

The Structure and Properties of Chitosan/Nylon6/Polyurethane Ternary Blends

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Abstract- The ternary blends consisting of Chitosan (CS), Nylon6 (Ny6) and Polyurethane foam (PUF) were prepared by solution blending method. The Structural, thermal and morphological studies were performed by Fourier transform infrared spectroscopy (FTIR), Thermo gravimetric analysis (TGA), X-ray diffraction (XRD) and Scanning electron microscope (SEM). The FTIR results showed intermolecular hydrogen bonds took place between CS, Ny6 and PUF. TGA studies reveal that the thermal stability of the uncross linked blend is higher than cross linked blend. Results of X-ray diffraction indicated that the intensity of diffraction peak at $2\theta = 20^\circ$ of CS and PUF become lower in uncross linked blends. In EG-CS/Ny6/PUF blend the diffraction peaks of CS and PUF at $2\theta = 20^\circ$ become wider and shifted to 23° indicating the amorphous nature and weak interaction between the constituent polymers. Morphologies of these blends were viewed using scanning electron microscopy; the studies revealed that rough and heterogeneous surface for uncross linked blend and a distinct phase separation with high porosity for cross linked blends.

Index Terms- Ternary blends, Chitosan, Ethylene glycol, Cross-linking

I. INTRODUCTION

Recently, natural polymers have been studied as biological and biomedical resources due to their unique properties including non-toxicity [1], bio degradability and biocompatibility [2, 3]. However, natural homopolymer by itself is inadequate to meet the diversity of demands for biomaterials. Biocompatibility had been considered as 'the ability of a material to perform with an appropriate host response in a specific application [1], taking into account the interactivity between the biomaterial and the host. Among the prominent applications for biomaterials are: controlled drug delivery [4, 5], orthopedic devices [6], sutures, cardiac pacemakers, and vascular grafts. Natural polymers such as konjac glucomannan [7], chitosan [8] and gelatin [9] have remained attractive primarily because they are economical, readily available, and potentially degradable and compatible due to their origin. Chitosan[Poly (1,4-b-D-glucopyranosamine)] is known to be non-toxic odorless, biocompatible with living tissues, biodegradable, and chemically functional. Due to these advantages, chitosan and its derivatives are seen in applications such as biomedical materials [10], biodegradable packaging and cosmetics. Chitosan has been well known as being able to accelerate the healing of wound in human [11,12]. It has also been documented that chitosan confers considerable antibacterial activity against a broad spectrum of bacteria [13, 14]. Owing to the advantages, some of the applications of chitosan have included wound dressings, gauzes, medical sutures [15] and metal ion-capturing materials for waste-water treatment [16].

The modification of chitosan by means of blending with other polymers may be a convenient and effective method to improve physical properties for practical utilization. Investigation of blends of chitosan with synthetic and naturally occurring macromolecules has attracted much interest in the recent years. It has been reported that the hydrophilic property of chitosan could be modified via blending with PEG and PVA [17, 18]. Chitosan was also blended with several polymers such as polyamides, polyurethane foam, poly (acrylic acid), gelatin, silk fibroin and cellulose to enhance mechanical properties [19-21].

Polyurethane foam (PUF) offers high porosity, low weight-to-volume ratios, good resilience abrasion resistance and moisture permeability properties along with high strength to weight ratio performance attributes. These properties have made PUF as one of the most common polymeric foam used on a global basis, which is reflected its multitude of applications [22].

Recently, Blending of synthetic with natural biopolymers has raised the attention of both the industrial and the academic world [23, 24]. Furthermore, cross linking treatment has emerged as another important strategy to improve the performance of the blends. In the present study we report on solution blending of chitosan with nylon6 and polyurethane foam with and without cross linking agent and subsequent characterization of the obtained blends using IR, TGA, XRD and SEM.

