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ORIGINAL PAPER

Physicochemical and morphological evaluation of chitosan/poly(vinyl alcohol)/methylcellulose chemically cross-linked ternary blends

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Abstract Chitosan/poly(vinyl alcohol)/methylcellulose (CS/PVA/MC) ternary blend was prepared and chemically cross-linked with glutaraldehyde. The prepared ternary blends were characterized by Fourier transform infrared spectroscopy (FTIR), Thermogravimetric analysis (TGA), and X-ray diffraction (XRD). The FTIR results showed that the strong intermolecular hydrogen bonds took place between CS and PVA. TGA showed the thermostability of the blend is enhanced by glutaraldehyde as crosslink agent. Results of XRD indicated that the relative crystalline of pure CS film was reduced when the polymeric network was reticulated by glutaraldehyde. Finally, the results of scanning electron microscopy (SEM) indicated that the morphology of the blend is rough and heterogenous, further it confirms the interaction between the functional groups of the blend components.

Keywords Chitosan · Glutaraldehyde · Ternary blends · Chemically cross-linked

Introduction

Chitosan (CS), a natural polysaccharide is known to be non-toxic, odorless, biocompatible with living tissues, biodegradable, and chemically functionalizable. Owing to these advantages, CS and its derivatives are seen in applications such as

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biomedical materials, biodegradable packaging, cosmetics, metal ion-capturing materials for wastewater treatment, and so on [1].

Poly(vinyl alcohol) (PVA) is a non-toxic, water-soluble synthetic polymer. Owing to the characteristics of easy preparation, good biodegradability, excellent chemical resistance, and good mechanical properties, PVA has been used widely in diverse fields, ranging from thickening agent to controlled release systems. Since CS contains hydroxyl and amine groups, it is potentially miscible with PVA due to the formation of hydrogen bonds [2]. Methylcellulose (MC) is a water-soluble cellulose polysaccharide derivative that is widely used as a binder or thickener in pharmaceuticals, foods, and ceramics [3].

Blending of synthetic with natural biopolymers is considered as a new class of materials that is of particular significance [4]. Recently, the study and development of blends formed by three or more components has raised the attention of both the industrial and the academic world [5]. Blending of CS with PVA and ternary blends of CS/PVA/gelatin, CS/PVA/pectin has been already reported in literature[4, 6]. Furthermore, cross-linking treatment has emerged as another important strategy to improve the performance of ternary blends. It has been reported that CS and PVA could be well cross-linked with some PVA- [7] and CS-based cross-linkers [8–11].

This article aims to prepare and comprehensively investigate the physical and chemical properties of polymer blends based on CS/PVA/MC and chemically cross-linked with glutaraldehyde. To our knowledge, this is the first report where such a system was synthesized and extensively characterized by spectroscopic and morphological aspects with different polymer contents, regarding to the hybrid network formation (polymer–polymer).

Experimental

Materials

Chitosan (92% deacetylated) was the kind gift of India seafoods Cochin, Kerala, India. PVA, MC, and glutaraldehyde (analytically pure) were purchased from S&D fine Chemicals, Mumbai, India.

Preparation of ternary blend

1 g CS powder was added into a 100 mL of formic acid and stirred to form a 1 wt% clear CS solution. Meanwhile 1 g PVA powder was charged into 100 mL purified water while stirring to form a 1 wt% clear PVA solution. Then CS and PVA were blended together to form a homogeneous CS/PVA binary blend solution. 1 g MC was charged into 100 mL purified water and stirred to form 1 wt% MC solution. Finally CS, PVA, and MC solutions in the weight ratio (1:1:1) was mixed and stirred. Then the cross-linker reagent glutaraldehyde (G) 0.75% (v/v) was slowly added under constant stirring. Further the solution was poured into plastic molds and allowed to dry for 72–120 h at room temperature (~25 °C) in the desiccator

followed by additional 24 h in an oven at 40 °C, in order to remove the residues of water and formic acid.

Characterization

The infrared spectra were recorded on Thermo Nicolet AVATAR 330 spectrophotometer in 4000–400 cm^{-1} wavelength range using KBr pellet method. X–ray diffraction (XRD) studies were performed using X-ray powder diffractometer (XRD—SHIMADZU XD—D1) using a Ni—filtered Cu Kα X-ray radiation source. Thermogravimetric analysis was conducted on a SDT Q600 V8.0 build 95 instrument. The morphology of the blend membranes was examined by a scanning electron microscopy (JEOL) Model JSM-6390LV.

