogravimetric analysis (TGA), diferential scanning calorimetry(DSC) and wide angle XRD analysis. The comparative study on the thermal stability of the pure chitin and the prepared blend was made.

MATERIALS AND METHODS

Materials

Chitin was obtained from India sea foods, Cochin which is 99% pure. All other materials such as glutaraldehyde 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 glutaraldehyde.

Fourier transform infra red spectroscopy 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 4cm^{-1} in the range of 400 – 4000 cm$^{-1.}$

X-ray diffraction studies

X-ray diffractometer was used to characterize the crystallinity of pure and the blend films. X-ray diffraction (XRD) patterns were recorded by reflection method with nickel-filtered Cu Kα radiation using a Rigaku X-ray diffractometer operated at 40kV and 30mA in the 2θ scanning mode from 5° to 80°.

Thermal gravimetric analysis

The thermo gravimetric analysis of the bentonite/chitin blends without and with cross linking agents such as formaldehyde and glutaraldehyde 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 analysed 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 DISCUSSION

FTIR

As shown in Figure 2(a), the spectrum of pure chitin film shows a broad band at 3434 cm^{-1} which is due to the OH stretching, NH stretching and intra-molecular hydrogen bonding. The band at 1561 cm^{-1} is assigned for the NH bending (amide II) (NH_2) [17] while the small peak at 1654 cm-1 is attributed to the C=O stretching (amide I) O=C-$NHCH_3$. The bands at 2926 cm^{-1} and1414 cm^{-1} are assigned to CH_2 stretching and CH_2 bending due to pyranose ring. The band at 1378 cm^{-1} is for CH_3 wagging. The characteristic features of chitin spectrum in this study are similar to that of previous reports [18]. Figure 2(b) represents the FTIR spectrum of chitin/bentonite (1:1) blend. The peak at 3434 cm^{-1} corresponding to OH group of chitin is significantly shifted to lower wave number at 3402 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 cm^{-1} of chitin to a higher wave number at 1658 cm^{-1}. In addition, the bands at 2926 and 1317 cm^{-1} of chitin disappeared in the spectrum of chitin/bentonite blend. These observations indicate the existence of good miscibility between chitin and bentonite.

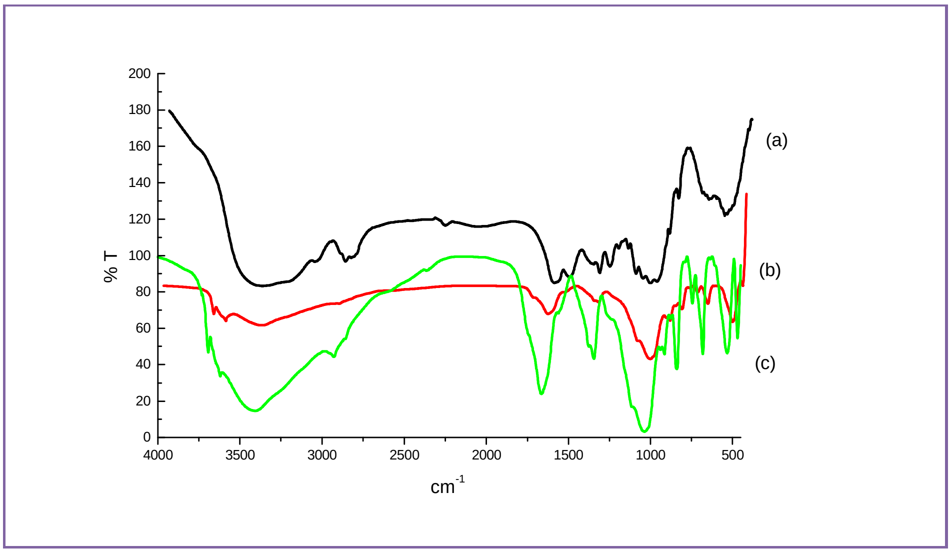

Figure-2: IR spectra of (a) pure chitin (b) CT/B E (1:1) (c) CT/BE (1:1) with glutaraldehyde