II. MATERIALS AND METHODS

A. Materials

Chitosan (92% deacetylated) was obtained from India sea foods, Cochin. Nylon6 was obtained from DuPont and had a molecular weight of 19,000. Polyurethane foam was obtained from Star foams, Ranipet. All the other materials chemicals are of AR grade from Sd-fine chemicals.

B. Preparation of ternary blend

The polymer solutions (1wt %) of Chitosan, Nylon6 and Polyurethane foam were prepared by using formic acid. The chitosan, nylon6 and polyurethane foam solutions of (1:1:1) weight ratios were blended together with and without cross linking agent (ethylene glycol) to form a homogeneous solution at room temperature with moderate agitation for 1h. Then the ternary blend solutions were poured onto cleaned Petri dishes and dried under vacuum in an oven at 70 °C for 10 h to ensure the removal of the solvent traces.

C. Sample Characterization

The FTIR spectra of the blends were recorded in the spectral range of 400–4000 cm^{-1} using Nucon Infrared spectrophotometer. The TGA analysis of the cross linked and uncross linked blend was performed using TGA Q500 V20.10 Build 36 instrument. X-ray diffraction patterns of blends were analyzed using an X-ray diffractometer (Model D8 avance Bruker, Germany) using a Ni-filtered Cu-K α radiation source power 12 kW, the Bragg's angle (2θ) in the range of 5-80° and scanning speed of $2\theta = 8/\text{min}$. The morphologies of cross linked and uncross linked blends were examined using a scanning electron microscopy (Hitachi – S3400N).

III. RESULTS AND DISCUSSION

A. Fourier transforms infrared (FT-IR) spectroscopy

The infrared spectra of pure chitosan, polyurethane foam and the blends are displayed in Fig.1(a-d). The typical absorption peaks of chitosan (Fig.1a) at 3427.83cm^{-1} correspond to stretching vibration of N-H and O-H; 2923cm^{-1} C-H stretching vibration and 1627cm^{-1} C=O stretching (amide I) and N-H bending (amide II) [25]. The spectra of PUF (Fig.1d) shows characteristic bands at 3442.66cm^{-1} , 2922.18cm^{-1} , 1743.04cm^{-1} and 1628.65cm^{-1} correspond to N-H stretching, CH_2 stretching, Urethane carbonyl and imine group respectively. The interferograms of the blends (Fig.1b &1c) were also observed with small changes in the intensity and wave number indicates obvious hydrogen bonding interactions among counterpart polymers [26].

B. Thermo gravimetric analysis

The TGA curves of CS, CS/Ny6/PUF and EG-CS/Ny6/PUF are shown in Fig. 2(a-c). Pure chitosan (Fig.2a) showed two discrete weight losses at around 100 °C and 272 °C, reflecting the loss of water by vaporization and degradation of CS chains respectively. The TGA curve of CS/Ny6/PUF exhibited two stages of degradation (Fig.2b); at the temperature ranges of 225 – 345 °C and 345 – 465 °C respectively, the thermal stability of the uncross linked blend is higher than pure chitosan due to strong hydrogen bonding between the polymers. On the other hand, the cross linked ternary blend EG-CS/Ny6/PUF (Fig. 2c) shows maximum degradation within the temperature range of 157 °C; due to weak hydrogen bonding and amorphous nature of the blend which is in agreement with XRD and SEM results.

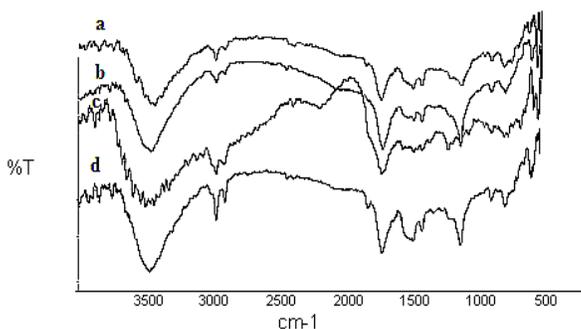


Fig. 1 FTIR spectra of (a) pure CS, (b) CS/Ny6/PUF blend, (c) EG-CS/Ny6/PUF blend (d)PUF

