Synthesis and characterization of ternary blends of Chitosan, Vermiculite and Montmorillonite clay

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ABSTRACT

In the present study the ternary blends of chitosan with inorganic clay vermiculite and montmorillonite clay at various ratios in presence and absence of crosslinking agent glutaraldehyde were prepared by the solution-casting technique. The structure and physical properties of the blend films were analyzed by advanced analytical tools such as Fourier transform resonance spectroscopy (FT-IR), X-ray diffraction (XRD), Differential Scanning Calorimetry (DSC) and Thermo gravimetric analysis (TGA). The obtained results of FT-IR studies reveal the presence of crosslinking between the polymers and crosslinking agent. The results of TGA and DSC studies confirms that the blend prepared with glutaraldehyde as a crosslinking agent was found to be highly thermally stable. The results are discussed.

Keywords: Chitosan, vermiculite, montmorillonite clay, crosslinking agent, blending.

INTRODUCTION

In recent years, much attention has been paid to natural polymers due to the energy crisis and environmental problem. Natural polymers have potential industrial applications because of their low toxicity and biocompatibility. The excellent biodegradable polymeric systems have gained importance [1] for many applications. The use of biopolymers as components of blends materials is a very popular topic for current studies. Chitosan as a biopolymer is also widely studied for development of a new blend material with vermiculite and montmorillonite (MMT) clay.

Chitosan, poly-b (1, 4)-2-amino-2-deoxy-D-glucose, is the deacetylated products of chitin, the second abundant natural polymer on earth [2]. Chitosan has been widely studied for biosensors, tissue engineering, separation membrane, water treatment cosmetics, food packaging and textiles and so on, which has several desirable properties like biodegradability, good biocompatibility and multiple functional groups. hydrophilicity, anti-bacterial property, and non-toxicity .It contains amino (−NH2) and hydroxyl (−OH) groups that can serve as coordination sites to bind heavy metals. However, low mechanical properties, thermal stability, and barrier of chitosan restrict its use in a wide range application. In order to improve the mechanical properties and thermal stability, it can be modified by several methods, such as blending with synthetic [3] or natural polymers [4], or with inorganic fillers. The addition of inorganic fillers into polymers is well known as an economical way to improve the properties of the polymers [5].

Many types of inorganic clay, such as kaolin [6], mica [7], vermiculite [8], bentonite [9], sepiolite [10], diatomite [11] and rectorite have been introduced into polymeric network to form organic inorganic composite. Clay minerals possess excellent properties such as low or null toxicity, good biocompatibility, and promise for controlled release,
thus give rise to the incessant interest to their development for biological purposes. These applications are mainly based on high cation exchange capacity, excellent swelling property, remarkable hydration ability, and structural plasticity of the cationic clays. Clay is a cheap natural raw material that has been widely used for many years as inorganic filler for plastics and rubbers to reduce the polymer consumption and cost.

Montmorillonite is a 2:1 layer-type clay mineral and its basic structural unit is composed of two tetrahedrally coordinated sheets of silicon ions surrounding a sandwiched octahedrally coordinated sheet of aluminum ions [12]. Montmorillonite clay is chemically hydrated sodium calcium aluminium magnesium silicate hydroxide (Na, Ca) 0.33(Al, Mg) 2(Si4O10) (OH) 2·nH2O. Its advantages of a high surface area, large aspect ratio and a platelet thickness of 10 Å make it suitable for reinforcement purposes [13]. The parallel layers in these structures are linked together by weak electrostatic forces. With many outstanding properties such as high specific surface area, high cation exchange capacity, layered structure, chemical and mechanical stability [14, 15, 16]. The variation of MMT concentration and dimensions to enhance the properties of the chitosan/MMT blends were studied [17].

Vermiculite (VMT) belongs to the general family of 2:1 layered silicates. Compared to other clay, VMT is abundant and has a larger cation exchange capacity. Furthermore, there are reactive OH groups on the surface of VMT and these groups are accessible to prepare organic inorganic blends. Recently, because of their availability, nontoxic characterization, biodegradability as well as biocompatibility. This work may be helpful in understanding the role of clay’s modification in chitosan blends. Chitosan/clay blends were described in some literatures [18].

In this study, chitosan/vermiculite/montmorillonite clay blends were prepared by the casting process. In order to produce chitosan film with homogeneous dispersion of fine clay particles, chitosan, the naturally cationic polymer was used as a compatibilising agent for montmorillonite modification. Glutaraldehyde was added to the blend as a crosslinking agent in various ratios and evaluate the performance of CTS/V/MMT blend. The hydrophobic behavior and an increase in spacing between the layers of silicate are important factors which make organophilic montmorillonite compatible with most hydrophobic polymers. Clay and silica has already proved to be an effective way to improve the mechanical, electrical, and thermal properties of polymers. This biopolymer can intercalate into the inorganic clay by means of cationic exchange process in the absence of other organic modifiers. The strong interactions between the clay and chitosan. The enhanced thermal stability properties of chitosan were reported [18]. Modified Ball clay (MBC) and chitosan composite (MBC–CH) was prepared by [19].