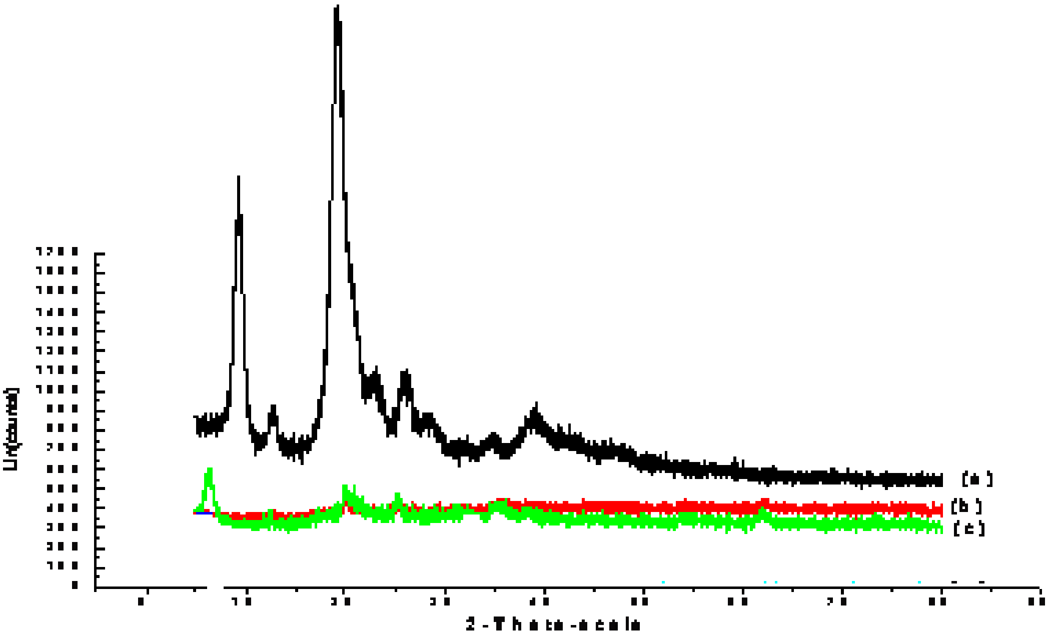

Figure-3: XRD of (a) pure chitin (b) CT/BE (1:1) with glutaraldehyde (c) CT/BE (1:1)

XRD

The X-ray diffraction analysis is used to determine the structure, complexation and crystallization of the polymer matrix [19, 20]. X- ray diffractograms (XRD) of chitin/bentonite composite films are shown in the Figure 3. As compared with chitin, CT/BE blend shows a weaker and broader peak at 2θ= 10-30° region, was a result of the loss of crystallinity due to the loss of hydrogen bonding [21], which demonstrated that the conjugation of bentonite (zeolite mineral) suppressed the crystallization to some extent. In the CT/BE blend films, the intermolecular interactions between the amide group of chitin and OH group of bentonite limited the molecular movement of chitin chain. So that the intensity of the peaks descends sharply. Hence, Crystallinity of the blended polymer had decreased much.

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 [22]. TGA thermograms of chitin, CT/BE (1:1) and CT/BE (1:1) with glutaraldehyde polymer blend are presented in Figures 4a, 4b, 4c. Chitin has two stages of degradation, the first stage is around temperature 30°C - 100°C indicating the loss of water. The second stage at 210°C – 450°C indicates the decomposition of pyranose ring structure.

The TGA of blended polymer shows mainly three decomposition temperatures, due to loss of water, breaking of the polymeric linkage and the decomposition of the polymer backbone. On comparing the TGA results of pure chitin, CT/BE (1:1) blend with and without the presence of glutaraldehye as the crosslinking agent, the thermal stability of the blend increases than the pure one. Also the blend prepared in the presence of crosslinking agents showed the high thermal stability when compared with the other. It was confirmed that the thermal stability of the polymer increased during blending in the presence of crosslinking agent.