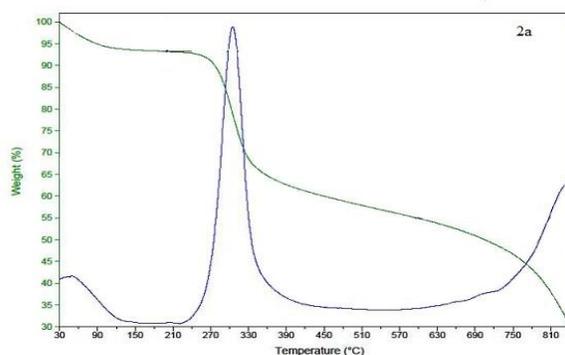


Fig. 2a TGA curves of pure Chitosan (CS)

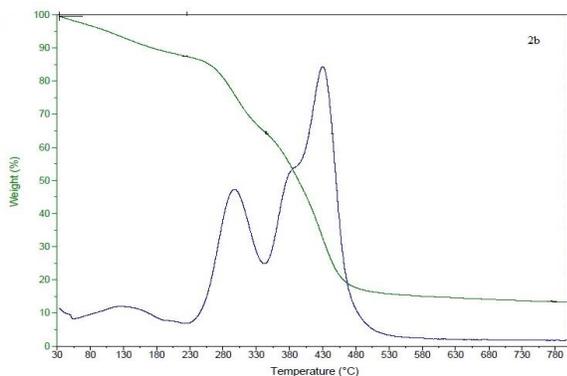


Fig. 2b TGA curves of CS/Ny6/PUF blend

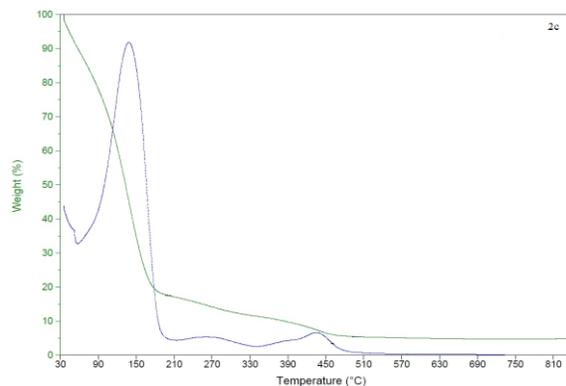


Fig. 2c TGA curves of EG-CS/Ny6/PUF blend

C. X-ray Diffraction

The X-ray diffraction spectra of CS, PUF, CS/Ny6/PUF and EG-CS/Ny6/PUF blends are shown in Fig. 3. The peaks (Fig. 3a) around $2\theta = 12^\circ$, 20° and 23° should be assigned to chitosan: the peak around $2\theta = 12^\circ$ corresponding to the hydrated crystalline structure; while the peaks around $2\theta = 20^\circ$ and 23° corresponded to the anhydrous crystalline and amorphous structure, respectively [27] and also PUF shows (Fig.3d) a wide diffraction peak at 20.45° and 41.55° indicating very low crystallization degree. The reflections for chitosan and PUF are diminished in the blend CS/Ny6/PUF and the intensity of diffraction peak becomes flat and broad gradually (Fig.3b), indicating the significant hydrogen bonding interaction among counterpart polymers.

The x-ray pattern of EG-CS/Ny6/PUF blend (Fig. 3c), in which the characteristic peaks of chitosan are less pronounced. The peaks of chitosan (20°) and PUF (20.45°) has been shifted to $2\theta = 23^\circ$; becomes wider and amorphous, indicating a weak hydrogen bonding interaction in EG-CS/Ny6/PUF blend.