Results and discussion

FTIR spectroscopy

Figure 1 shows the FTIR spectra relative to CS, PVA, CS/PVA, and CS/PVA/MC (1:1) blend membranes both cross-linked and uncross-linked. The spectrum of pure CS (Fig. 1a) shows peaks around 899 and 1070 cm^{-1} corresponding to sugar structure and a peak around 1570 cm^{-1} corresponding to NH bending (amide II). The peaks at 1639 and 3454 cm^{-1} are attributed to C=O stretching (amide I) and OH stretching. Figure 1b PVA shows absorption peak at about 3406 cm^{-1} of the hydroxyl groups, at 1094 and 1441 cm^{-1} related to C–O bonds. In the CS/PVA blend the change in the characteristic shape of the CS spectrum is due to hydrogen bonding between –OH of PVA and –OH or –NH_2 of CS is evident from Fig. 1c. Absorption bands of natural and synthetic polymers are observed due to the integration of the three components (CS, MC, and PVA) in the hybrid. Common interactions in hybrid polymers based on CS occur between the primary hydroxyl groups of CS [12, 13]. Other suggested interactions are between the CS hydrogen bonds, related to NH_2 groups [14] and C=O groups [15].

In the spectra of the blend film we see interactions involving natural and synthetic polymers: C=O at 1639 cm^{-1} (amide I) and NH at 1570 cm^{-1} (amide II). These bands change their intensity in the hybrid blend film of CS/PVA/MC spectra (Fig. 1d) to 1595 cm^{-1}. This indicates the interaction among the blend components, probably through formation of hydrogen bonds. Further cross-linking with glutaraldehyde (G-CS/PVA/MC) (Fig. 1e) showed absorption peak at 1625 cm^{-1} corresponding to imine linkage (C=N) [16].

Thermogravimetric analysis

Figure 2 shows TGA curves of CS, CS/PVA, CS/PVA/MC, and G-CS/PVA/MC. Two weight losses are observed in the (Fig. 2a) CS TGA curve. The weight loss at 50–150 °C is due to the moisture vaporization. The other weight loss at 200–300 °C is due to the degradation of CS molecule. Figure 2c depict the weight losses

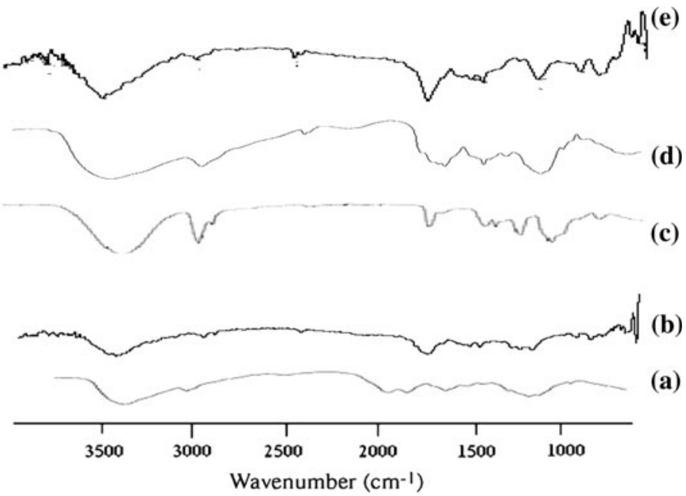

Fig. 1 FTIR spectra of various blends: *a* pure CS, *b* pure PVA, *c* CS/PVA blend, *d* CS/PVA/MC blend, and *e* G-CS/PVA/MC blend

resulting from CS, PVA, and MC. The first weight loss at 50–150 °C is due to the moisture vaporization while the second weight loss at 250–350 °C is due to the thermal degradation of CS, PVA, and MC. The third weight loss at 400–450 °C is due to the by-products generated by PVA during the TGA thermal degradation process as mentioned by Hay [17].

The cross-linked ternary blend membrane G-CS/PVA/MC (Fig. 2d) on the other hand, shows two step weight loss between 270–340 °C and 410–480 °C, corresponding to the decomposition of CS and PVA polymers, respectively. The maximum decomposition temperatures of CS/PVA/MC blended membranes with glutaraldehyde treatment are higher than those membranes without glutaraldehyde treatment. From the results of Fig. 2 it can be concluded that the thermal stability of blended membranes increases with the treatment of glutaraldehyde.