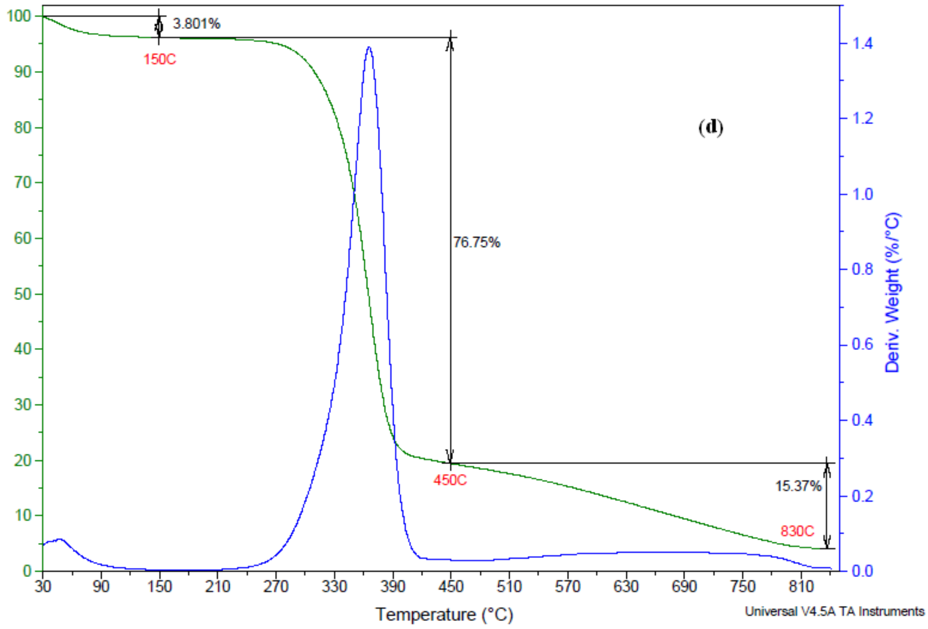

Figure-4a: TGA of Pure chitin

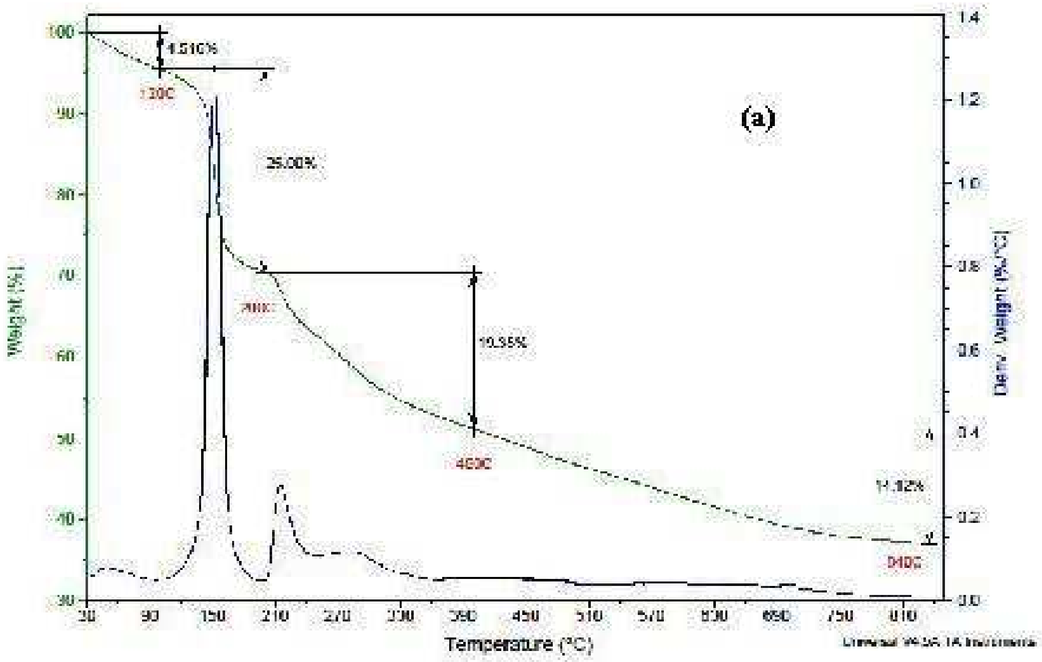

Figure – 4b: TG curves of chitin/bentonite (1:1)