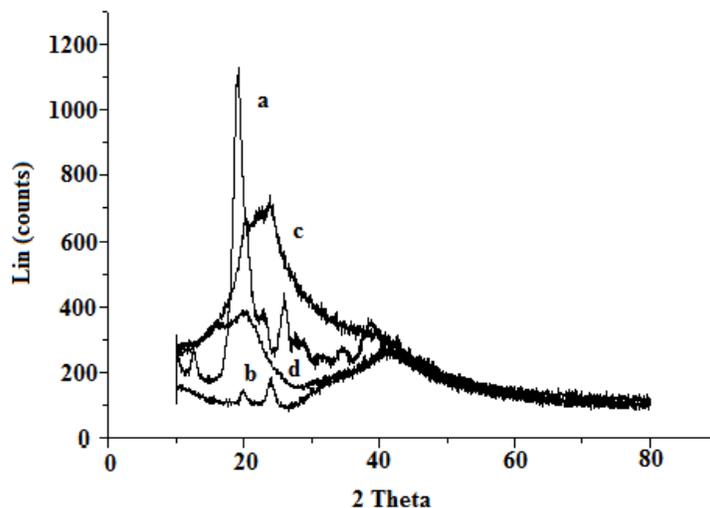


Fig. 3 XRD curve of (a) pure CS, (b) CS/Ny6/PUF blend, (c) EG-CS/Ny6/PUF blend (d) PUF

D. Morphology Characterization

The scanning electron micrographs of prepared blends are shown in Fig. 4(a–c). Pure chitosan exhibit uniform and dense micro structure without pore (Fig. 4a); whereas the CS/Ny6/PUF (Fig. 4b) blend morphology indicates heterogeneous rough surface resulted from the reorientation of polar functional groups toward to the top surface of ternary blend [28]. However, the morphology of EG-CS/Ny6/PUF (Fig. 4c) displayed a trend of self gathering due to limited compatibility; as a result of migration many holes were generated at the surface affecting the thermal stability of the blend, though they can form hydrogen bonding interaction.

