Preparation and characterization of short sisal fiber reinforced chitin (CN)/starch (ST) ternary blend

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Abstract
In the present work, a novel series of ternary blends Chitin(CN)/Starch(ST)/Cellulose fiber(CF) were prepared in different ratios (1:1:1, 1:2:1, and 2:1:1) in the presence of cross-linking agent glutaraldehyde. The prepared ternary blends were characterized using FTIR, XRD, TGA and SEM. From the FTIR results, the shift in peaks to higher wavenumber confirms the formation of blend. XRD studies were conducted to find out the amorphous or crystalline nature of the ternary blend. XRD analysis revealed in the presence of cross-linking agent glutaraldehyde enhances the amorphous nature of the ternary blend. The TGA result shows the thermal stability for the blends prepared in the presence of glutaraldehyde. The preliminary studies supported that the ternary blend formed in the presence of cross-linking agent is suitable for heavy metal removal.

Key words: Chitin, Starch, Cellulose fiber, FTIR, XRD, TGA, SEM.

INTRODUCTION
In the last few years, the use of natural biopolymers as adsorbent for heavy metal removal has received considerable attention, especially from the viewpoint of environmental pollution, biodegradability, safety and cost [1]. Biopolymers are the polymeric biomolecules. They contain monomeric units that are covalently bonded to form larger structure [2]. Considering the availability and structural properties of the biopolymer, in this present research work the most advantageous marine biopolymer chitin was blended with starch and cellulose fiber.

Chitin (β-(1-4)-poly-N-acetyl-D-glucosamine) is widely distributed in nature [3] and is commonly found in the exoskeletons of crustacean and insects as well as the cell walls of fungi [4]. Chitin shows a highly ordered structure [5] and it is widely used as a better adsorbent due its versatile properties such as non-toxic [6], non-allergenic, anti-microbial and biodegradable [7, 8]. However, low mechanical properties, thermal stability, and poor solubility of chitin restrict its use in a wide range application. In order to improve its thermal and mechanical properties of chitin, it can be modified by several methods such as blending and grafting. In this research work starch and cellulose fiber were chosen for blending.

Starch is a polysaccharide which consists of repeating D-glucopyranose units, linked together by α-1, 4 linkages. Starch is a renewable and biodegradable compound [9] which can easily form complexes with different metal particles. Starch is water-soluble, making it easy to be modified by blending to improve its applications [10, 11]. Cellulose was processed from sisal fiber. These fibers have abundant and specific functional group such as hydroxyl groups which have affinities for heavy metal ions [12].

In the present work, efforts has been made to prepare ecofriendly adsorbent based on natural biomaterials such as chitin, starch and cellulose fiber in the presence of cross linking agent glutaraldehyde. The prepared ternary blend was characterized with reliable techniques such as FTIR, XRD, TGA and SEM.

The XRD study indicated that the crystallinity of polymer blend decreased which shows that the blends were changing into amorphous character. The thermal analysis showed that blending compound had higher thermal stability.

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EXPERIMENTAL
Material and Methods
Materials
Corn starch (12% moisture) was purchased from Sigma Aldrich, India. Chitin was obtained from India Sea Foods, Cochin and Sisal Fibers was purchased from Vibrant Nature, Chennai, India. Glutaraldehyde was procured from S.D. Fine Chemicals. All chemicals used in the study are of analytical grade.

Preparation of chitin/starch/cellulose fiber blend with crosslinking agent glutaraldehyde
A known amount of chitin was dissolved in 5% CaCl₂ in methanol solution. Starch was mixed with minimum amount of water to make an emulsion. Chitin and starch solutions were mixed in different ratios with glutaraldehyde as crosslinking agent. Cellulose fiber was processed from sisal fiber by steam explosion method. The chitin starch blend solutions with glutaraldehyde were reinforced with modified Cellulose fibers in different proportions in the high speed mixer Remi India and then stored overnight. The blend was casted in plastic petri plates with the dimension 50cm X 50cm.

Characterization of polymer blends
FT-IR spectroscopy
The Fourier transform infrared (FTIR) investigation was carried out using PERKIN ELMER spectrometer in the range of 400 cm⁻¹ to 4000 cm⁻¹. The IR spectrum was recorded in a solid state using KBr pellet method.

X – Ray Diffraction Studies
It was carried out using (XRD – SHIMADZU XD – D1) a Ni – filtered Cu Kλ X-ray radiation source. The blends were scanned within the range of 10° - 90° (2θ) at a scanning rate of 5°/min.

