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Physicochemical characterisation and thermal sensitivity of chitin polymer blend by crosslinking with formaldehyde

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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). FTIR analyses confirmed that interactions were present between the hydroxyl groups of bentonite and amide group of chitin. From TGA studies, it was found that the onset degradation temperature of the blends almost changed due to the presence of strong interaction between bentonite and chitin chains. The DSC analysis showed a single glass transition temperature for all the blends, indicating that these polymers are miscible over the entire composition range.

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KEYWORDS

Chitin;
Cross linking agent;
Thermal stability;
Polymer blend.

INTRODUCTION

Chitin, a naturally occurring polysaccharide, is one of the principal ingredients of the carapaces, crust and shells of crustacean. It is the second most abundant natural polysaccharide in nature^[1]. It consists mainly of β - (1→4)-2- acetamido- 2- deoxy-D-glucopyranose units^[2].

Chitin possesses many beneficially biological properties such as biocompatibility, biodegradability, non-

toxicity, haemostatic activity adsorption properties and wound healing property, much attention has been paid to its biomedical applications^[3,4]. They have been broadly applied in waste water treatment^[5]. Nowadays natural polymeric materials have become increasingly important due to their natural abundance and low cost^[6]. While addition of synthetic polymers increased its properties tremendously. The mechanical properties of chitin film can be improved by blending with other natural^[7] or synthetic polymers^[8].

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Polymer blending is an attractive alternative for producing new polymeric materials with tailored properties without having to synthesize totally new materials. Other advantages of polymer blending are versatility, simplicity, and inexpensiveness. 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^[9,10] with a network of organized fibers, this structure confers rigidity and resistance to organisms that contain it^[11] Chitin is known as potential useful biomedical materials for wound healing, artificial skin, suture and drug carrier.

Different kinds of substances have been used to form composite (blend) with chitin and chitosan such as montmorillonite^[12] polyurethane^[13] activated clay^[14] bentonite^[15] poly vinyl alcohol, poly vinyl chloride, kaolinite^[16] oil palm ash^[17] and perlite^[18] Chitin composites have been proven to have better adsorption capacity and resistance to acidic environment^[19]. Bentonite contains a high proportion of swelling clays. It mainly composed of montmorillonite with a composition of SiO_2 , Al_2O_3 , CaO , MgO , Fe_2O_3 , Na_2O , and K_2O ^[20,21]. Bentonite is a 2:1 type aluminosilicate, the unit layer which consists of one Al^{3+} octahedral sheet between two Si^{4+} sheets^[22]

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 in the presence of crosslinking than 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 polysty-

rene 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 4cm^{-1} in the range of 400 – 4000 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 Figure 1, the spectrum of pure chitin film shows a broad band at 3434 cm^{-1} which is due to the OH stretching. The band at 1561 cm^{-1} is assigned for the NH bending (amide II) (NH_2)^[23] while the small peak at 1654 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 cm^{-1} are assigned to CH_2 bending due to pyranose ring. The band at 1378 cm^{-1} is due to CH_3 wagging. The characteristic features of chitin spectrum in this study are similar to that of previous reports^[24]. Figure 2 represents the FTIR spectrum of chitin/bentonite (1:1) blend in the presence of cross linking agent. 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 in the presence of cross linking agent.

