

Electrical and mechanical characterization of Gelatin/poly (aniline) composite films

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Abstract

The method of preparation of Gelatin/poly (aniline) composite films has been discussed. Gelatin was cross linked with glyoxal (Glox) in aqueous medium. The composite film was prepared by *in-situ* polymerization of Aniline within the Gelatin film matrix. The films so prepared have been characterized with XRD, tensile testing and conductivity measurements. The variation in mechanical/electrical properties of Gelatin/poly(aniline) composite films with varying concentration of aniline have been investigated. It was observed that the electrical conductivity of the films increase appreciably with the concentration of aniline in the film. In addition, the tensile strength of the films was also found to increase with aniline concentration. The results from XRD, conductivity test and tensile testing were correlated. A stronger material having added advantage of conductivity has been reported. Copyright © 2017 VBRI Press.

Keywords: Gelatin, poly (aniline), in-situ polymerization, elastic strength, conductivity.

Introduction

Conducting polymers are gathering lot of interest in the area of organic electronics due to their potential application in energy conservation systems such as photovoltaic cells, solar cells etc.(1). In last decade researchers around the world have their focus on biomedical applications of electrically conducting polymers. Researchers in tissue engineering field are looking forward to develop stimulus-responsive biomaterials with easy-to-tailor properties. Indeed, electroactive biomaterials belong to a new class of 'smart' biomaterials that are capable of delivering electrical, electrochemical and electroanalytical stimulations to cells. The conducting polymers are very important members of this group of electroactive biomaterials, due to their excellent properties such as a good control on electrical stimulus, fair optical and electrical properties, a high conductivity to weight ratio, and the ease with which they can be made biocompatible, biodegradable and porous. Bioinspired Intelligent Materials and Devices with conducting polymers were described in detail by Toribio Fernández Otero [2]. Co-polymerization of these conducting polymers with other non-conducting polymers may impart some of their properties to the resultant composite material.

Gelatin, usually referred to as the most common protein in animal kingdom, is usually termed as a pure protein. Apart from having fair ability to form transparent film and to undergo biodegradation, it also acts as diffusion barrier for various gases and aroma. This allows it to be in a large number of food and biomedical applications such as food packaging, absorbent pads, bio sensing, wound dressings, porous scaffolds, drug delivery systems, tissue engineering, bone grafts, plasma expander etc. (3,4,5,6).

Poly(aniline) (PANI) as a conducting polymer has an immense potential to be used in biomedical field [7-9]. Due to ease of synthesis, environmental stability and high electrical conductivity and its ability to be electrically switched between its conductive and resistive states, poly(aniline) has captured the intense attention of the scientific community. Poly(aniline) (PANI) has appreciable conductivity with added advantage of hemocompatibility makes it useful to be used as biosensors [10].

Several researchers all over the world are doing research on biosensors, neural probes, controlled drug delivery and tissue engineering applications of PANI and its composites. Yibo Yo *et al.* (11) have reported fabrication of conductive gelatin

methacrylate–polyaniline hydrogels which will be useful in developing next-generation bioelectrical interfaces. The polymerization of aniline at a solution–gelatin gel interface was reported by Natalia V. Blinova *et al.* (12). Still electrical and mechanical characterization of composite of gelatin and aniline was never done before.

After carrying out a thorough literature survey, we observed that *in-situ* polymerization of aniline within a polymeric film has not been reported. The advantage with this novel strategy could be the fact that a uniform distribution of poly (aniline) chains within the polymer matrix might be obtained. Therefore, we hereby report a unique strategy to prepare poly(vinyl alcohol)/poly (aniline) composite film by carrying out *in-situ* polymerization of aniline within the poly(vinyl alcohol) film. The present work is confined only to the study of on electrical and mechanical properties of composite film thus produced. A correlation of these findings with results obtained from XRD studies has also been attempted. In order to prepare the poly (aniline)/gelatin composite film, aniline was polymerized *in-situ* within the gelatin film matrix. This enabled us to obtain a uniform distribution of poly(aniline) macromolecular chains within the gelatin film. The variations in tensile strength and electrical conductivity with change in concentration of aniline in composite samples were investigated.

Experimental

Materials

Aniline (Ani) (Molecular Weight-93.13) and gelatin (Gel) of GR grade were purchased from Hi Media Chemicals, Mumbai, India. Potassium Persulphate (Molecular Weight-270.31) Ammonium persulphate (APS), glyoxal (Glox)(40% LR), hydrochloric acid(35%), and other chemicals of analytical grade were obtained from Research Lab, Pune India. The double distilled water was used throughout the investigation.

