

Spectroscopic Studies on PVA-Chitosan Blend with Potassium Nitrate as Ionic Crosslinker for Biomedical Application

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Abstract— The present research aimed to study the energy band gaps of Chitosan (CS) -Polyvinyl Alcohol (PVA) blend films crosslinked with Potassium nitrate (KNO₃). The morphology of the film surface and blending were investigated by Scanning Electron Microscopy (SEM). The UV-visible spectroscopic studies were done by Parking Elmer UV/Vis Spectrometer Lambda-35. The increase in the absorption intensity and decrease in the optical band gap may be due to a larger absorption increment associated with the charge transfer transition and a similarly Optical conductivity of samples increases due to the decrease in optical band gap and hence promises to be a good material for the biomedical and battery applications.

Keywords— Chitosan-Polyvinyl Alcohol blend, Potassium nitrate, absorption maxima, direct and indirect energy band gap

I. INTRODUCTION

Polymer blending is a method that is commonly used for providing desirable polymeric materials with the combined properties suitable for particular applications. Investigation of blends of chitosan with synthetic and naturally occurring macromolecules has attracted much attention in the recently years in various occasions [1-5]. Blending of chitosan with synthetic polymers is a convenient method for preparation of synthetic biodegradable polymers having versatile properties such as good water absorbance and enhanced mechanical properties while maintaining biodegradability[6] and chitosan [poly-b(1-4)-d-glucosamine], have recently been re-evaluated and found to be useful resources and functional materials [7-8]. However, their homopolymers are inadequate to meet the diversity of our demands for materials. Polymer blending is one of the most effective methods for providing new, desirable polymeric materials for practical applications. Chitosan membranes blended with poly(vinyl alcohol)(PVA) have already been reported to have good mechanical properties because of the specific intermolecular interactions between PVA and chitosan in the blends.

polymeric chains are interconnected by crosslinkers, leading to the formation of a 3D network. Crosslinkers are molecules of MW much smaller than the MW of the chains between two consecutive crosslinks. The properties of crosslinked hydrogels depend mainly on their crosslinking density, namely the ratio of moles of crosslinking agent to the moles of polymer repeating units. Moreover, a critical number of crosslinks per chain is required to allow the formation of a network, such as that of a hydrogel.

Depending on the nature of the crosslinker, the main interactions forming the network are covalent or ionic bonds. The structures and interactions forming the covalently and ionically crosslinked polymers will be presented, their principles of formation and properties will be considered and examples of medical or pharmaceutical applications will be given. Their potential biocompatibility will be discussed, although some examples will refer to systems that are still in development.

Ionic crosslinking is a simple and mild procedure. In contrast to covalent crosslinking, no auxiliary molecules such as catalysts are required [9], which is of great interest for medical or pharmaceutical applications. Indeed, ionic crosslinking can be ensured by the classical method of preparing a crosslinked network, namely by the addition of the crosslinker, either solubilised [10] or dispersed [11], to the chitosan solution. Chitosan can be crosslinked by simply dipping pieces of chitosan film into the crosslinker solution [12] or by adding the chitosan solution to the crosslinker solution [13,14,15] through a syringe for example. These latter methods induce the formation of systems that are similar to gel particles.

The objective of this study was to develop chitosan based film by blending and crosslinking with polyvinyl alcohol and Potassium nitrate(KNO₃) in order to study the energy band gaps of chitosan biopolymer. This modified PVA-CS film may be a promising material in packaging applications, battery and biomedical applications.

II. MATERIALS AND METHODS

Shrimp source Chitosan in a form of white flakes with a degree of deacetylation of 88.1% defined by UV method [25] was obtained from commercial source. Polyvinyl alcohol was purchased from Sigma Chemicals Co. (UK). Acetic acid (glacial 100%, pro analysis) was purchased from Merck (Germany). Potassium nitrate (KNO_3) ($M = 101.1032 \text{ g mol}^{-1}$) was purchased from Merck (Germany), Methanol AR (CH_4O) ($M = 32.04$) was purchased from S D Fine chemical Mumbai. Ultra pure water (Elga-Prima Corp, UK) with a resistivity higher than $18 \text{ M}\Omega \text{ cm}^{-1}$ was used to prepare all solutions. All chemicals were used without further purification and freshly prepared solutions were always used in all experiments.

1: Synthesis of CS/PVA blend and its crosslinked films:

Chitosan was grounded and dried in an oven until a constant weight was observed. A 10 g L^{-1} solution of Cs was prepared by dissolving 5g of chitosan in 500 ml of acetic acid (0.1 M) followed by stirring and heating at 60°C for 14 to 16h. The solution was filtered before being used to remove the undissolved particles. The PVA powder was dissolved in preheated ultra pure water, followed by stirring at a temperature of 90°C for about 2 hours until clear solutions were obtained. To prepare the CS-PVA blend, 50ml of Cs and 50ml of PVA solutions were mixed and stirred at 90°C for 30 min to obtain homogeneous blended solutions. The pH of the solution was maintained at levels higher than $\text{pH} \sim 6$ to avoid Cs precipitation.