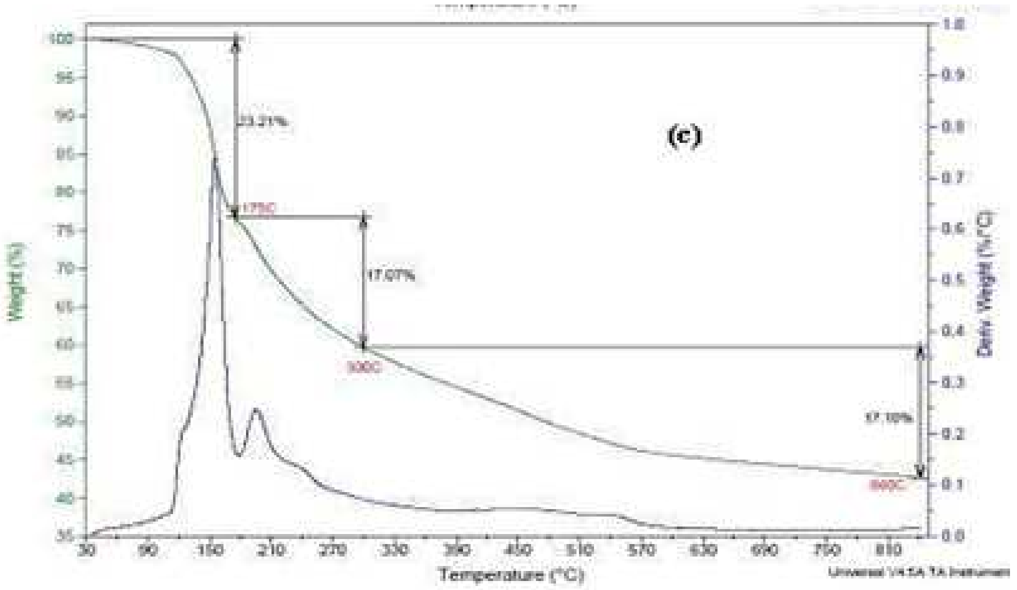

Figure – 4c: TG curves of chitin/bentonite (1:1) with glutaraldehyde

DSC analysis

The Figure 5a, 5b and 5c shows the DSC curves of pure chitin, CT/BE (1:1) blend without crosslinking agent, CT/BE (1:1) blend with glutaraldehyde as the crosslinking agent. Broad endothermic peaks are observed at various temperatures indicating the crystallization of the blend polymers as well as evaporation of water in the films, and appeared in all the film samples, as has been reported earlier [23, 24] 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 without crosslinking agent (1:1) is 82.5 °C and CT/BE blend (1:1) with cross linking agent (Glutaraldehyde) is 114.3.7 ° C. On comparing the DSC curves of CT/BE (1:1) with and without the cross linking agents, it was found that the endothermic peaks and the glass transition temperatures of chitin/bentonite with crosslinking agent are shifted to higher values. It confirms that the CT/BE (1:1) blend in the presence of cross linking agent has higher thermal stability than the blend without crosslinking agent with the formation of different crystalline forms.