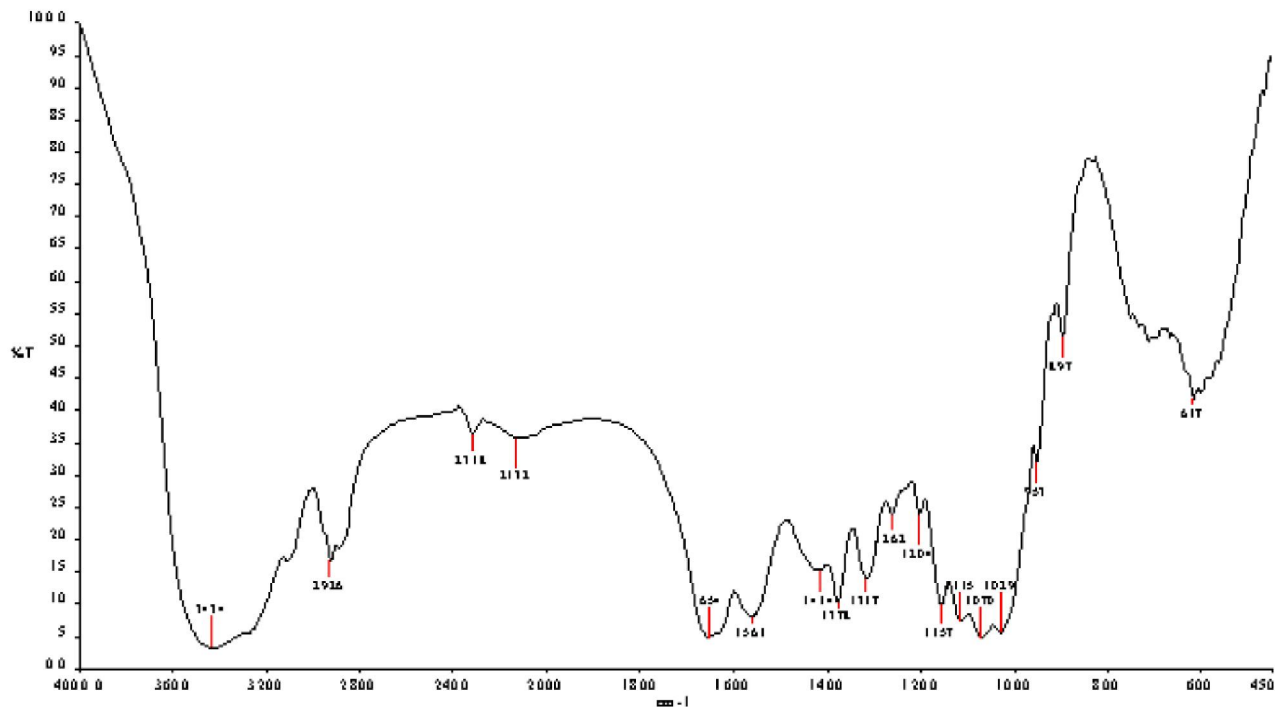


Figure 1 : FTIR spectrum of pure chitin

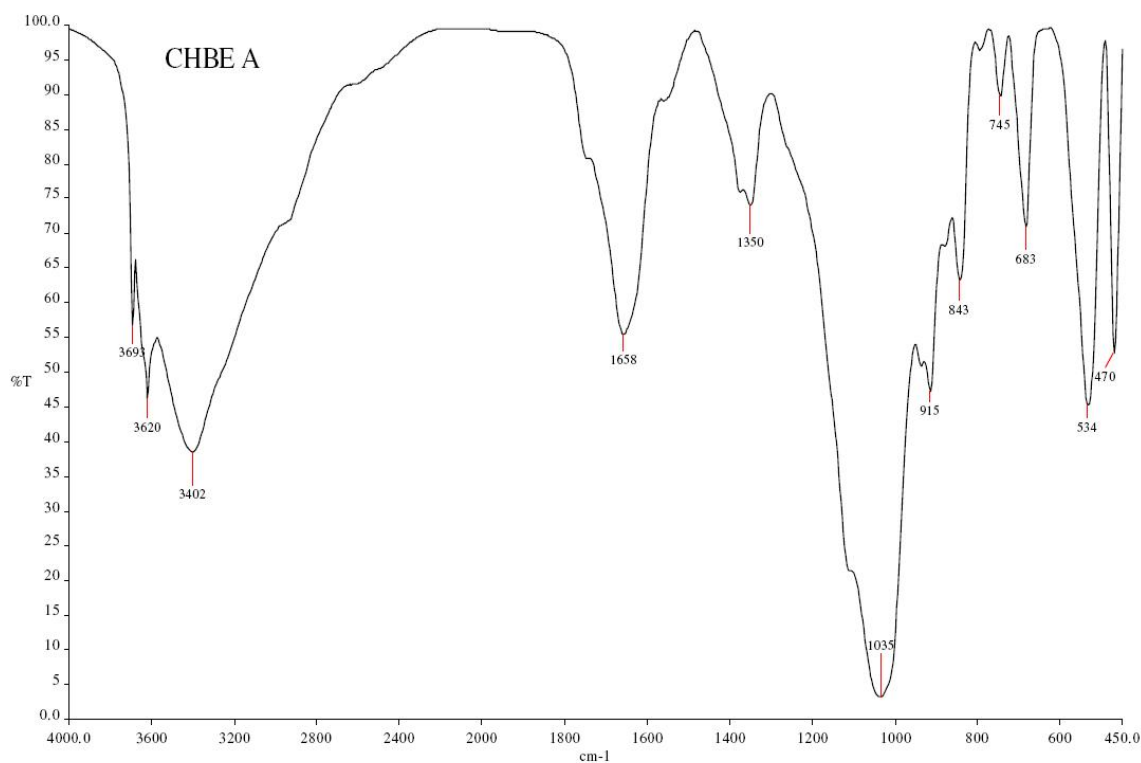


Figure 2 : FTIR spectra of CT/BE (1:1) blend

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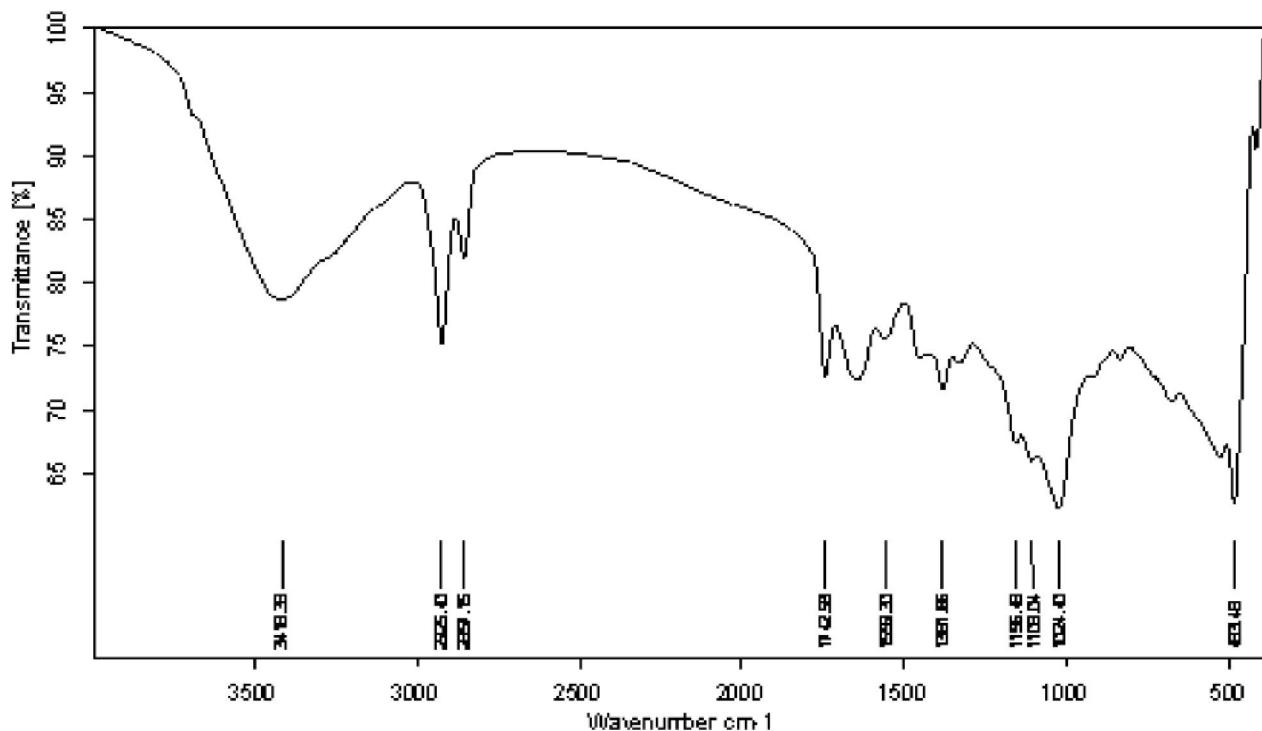


Figure 3 : FTIR spectra of CT/BE (1:1) with cross linking agent (Formaldehyde)

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^[25]

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. Maximum decomposition was observed around from 370 °C in CT/BE