In this paper, the main objective was to prepare the polymer blend (Cs/V/MMT clay) whose chemical structure and physical properties of blend were characterized by FTIR, XRD, TGA, DSC and SEM analysis. 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.

MATERIALS AND METHODS

Chemicals and Materials
Chitosan was kind gift from India Sea Foods, Cochin, Kerala which is 92% deacetylated. Glacial acetic acid were purchased from Sisco Research Laboratories PVT, LTD, India. Montmorillonite (MMT) employed in this study was K10 montmorillonite from Sigma-Aldrich vermiculite was obtained from Fisher Scientific Pvt Ltd, India. The cross linking agent glutaraldehyde was purchased from SDFine-Chem Ltd, India.

Preparation of chitosan/vermiculite/montmorillonite clay blend
Chitosan/vermiculite/montmorillonite blend films were prepared by casting technique. Chitosan Solutions were prepared by dissolving chitosan in 2% glacial acetic acid solution at room temperature with stirring. Ion-exchanged vermiculite (VMT) powder was added with water. A montmorillonite clay dissolved in water was also prepared. Subsequently, the dispersion was mechanically stirred at 1000 rpm for one hour. The product was poured into petri dish and allowed to dried. The same procedure was carried out in presence. The prepared ratios were tabulated below, Table -(1)
Characterizations

FTIR measurements of the prepared polymeric samples was recorded by Fourier transform infra-red spectrophotometer (FT-IR) using the Perkin Elmer 200 FTIR spectrophotometer, in the range of 400-4000cm⁻¹ at 25°C with a resolution of 4 cm⁻¹. The thermal analysis (TGA and DSC) was carried out on a Perkin Elmer thermal analysis instrument. TGA were recorded with 2.0mg of this sample was heated from 30 °C to 870°C at a heating rate of 10 °C /min at N2 atm. In this technique thermal decomposition of polymer blend are measured as a function of temperature. For DSC analysis the pierced lid in the nitrogen atmosphere at a heating rate of 10° K/min was used. The XRD Pattern of the various polymeric blend samples were tested by an X-ray scattering SHIMADU XD-DI Diffractometer using Ni filter Cu Kα radiation source (λ=0.154nm), set as scan rate =10/min, using a voltage of 40kv and a current of 30mA.The particles are having cubic to cuboid shape with 100-300nm particle size as given by Nanotrac particle analyzer.

RESULTS AND DISCUSSION

FTIR analysis

The FTIR spectra of Chitosan /Vermiculite/Montmorillonite clay (1:1:1) are depicted in Figure-(1A). The main characteristics bands of chitosan blend at 3679.08 cm⁻¹, 3619.15 cm⁻¹ are ascribed to O-H, and intermolecular hydrogen bonded O-H (Polymeric association). The absorption bands at 3009.65 cm⁻¹ (C-H stretching), 2882.45 cm⁻¹ (C-H stretching in CH₃), 2591 cm⁻¹ (O-H stretching in alcohol (chelate compound)). Absorption bands at 1835.20 cm⁻¹, 1790. 1790. cm⁻¹ (C=O stretching in amide group, amide vibration), 1517 cm⁻¹ (N-H bending in primary amines) and 1398.93 cm⁻¹, 1338.82 cm⁻¹ (skeleton vibrations involving C-O-C linkage) are characteristics of modified chitosan blends.

IR spectra of Chitosan/Vermiculite/Montmorillonite clay (1:2:1) are shown in Figure- (1B). The N-H bending in primary amine band of chitosan was found at 1517.51 cm⁻¹. The peak obtained at 1425.17 cm⁻¹ (C=C stretching) the band of Cs/VMT/MMT blends at 1398.94 cm⁻¹, 1338.66 cm⁻¹, 1131.47 cm⁻¹ are ascribed to C-O stretching in alcohol and (skeleton vibrations involving C-O-C linkage) respectively.

The FTIR spectra of modified in chitosan blend in the presence of glutaraldehyde (1:1:1-glu) and (1:2:1-glu) are depicted in Figure-(1C&1D). After crosslinking process it showed a shift from 1586 to 1564 cm⁻¹ in the– NH₃⁺ vibration upon interaction of the poly-cation with the clay [20], that can be assigned to N=O stretching and C=N stretching was observed that the formation of ionic crosslinks between chitosan and glutaraldehyde This band is attributed to the –NH₃⁺ groups that do not interact with the clay and vermiculite.

X-RAY DIFFRACTION

X-ray diffractograms of Cs/VMT/MMT (1:1:1) blend films are shown in Figure-(1A). As observed, the chitosan based film was in a semi-crystalline state with 3 main diffraction peaks 2θ=19.74°, 26.26°, 31.05°, 34.65° present in its X-ray diffraction pattern. The semi-crystalline character of Cs/VMT/MMT (1:2:1) is revealed from its respective diffractogram are shown in Figure -(1B), which showed peaks at 2θ=19°, 24°, 26°, 21.90° correspond to crystal form.