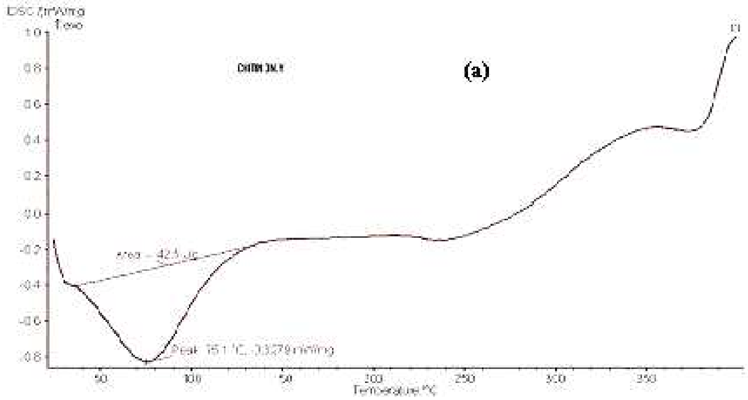

Figure -5a: DSC Thermogram of chitin

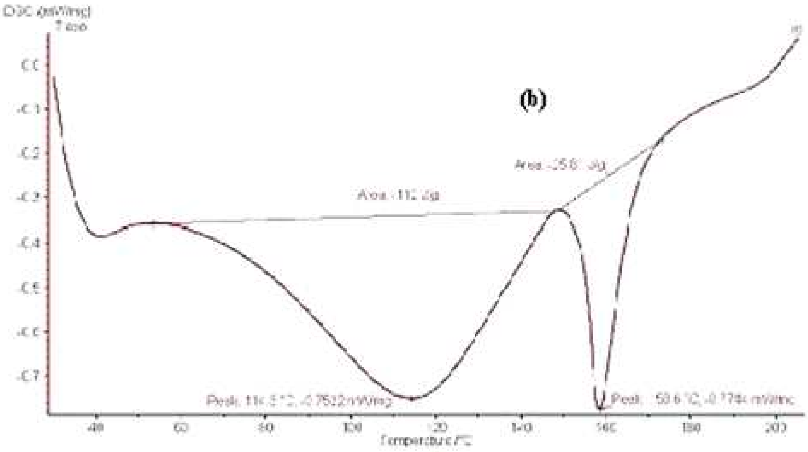

Figure -5b: DSC Thermogram of chitin/bentonite (1:1)

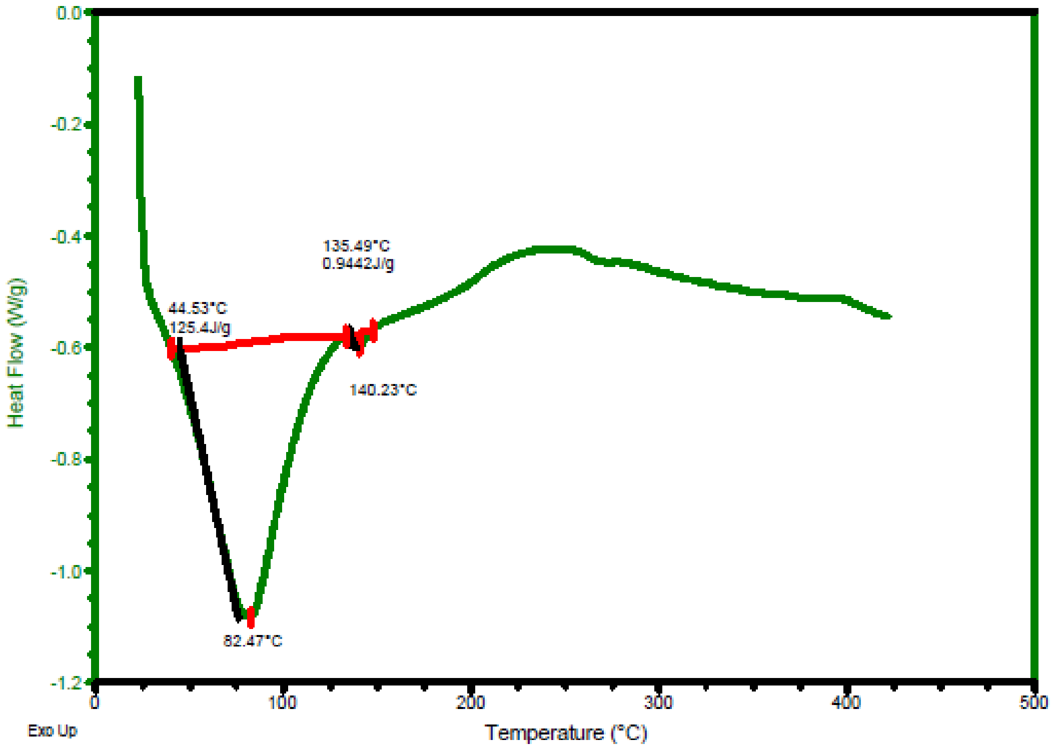

Figure -5c: DSC Thermogram of CT/BE (1:1) blend

CONCLUSION

The 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 FTIR results, it was found that the C=N type of linkage were observed in the cross linked polymers showing the new bond formation between the polymer and the crosslinking agent. From the results of DSC and TGA analyses, it was observed that the crosslinking agents enhanced the thermal stability of the polymer blend. While the XRD studies shows that the films to exhibit an amorphous character. The high molecular weight chitin employed was found to have good film-forming properties, because of intra and intermolecular hydrogen bonding, and the optimum ratio of blended bentonite – chitin film lead to strong and stable.