X-ray diffraction

The XRD patterns of CS, PVA, CS/PVA, CS/PVA/MC, and G-CS/PVA/MC blends are shown in Fig. 3. In Fig. 3a CS exhibits reflection fall at about 20°. The CS/PVA blend (Fig. 3b) shows two diffraction peaks at 18° and 41°, which are the characteristic of crystalline peaks of PVA and hydrated crystalline structure of CS, respectively. In Fig. 3c as MC is added to the CS/PVA/MC ternary blend the intensity of diffraction peak at 18° for PVA becomes flat and broad gradually. The peak of the hydrated crystalline structure of CS at 41° shows the same tendency. Thus, it becomes evident that the existence of MC decreases the crystalline nature of PVA and CS. This phenomenon is due to the significant hydrogen bonding interaction among CS, PVA, and MC molecules. In other words, the addition of MC improves the compatibility between CS and PVA. In Fig. 3d G-CS/PVA/MC the

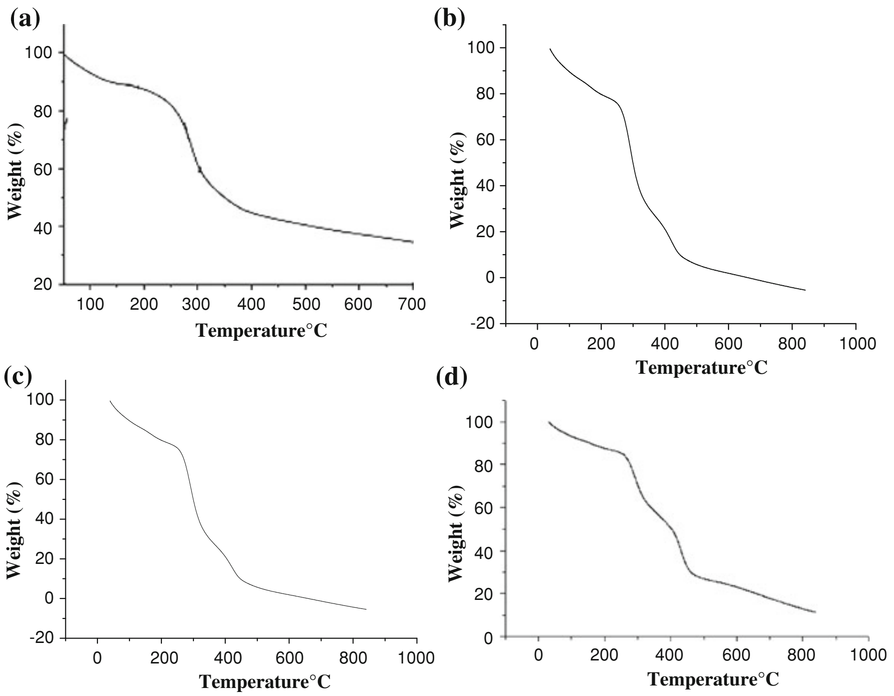

Fig. 2 TGA curves of various blends: **a** pure CS, **b** CS/PVA blend, **c** CS/PVA/MC blend, and **d** G-CS/PVA/MC blend

peak at 20° becomes flat and broad gradually to higher diffraction value of 41° is proved by the chemical crosslinking. The average crystallinity index (ratio of the areas) of pure CS was reduced when the ternary blend was reticulated with glutaraldehyde. So the cross-linking inhibits close packing of the polymer chains by reducing the degree of freedom in the 3-D conformation, preventing the formation of crystalline regions [18]. This reduction of crystallinity would play a crucial role on influencing the blend degradability, water absorption, and swelling.

SEM examination

The SEM photographs of the CS/PVA/MC blended films and G-CS/PVA/MC is shown in Fig. 4. The surface morphology of CS/PVA/MC and G-CS/PVA/MC ternary blend membrane is rough and heterogeneous indicating more hydrophilic top surface as evident from Fig. 4a, b. According to Chen et al. [6] such a rough surface could be due to the reorientation of polar functional groups toward to the top surface of the ternary blend membranes. It is suggested that polymer, CS/PVA/MC prior to chemical cross-linking have their chains mostly physically entangled in the blend network, but formed a chemically bonded blend after glutaraldehyde cross-linking has taken place.