The obtained homogeneous of CS-PVA (50-50) solution was cast into a polystyrene Petri dish, after removing all trapped air bubbles. The cast solution was then allowed to dry in a vacuum oven at 60°C to form a uniform and homogenous film with a thickness of about $14 \pm 2 \mu\text{m}$. The film thicknesses were obtained at various positions of the samples using a digital thickness gauge and the reported data is the average of 3 readings.

The blended films were ionically crosslinked using the method described by Huang *et al.* [26]. The dried of CS-PVA (50-50) films were immersed in a different weight percentages of Potassium nitrate in aqueous methanol solution, as shown in table 1. The crosslinking reaction was allowed to continue for 30-40 min at room temperature under continuous stirring. The crosslinked films were removed, and then placed under vacuum for drying.

Table 1: Polymer blend samples with KNO_3 as Crosslinker.

Sl.No	Films designation PVA/CHITOSAN(50/50) blend films	Potassium Nitrate in Methanol (wt%) as crosslinker
01	PVA/CS (50/50) blend (PC blend)	0
02	PVA/CS (50/50) blend (CPKN-1)	0.1
03	PVA/CS (50/50)blend (CPKN-2)	0.2
04	PVA/CS (50/50)blend (CPKN-3)	0.3
05	PVA/CS (50/50)blend (CPKN-4)	0.4
06	PVA/CS (50/50)blend (CPKN-5)	0.5

III. RESULTS AND DISCUSSION

1: MORPHOLOGICAL STUDIES OF CS-PVA BLEND AND ITS CROSSLINKED FILMS:

Figure 1 shows the SEM images of the surfaces of PVA-CS blended film and its corresponding crosslinked films as ionic crosslinker. In fig 1 (a) shows smooth and homogenous surface with no straps or lumps unlike that of (b) and (c) where some straps are seen because of the ionic salt, which is deposited on the surface of the blended film [18,19]. This indicates the uniform distribution of CS and PVA molecules throughout the films and is caused by the interaction of hydrogen bonds between the functional groups of the blended components ($-\text{OH}$ and $-\text{NH}_2$ groups in chitosan and $-\text{OH}$ groups in PVA), further, the images (b) and (c) (CPKN-1,CPKN-2) shows that the crosslinking is achieved by completely modifying the surface morphology of crosslinked of PVA-CS (50-50) blend.

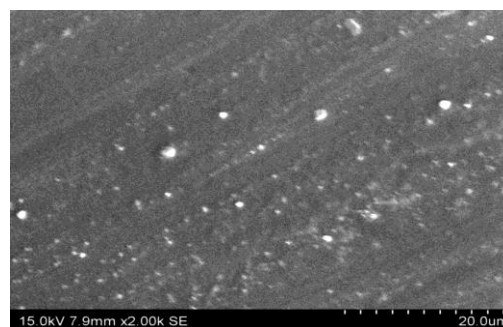
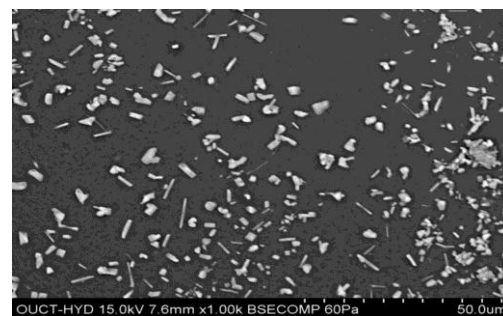
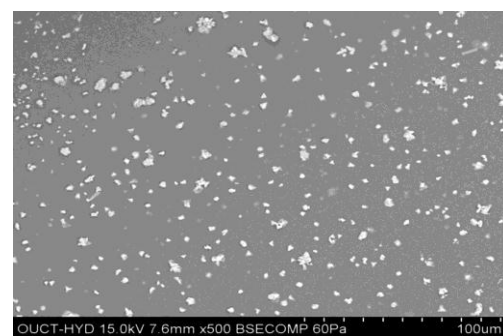


FIGURE 1: (a) SEM image of PVA/CS (50/50) blend film



(b): SEM image of CPKN-1 film



(c): SEM image of CPKN-2 film

2. OPTICAL PROPERTIES:

Figure 3 of (a) shows optical absorption spectra recorded for blend PVA-CS polymer in the region 200–900 nm. The optical band gap of films can be calculated by using the intercept method and the following formula.