REFERENCES

[1] Gonzalez-Davila M, Santana-Casiano M J and Millero F J **(1990)**. *J.Colloidal .inter. Sci*. **137,** 102.

[2] Shahidi, F., and Synowiecki, J. **(1991).** *Journal of Agricultural and Food Chemistry, 39*, 1527-1532.

[3] Hirano, S., Hutadilok, N., Hayashi, K. I., Hirochi, K., Usutni, A., and Tachibana, H. **(1993)**. In M. Yalpani (Ed.), *Carbohydrates and carbohydrate polymers: analysis, biotechnology,*

Polymer Science. Part A: Polymer

Chemistry. 31 : 485-491.

modification, antiviral, biomedical and others applications (pp. 253-264). vol. 1, IL, USA: Mount Prospect, ALT Press.

[4] Muzzareli, R. A. A. **(1985)**. Chitin. In *Encyclopedia of polymer science and engineering* (pp. 430-440), Vol. 3, New York: John Wiley.

[5] Binachi, E., Marsona, E., and Tacohino, A. **(1997).** Thermo reversible gels of chitin. *Carbohydrate Polymers*, *32*, 23-26.

[6] Khor, E., Wan, A. C. A., Tee, C. F., and Hastings, G. W. **(1997).** *Journal of Polymer Science. Part A. Polymer Chemistry*, *35*, 2049-2053.

[7] Rathke, T. D., and Hudson, S. M. **(1994).** *Journal of macromolecular Science Review. Macromolecular chemistry and Physics*, *34*(3), 375-437.

[8] Freddi, G., Romano, M., Massafra, M.R. and Tsukada, M. **(1995).** *Journal of Applied Polymer Science*, 56: 1537-1545.

[9] Minke, R., and Blackwell, J. **(1978).** *Journal of Molecular Biodegradation*, *120*, 67–81.

[10] Gonzalez, V., Guerrero, C., and Ortiz, U. **(2000).** *Journal of Applied Polymer Science*, *78*, 850–857.

[11] Sugimoto, M., Morimoto, M., Sashiwa, H., Saimoto, H., Shigemasa, Y., **(1998).** *Carbohydr. Polym*; 36: 49-59.

[12] Lee, Y.M., Kim, S.H. and Kim, S.J. **(1996).** *Polymer*. 37(26), 5897.

[13] Lerivrey, J., Dubois, B., Decock, P., Micera, G., Urbanska, J., and Kozlowski, H. **(1986).** *Inorganica Chimica Acta*, 125, 187–190.

[14] Folkes, M. J., and Hope, P. S. **(1985)**. In *Polymer blends and alloys* (pp. 430-440). London: Chapman & Hall.

[15] Cascone, M. G. **(1997)**. *Polymer International*, *43*, 55- 69.

[16] Fukae, R., Yamamoto, T., Sangen, O., Saso, T., Kako, T., and Kamachi, M. **(1990).** *Polymer Journal*, *22*, 636-637.

[17] Kurita, K., Tomita, K., Tada, T., Ishii, S., Nishimura, S., and Shimoda, K**.(1993).** *Journal of Polymer Science.Part A: Polymer Chemistry*. 31: 485-491.

[18] Chunhua Xiong, **(2010).** *J.Chem.Soc.Pak*., Vol..32, No.4,.

[19] Pradhan, D. K., Samantaray, B. K., Choudhary, R. N. P., Thakur, A. K., **(2005).** *J Power Sources* 139: 384-393.

[20] Rajendran, S., Sivakumar, M., Subadevi, R., **(2004).** *Mater. Lett*. 58: 641-649.

[21] Zong, Z., Kimura, Y., Takahashi, M., Yamane, H., **(2000)**. *Polymer*, 41, 899.

[22] Stephan, A. M., Saito, Y., Muniyandi, N., Renganathan, N. G., Kalyanasundaram, S., Elizabeth, R. N., **(2002)**. *Solid State Ionics* 148:467-473.

[23] Li, Z., Zhuang, X.P., Fei Liu, X., Guan, Y.L., Yao, K.D., **(2002).** *Polymer*, 43, 1541- 1547.

[24] Mucha, M., Pawlak , A., **(2005).** *Thermochim Acta*, 427, 69-76.