Method of preparation of composite films

Preparation of glyoxal (Glox) crosslinked gelatin film

Gelatin film, crosslinked with glyoxal, was prepared by following the procedure reported by J. Vartiainen [13]. In a typical experiment, a pre-calculated quantity of gelatin was put in distilled water and allowed to keep for a period of 12 h to ensure complete dissolution. The solution was stirred gently on a magnetic stirrer at 40⁰C for a period of 1h and then filtered to obtain transparent solution. Now, 0.5 ml of 40 % glyoxal solution was added in to 20 ml of gelatin solution and the final volume was made to 25 ml by using distilled water. The cross linking reaction was performed by pouring the above solution in a Petri plate (id 74 mm) and placing it in an electric oven (Temp star, India) at 60⁰C for a period of 12h. After the reaction was over, the film was peeled off, equilibrated in distilled

water for 6 h to remove unreacted chemicals and finally dried in vacuum chamber till they attained constant weight. We prepared six samples, having different concentrations of glyoxal and gelatin in the feed mixture.

Preparation of Glox-crosslinked Gel/poly (Ani) composite films

In order to prepare Gelatin/poly(aniline) composite film, aniline was polymerized *in-situ* within the gelatin film. In a typical experiment, 30 ml of aniline solution was taken in a beaker and allowed to cool till 5⁰ C in ice bath. This, 30 ml of aniline was then taken in a 150 ml beaker (corning, India). Aniline was dissolved by the slow addition of 30 ml of HCl (2M) in drop-wise manner. Now, to this solution, 50 ml of 2% KPS solution was added. In the above reaction mixture, a pre-weighed piece of Glox-X- Gel film was equilibrated for a period of 12 h. Finally, the film was taken out, washed with distilled water and allowed to dry at 40⁰C till constant weight.

Characterization of Glox-X-Gel/PANI films

The crystalline nature of the Glox-X-Gel/PANI film was investigated by X-ray diffraction technique. ARikagu Diffractometer (Cu radiation = 0.1546 nm), operating at 40 kV and 40 mA was employed to record the diffraction pattern in the range of 2 from 3 to 50⁰ at the speed rate of 2 degree/ min. The mechanical properties of Glox-X-Gel/PANI films were investigated using tensile testing machine (Make: Unilab Lab Testing Equipments, Delhi, India). For measuring conductance of Glox-X-Gel/PANI films Impedance Analyzer (Make, Wayne Kerr Electronics, UK) was used. Conductance was recorded by using this apparatus at a frequency of 1 MHz using parallel equivalent circuit at a temperature of 30⁰celcius keeping drive level of 1000 volts.

We have studied variation in elongation, tensile strength vice versa elasticity and electrical conductance with variation of concentration of aniline in composite sample. The results obtained with these studies were correlated with results from XRD studies.

Results and Discussion

Preparation of Glox-X-Gel film

Because of presence of amino groups within the structure, polysaccharides and proteins are usually crosslinked by aldehyde group containing monomer such as glyoxal, formaldehyde, glutaraldehyde etc. The chemical cross linking between gelatin and glyoxal involves reaction between free amino groups of lysine residues of proteins and aldehyde groups of glyoxal. In addition, other functional groups of gelatins such as carboxyl, amide, imidazolyl, or guanidine also occasionally take part in the cross-linking reaction. The overall scheme of formation of hydrogel is shown in **Fig. 1**.

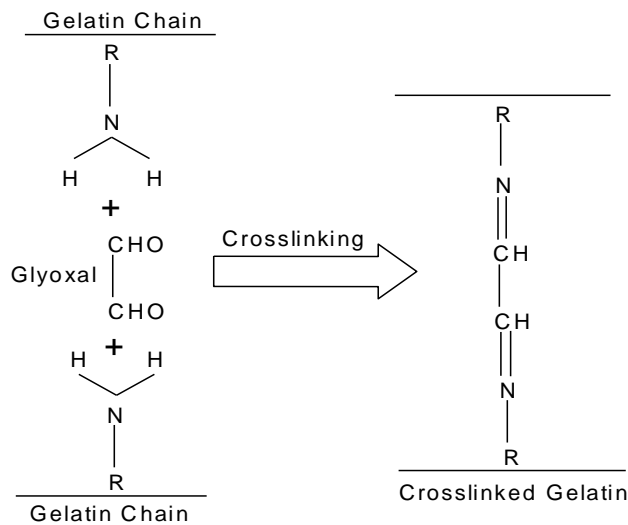


Fig. 1. Scheme showing crosslinking of gelatin chains by glyoxal.