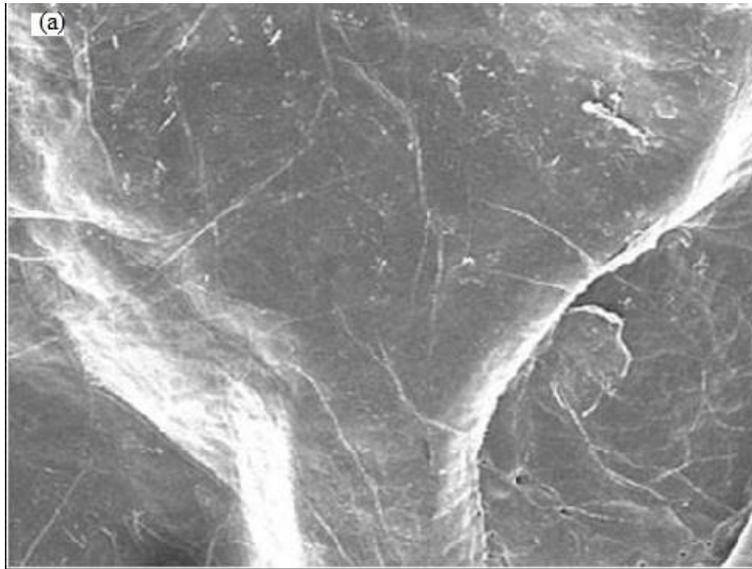


Fig. 4a SEM micrographs of CS

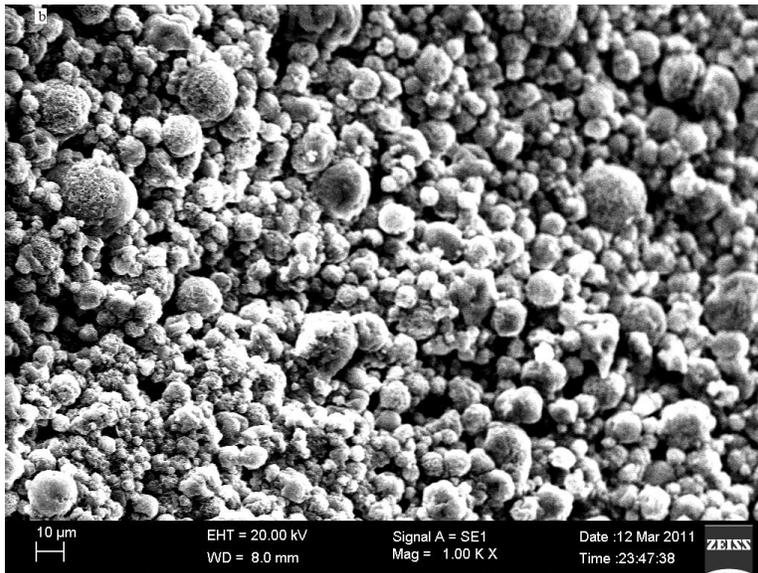


Fig. 4b SEM micrographs of CS/Ny6/PUF blend

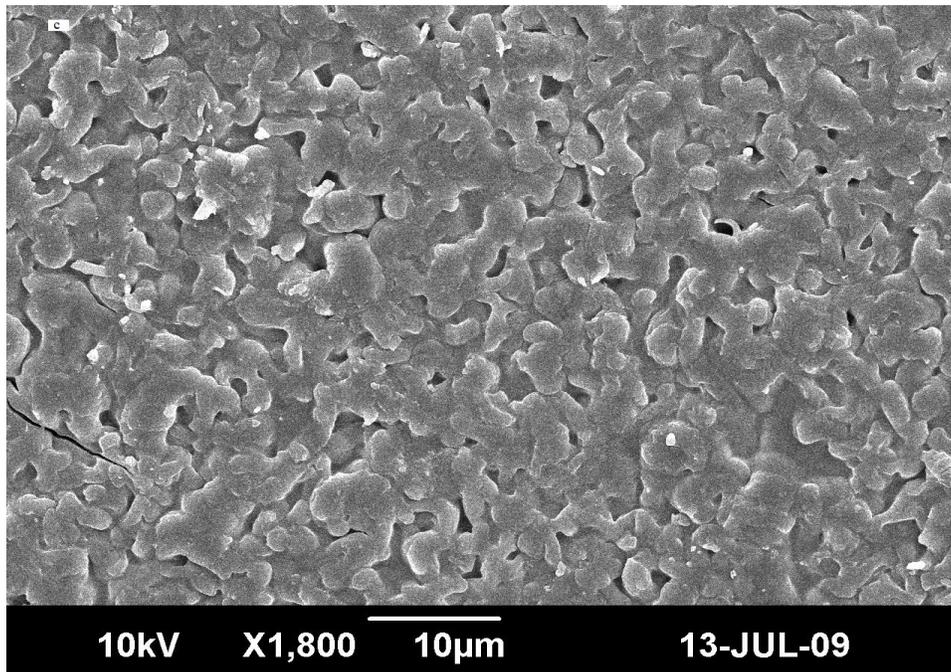


Fig. 4c SEM micrographs of EG- CS/Ny6/PUF blend

IV. CONCLUSION

Ternary blends composed of Chitosan, Nylon6 and Polyurethane foam with and without cross linking agent in 1:1:1 ratio were prepared. The FT-IR studies indicate the existence of inter-molecular interaction between the counterpart polymers. The XRD spectra results revealed that the decrease in crystallinity of pure CS; this is due to significant interaction among CS, Ny6 and PUF molecules. The TGA studies revealed the improved the thermal stability of the uncross linked blend whereas ethylene glycol cross linked blend show low thermal stability. The surface micro structure of the uncross linked blend show rough and heterogeneous surface whereas the ethylene glycol cross linked blend show distinct phase separation with high porosity indicating low compatibility between counterpart polymers.

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