Thermo Gravimetric Analysis (TGA)
Thermo gravimetric analysis (Perkin Elmer Model, USA) was used having unit of microprocessor temperature control with TA data station. The sample mass generally in the range of 2 - 3 mg was used. An equipment consist of both sample pan with balance system was placed in temperature ranges from 25°C to 800°C with 50 cm³/min flow rate of nitrogen. The mass of sample pan was recorded constantly as a function of temperature.

Scanning Electron Microscopy (SEM)

RESULTS AND DISCUSSION

FTIR spectroscopy
The FTIR spectral details of the ternary blend prepared using Chitin(CN)/Starch (ST)/Cellulose fiber (CF) with crosslinking agent glutaraldehyde of ratio 1:1:1 was shown in Figures 1. The main characteristics broad peak at 3459.7cm⁻¹ corresponds to O-H and N-H stretching, intermolecular hydrogen bonding and polymeric association. This broader peak confirms that the individual polymers were blended well [13]. The absorption bands at 2947.9 cm⁻¹ (C-H stretching) [14], 1599.8 cm⁻¹ (Amide II band (NH bending), 1381.8 cm⁻¹ (C-O-C glycosidic linkage in Cyclic ether group) 1052.3 cm⁻¹ (C-N stretching), and 466 cm⁻¹ (C-C bending, O-H out of plane bending) of the ternary blend. The frequencies were disappeared or shifted during blending confirm the formation of polymer blends [15].

X-Ray Diffraction studies (XRD)
The Figure (2) shows the XRD spectrum of Chitin(CN)/Starch (ST)/Cellulose fiber (CF) blend (1:1:1) in the presence of cross linking agent glutaraldehyde. The XRD spectrum of the prepared blend shows two peaks around 2θ = 22° and 40°. The broad peak observed at two different 2θ values indicates that the sample has a semi crystalline nature [16]. The crystallinity of the blend is generally lower than pure chitin, which confirms that the amorphous nature increases during the blending of polymeric mixture [17].

Thermogravimetric Analysis (TGA)
Thermogravimetric analysis (TGA) is a thermal analysis technique, used to determine the sample stability and loss of weight in diverse temperature [18]. Thermal details of ternary blend of CN/ST/CF of 1:1:1 in presence of glutaraldehyde is discussed below. From the figure it is found that the heating rates were suitably controlled at 10°C min⁻¹ under nitrogen atmosphere, and the weight loss was measured from the ambient temperature up to 800°C. Around 70% of the specimen had crumbled in the temperature scope of 390°C. Around 84.4% of the specimen had broken down toward the end of the
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analysis deserting 13.6% of the blend as a deposit. Most extreme weight reduction happens at the scope of 220°C to 400°C. The remaining temperature was observed to be 785°C (Fig.3a and 3b).

Scanning Electron Microscopy
The SEM images of ternary blend are shown in Figure 4 (a) and 4 (b). It can be seen in Fig. 4a that the surface morphology of the blend is quite smooth with fortified filaments and the normal communication between the sisal filaments and the CN/ST mix lattice is hydrogen holding which make the composite stable with numerous hydrophilic centres at the surface. This hydrophilic centre will be favorable for metal ions to diffuse and penetrate into the interior part of each adsorbent and be trapped on the copolymer. The cross section morphology of the same blend is shown in Fig. 4 b. The voids and the microvoids in the figure illustrates the smooth blending of the chitin, starch and the cellulose fiber which explains that the ternary blend is highly suitable for the metal ion adsorption.

Fig 1. FTIR spectrum of CN/ST/CF (1:1:1) with GLU ternary blend

Fig 2. XRD pattern of the blend CN/ST/CF (1:1:1) with GLU

Fig 3. (a) TGA thermal studies of the blend CN/ST/CF (1:1:1) with GLU (b) Thermal decomposition (TGA) details of CN/ST/CF blend (1:1:1) with GLU
CONCLUSION
In this study, the Chitin / Starch / Cellulose fiber blend were prepared at various ratios with crosslinking agent glutaraldehyde. The results suggest that there is strong interaction between the molecular chains of chitin, starch and cellulose fiber, which may lead to the miscibility at specific ratios during blending. The blends were characterized using various physicochemical methods such as FTIR, XRD, TGA and SEM. From the FTIR results, it was found that the peaks were shifted to higher wave number during blend formation. This confirms the crosslinking had taken place between the polymer and the crosslinking agents. The XRD studies elucidate the reduction in the crystallinity of the ternary blends. The morphology as well as the compatibility of the blends has been studied using SEM and XRD methods. TGA results indicate that the addition of glutaraldehyde enhanced the thermal stability of the polymer blends. It was concluded that the prepared blend is highly suitable as sorbent for heavy metal removal.

ACKNOWLEDGEMENT
None.

CONFLICT OF INTEREST
No conflict of interest.

REFERENCES
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