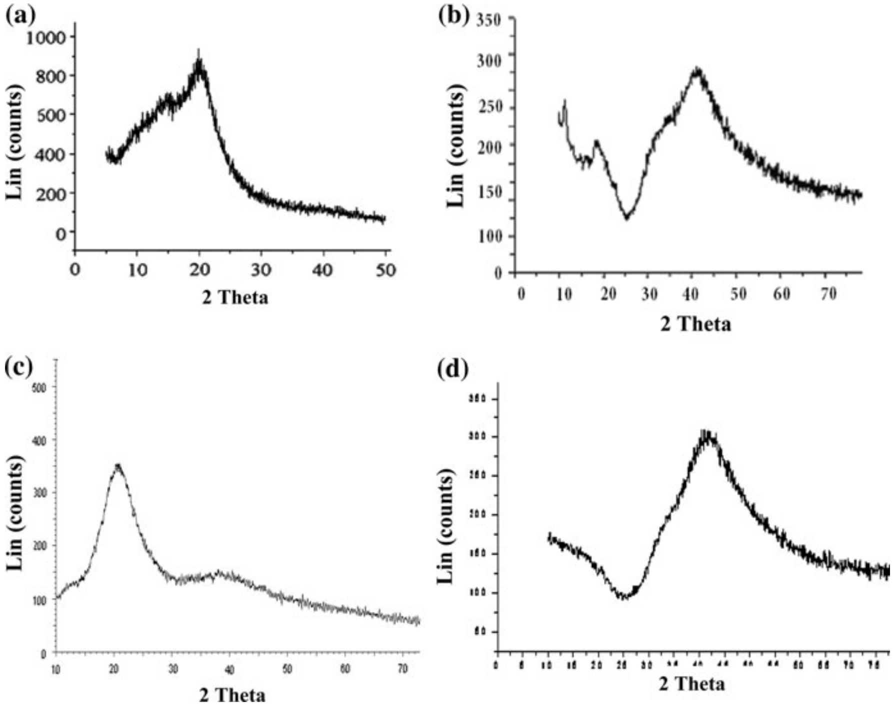

Fig. 3 XRD patterns of **a** pure CS, **b** CS/PVA blend, **c** CS/PVA/MC blend, and **d** G-CS/PVA/MC blend

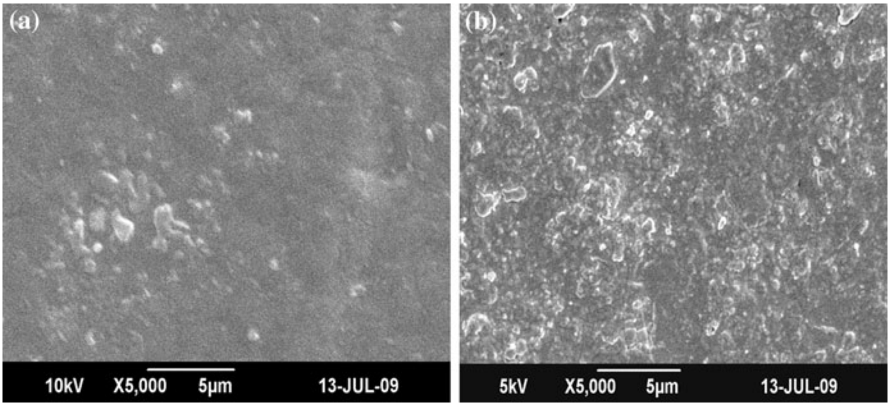

Fig. 4 SEM micrographs of blend films: **a** CS/PVA/MC blend and **b** G-CS/PVA/MC blend

Conclusion

Novel CS/PVA/MC blends were synthesized and chemically cross-linked in this study. The results have shown that the overall properties of ternary blend can be tailored associated with addition of cross-linker. Characterization of cross-linked membrane by FTIR and XRD confirmed the cross-linking reaction. FTIR spectroscopy revealed the interaction between CS, PVA, MC, and glutaraldehyde. XRD spectra illustrate that the existence of MC decreases the crystalline of PVA and CS. This is because of the significant hydrogen bonding interaction occurs among CS, PVA, and MC molecules and further demonstrated that the cross-linker enhanced the amorphous nature of ternary blend. Thermogravimetric analysis showed that blending and cross-linking improved the thermal properties of CS. The result of SEM indicated the surface of the ternary blend after the addition of cross-linker is rough and heterogeneous indicating more hydrophilic top surface.

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