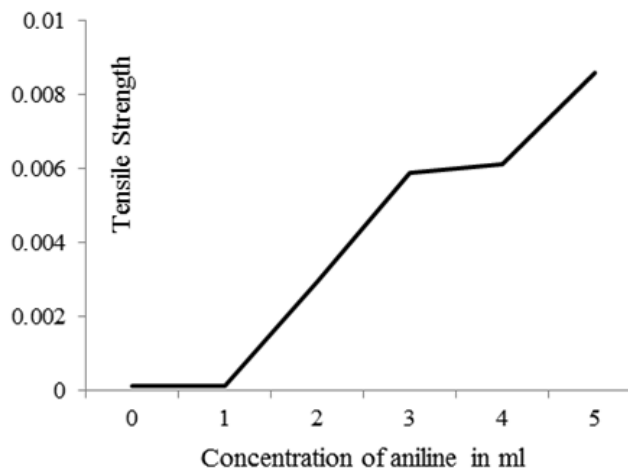


Fig. 2. Plot of tensile strength versus concentration of aniline in composite samples.

Preparation Glox-X-Gel/PANI film

The *in-situ* polymerization of aniline within the gelatin film occurs when gelatin film is placed in the 2M HCl solution containing the dissolved Ani and initiator APS. The Ani molecules, along with persulfate ions, enter into the gelatin film matrix and poly(aniline) formation takes place. The gelatin film turns blackish-brown, which is an indication of the formation of poly (Ani) within the film matrix.

Characterization of films

The X-ray diffraction pattern for pure Gelatin and Glox-X-Gel/PANI, as in Fig. 4(a) and Fig. 4(b) respectively, indicates partially crystalline gelatin with peaks at $2\theta=7.8^\circ$ ($d_{101}=11.08 \text{ \AA}$) and at 22.12° ($d_{101}=4.01 \text{ \AA}$). Indeed, the triple helical crystalline structure in collagen and gelatin is responsible for these peaks. The XRD pattern of Glox-X-Gel/poly(Ani) composite film, as shown in Fig. 4(b) is indicative of purely amorphous

nature of component poly(Ani) with a broad peak at 23° which is a characteristic peak of PANI.

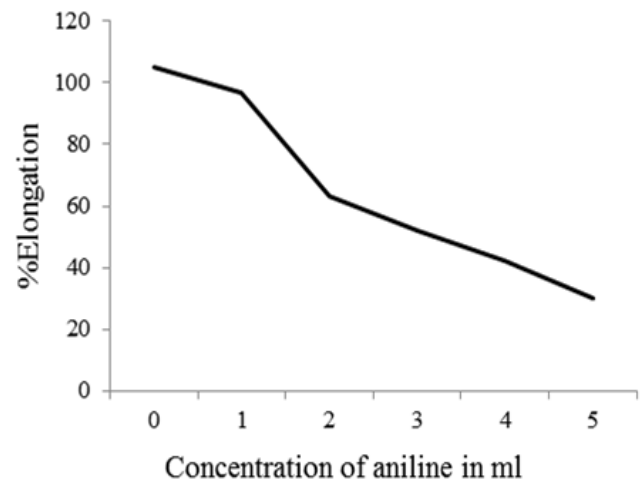


Fig. 3. Plot of elongation versus concentration of aniline in composite samples.

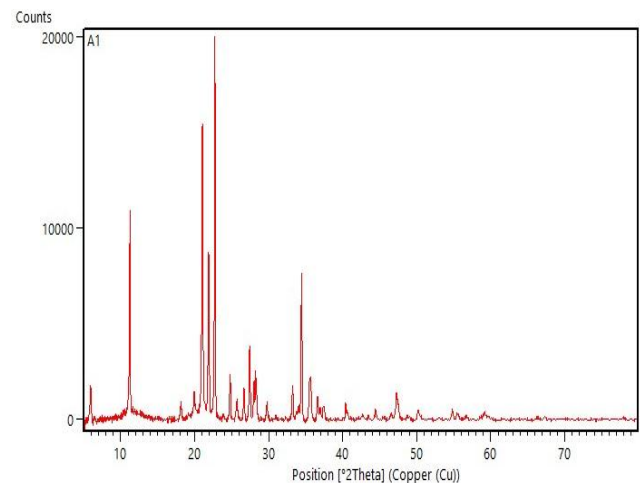


Fig. 4 (a) XRD pattern for Glox-X-Gelatin.