The XRD pattern of Cs/VMT/MMT (1:1:1) blend with glutaraldehyde film are shown in Figure-(1C), which showed Amorphous in nature. The peaks observed at 2θ=26.18°, 43.16°, 43.16° and XRD pattern of Cs/VMT/MMT (1:1:2)-Glutaraldehyde shown in Figure-(1D). As observed the peaks at 2θ=42° was amorphous.
Figure- (1). FTIR spectra (3500–1000 cm$^{-1}$) of (A) Cs/V/MMT clay (1:1:1) (B) Cs/V/MMT clay (1:2:1) (C) Cs/V/MMT clay (1:1:1-Glu) and (D) Cs/V/MMT clay (1:2:1-Glu).
On comparing the pure chitosan, with prepared Cs/VMT/MMT clay in presence and absence of glutaraldehyde shows almost amorphous in nature. It was observed that the degree of crystallinity was found to be decreased for the blends in the presence of cross linking agent. This indicates most probably that the formation of a disordered intercalated structure of Cs/VMT/MMT blend has occurred, where the silicate layers are homogenously dispersed in the polymer matrix and crosslinking agent forms bonds between polymers and the coherent order of the chitosan was destroyed more [18].

The above results were investigate the effect of glutaraldehyde and molecular weight upon the intercalation with vermiculite and montmorillonite clay. The crosslinking agent glutaraldehyde increases the mechanical strength and thermal stability of ternary blends when compare to absence of crosslinking agent.

**SEM analysis**

SEM is a widely used technique to study morphology and surface characteristics of the prepared blend. In the present study, SEM is used to assess morphological changes in modified chitosan with crosslinking agent glutaraldehyde surface at various combination of chitosan/vermiculite/montmorillonite clay were recorded at Fig. 3. It can be observed that the mean particle size of the microsphere is about 10µm. The surface of microsphere is uneven and rough surface [21] shown in figure-(3A) & (3B) suggesting that parts of the blend are likely to absorb on the surface. It is visible from micrographs that the samples without crosslinking agent have roughening the surface, while after adding of glutaraldehyde, together with smoothen the surface shown in figure- (3C) & (3D).
Thermal analysis
Thermo gravimetric analysis
The TGA thermogram details of Cs/V/MMT clay in presence and absence of glutaraldehyde were represented in the Figures-4 (A-D). Generally, three stages of decomposition were attributed. The first stage of transition falls in the range of 30ºC -150ºC shows about 4 - 5% weight loss due to the evaporation of loosely bound water molecules from the samples. The second stage—a predominant one, was the maximum weight loss which had taken place indicating the breaking of the polymer structure. The maximum decomposition taking place at the temperature range from 150 to 540ºC for the prepared blend with and without glutaraldehyde. In the third stage, the breakdown of the polymeric backbone took place [22], around 31.09%, 64.48% , 27.95% and 25.95% of the sample had disintegrated at the temperature of 783.42ºC, 783.30ºC,783.35ºC and 783.31ºC respectively. It is known from the literature [23].On comparing the prepared blend of Cs/V/MMT clay without and with crosslinking agent glutaraldehyde, the thermal stability of Cs/v/MMT clay (1:1:1-Glu) & (1:2:1-Glu) shown in figure-(4A-B) is higher with addition of glutaraldehyde when compare with absence of glutaraldehyde shown in figure-(4C-D).
Differential Scanning Calorimetry Analysis

Figure 5(A-D), represent the DSC details of Cs/VMT/MMT clay in presence and absence of glutaraldehyde. DSC shows one broad endothermic peak and one exothermic peak for all the samples, at the temperatures of 118.4°C, 114.2°C, 114.8°C and 79.6°C indicating the crystallization temperature and 304.2°C, 311.6°C, 245.2°C and 251.9°C indicating the melting temperature respectively. This is due to the loss of water. The single glass transition temperature was observed at 220°C, 230°C, 280°C and 320°C respectively showing the compatibility of the sample. On comparing the DSC curve of the prepared samples with presence of glutaraldehyde, the samples show a shift in the glass transition temperature. From the above results, it is concluded that the presence of crosslinking agent is increases the thermal stability of the blend.
CONCLUSION

In this study, the Chitosan / Vermiculite / Montmorillonite clay blend were prepared at various ratios with and without crosslinking. The blends were characterized using various physicochemical methods such as FTIR, TGA, DSC, SEM and XRD. From the FTIR spectra the different pendant groups present in the blends have been ascertained that the cross-linking agents enhanced the thermal stability of the polymer blend. The morphology as well as the compatibility of the blends has been studied using SEM and XRD methods. The TGA and DSC analysis predicted the samples are highly thermally stable with crosslinking agent. It was concluded that the cross-linking agents enhanced the thermal stability of the polymer blend.

REFERENCES

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