$$(ahv)^n = A(hv - E_g) \tag{1}$$

Where α is the absorption coefficient near the absorption edge, A is a constant and n characterizes the transition process. Here $n = 2$ and $1/2$ stands for the direct band gap and indirect band gap, respectively. A shift in absorption towards the higher wavelengths has been observed, these shifts indicate the formation of inter/intra molecular hydrogen bonding mainly between nitrate ions with that of these adjacent OH groups, The decrease in transmission for crosslinked PVA-CS films reflect the variation in the optical band gap which arises due to the change in polymer structure. We have made an attempt of evaluating optical band gap of these crosslinked polymer films using Tauc plot. **Figure 3 of (b) and (c)** shows the photon energy ($h\nu$) is plotted against $(ahv)^2$ and $(ahv)^{1/2}$. It gives a straight line fit, which implies that the samples undergo direct and indirect transition. Then the band gap has been extracted by extrapolating the straight portion of the graph on $h\nu$ axis at $\alpha = 0$. The calculated values of the optical band gap for all prepared polymer electrolyte films are given in table 2.

Table 2. The values of the optical band gap decreasing with increasing concentration of KNO₃.

SL.NO.	FILM DESIGNATION	DIRECT E _g (eV)	INDIRECT E _g (eV)
01.	PVA-CS(50-50)blend	2.80	2.6
02.	CPKN-1	2.65	2.4
03.	CPKN-2	2.55	2.2
04.	CPKN-3	2.45	2.1
05.	CPKN-4	2.30	1.8
06.	CPKN-5	2.20	1.5

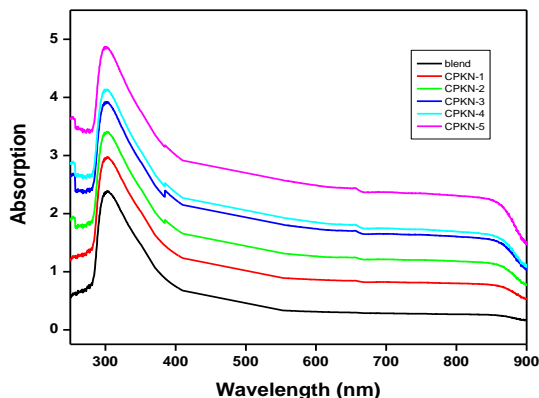


Fig 5.4.3(a): Optical absorption spectra for various blend and its crosslinked films.

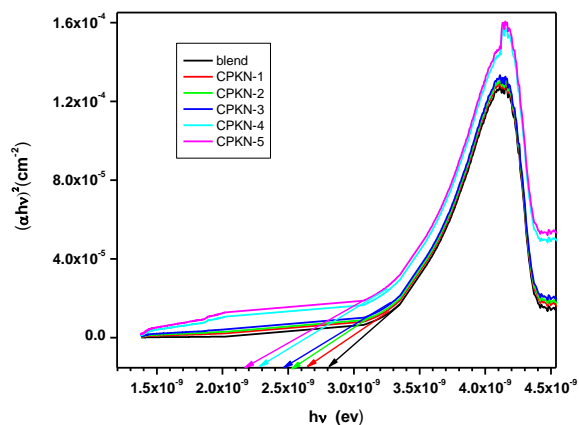


Fig 5.4.3(b): Plot of $(ahv)^2$ v/s (hv) for various blend and its crosslinked films.

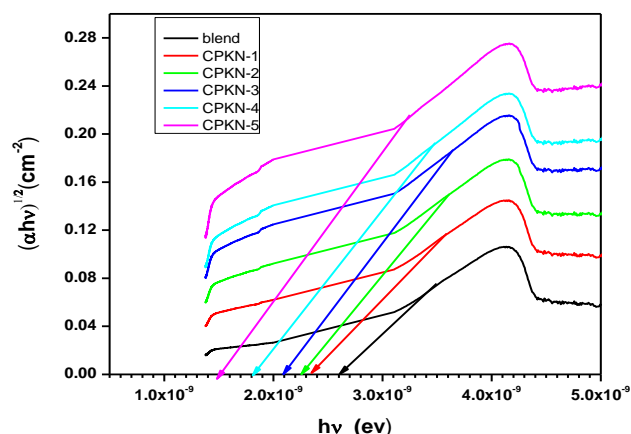


Fig 4.4.3(c): Plot of $(ahv)^{1/2}$ v/s (hv) for various blend and its crosslinked films.

IV. CONCLUSION

PVA-CS blend and its crosslinked films with ionic crosslinker KNO₃ is prepared. From SEM it is clear that PVA-CS blending along with its crosslinker is achieved successfully. The UV-Vis spectra show the existence of optical energy band gap in these crosslinked films and the values of optical band gaps are decreasing with increasing concentration of KNO₃. The decrease in transmission for crosslinked PVA-CS films reflects the variation in the optical band gap which arises due to the change in polymer structure. This modified chitosan film may be a promising material in packaging, biomedical and battery applications.

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