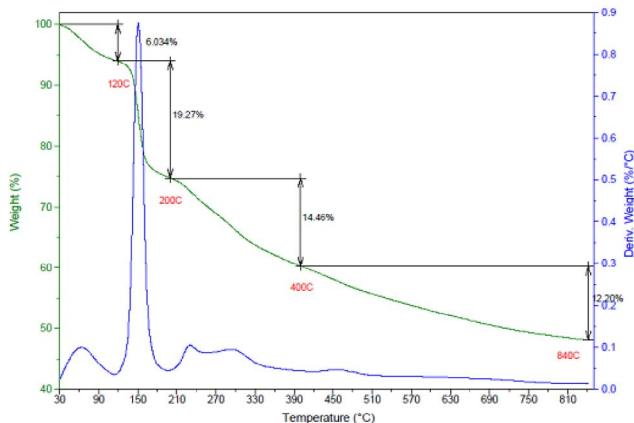


Figure 4 : TGA spectra of pure chitin

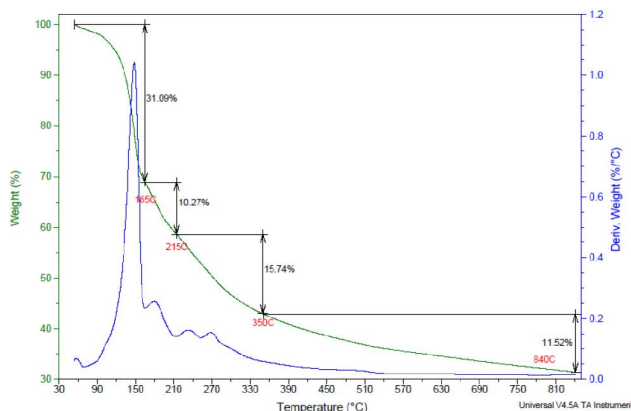


Figure 5 : TGA spectra of CT/BE (1:1) blend

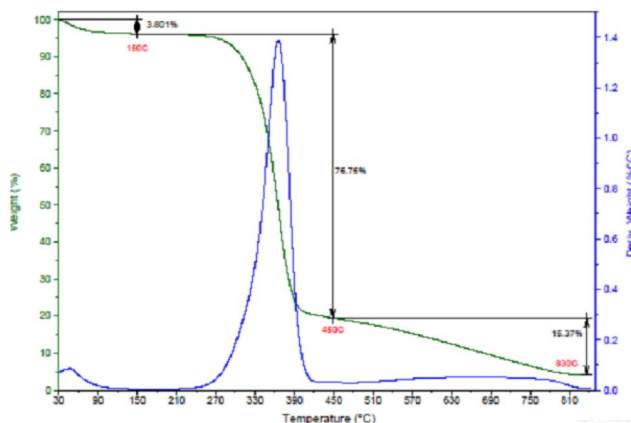


Figure 6 : TGA spectra of CT/BE (1:1) with cross linking agent (Formaldehyde)

(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.

DSC analysis

The Figures 7-9 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^[26,27] 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.

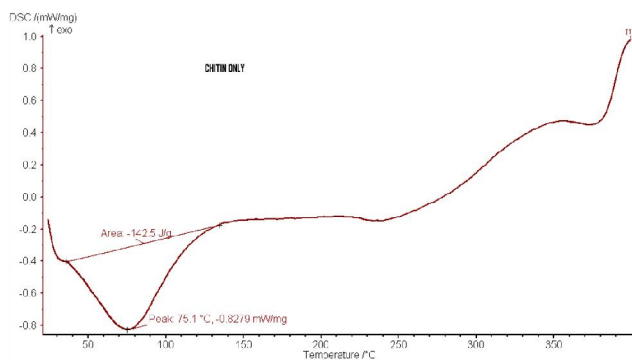


Figure 7 : DSC spectra of pure chitin

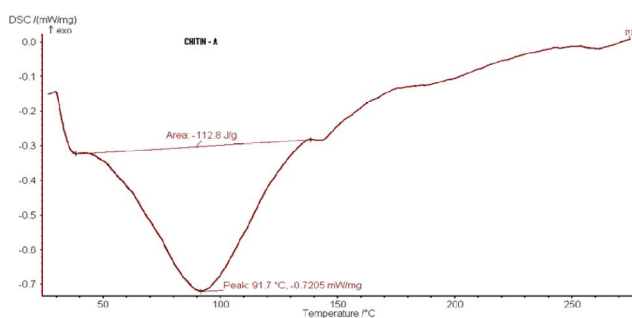


Figure 8 : DSC spectra of CT/BE (1:1) blend

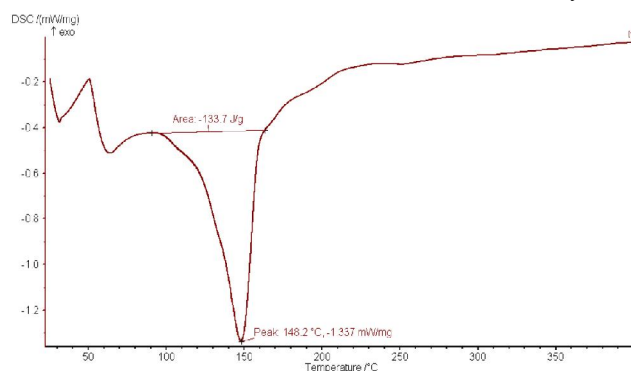


Figure 9 : DSC spectra of CT/BE (1:1) with cross linking agent (Formaldehyde)

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 had higher thermal stability in the presence of cross linking agent.

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