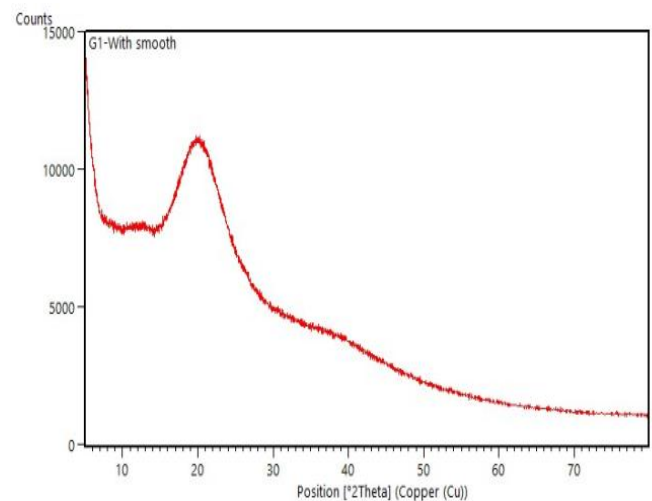


Fig. 4(b) XRD pattern for Glox-X-Gel/PANI composite.

Mechanical properties of film

The plot of tensile strength versus concentration of aniline in composite samples is shown in **Fig. 2**. The plot of elongation versus concentration of aniline in composite samples is shown in **Fig. 3**. Again, the variation in elongation with load for various samples having varying composition of aniline is plotted in **Fig. 4**.

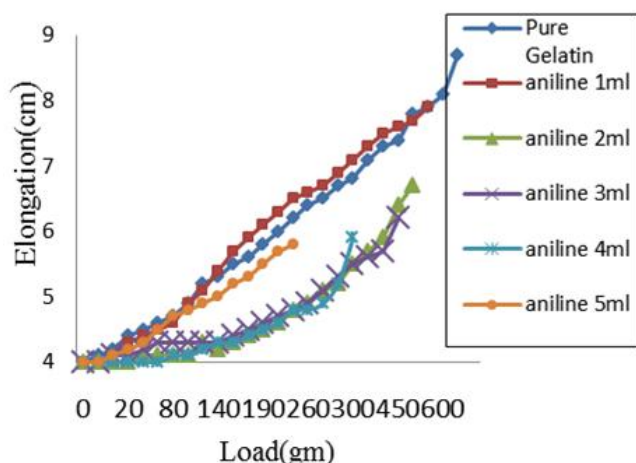


Fig. 4. Variation in elongation with load for various samples having varying composition of aniline.

It is evident from **Fig. 2** that Glox-X-Gel film in absence of aniline has minimum strength. With increase in aniline concentration strength of composite film increases, however for sample having 1 ml of aniline, the strength is almost equal to pure Glox-X-Gel sample. For samples having concentration of aniline more than 1ml, increasing trend continues, however the rate of increase stabilizes for samples having concentration of aniline around 4ml.

The graph of elongation versus load of **Fig. 3** is typical of elastic behavior of solid material, however this graph clearly shows that yield strength increases with concentration of aniline in composite samples.

When gelatin reacts with the crosslinking agent glyoxal, there is Schiff base reaction between amino group of lysine and aldehyde group of glyoxal. It is evident from **Fig. 4(b)** that addition of amorphous aniline, increases crystallinity while crosslinking with Glox as reported elsewhere increases thermal stability [14]. Increase in elastic strength that is yield strength is attributed to increase in crystalline which is due to introduction of PANI in composite material. Insertion of poly(aniline) in Glox-X-Gel film, increases crystallinity and elastic strength which infers that PANI acts as a plasticizer.

Electrical properties of film

The plot of variation in conductance measured at frequency of 1 MHz, plotted against concentration of aniline in composite sample is shown in **Fig. 5**. It is

evident that conductance of the composite samples increases with concentration of aniline. Appreciable conductivity of Glox-X-Gel/PANI composite has been reported which shows that on insertion of conducting poly(aniline) in otherwise non-conducting Glox-X-Gel makes the resulting composite conducting.

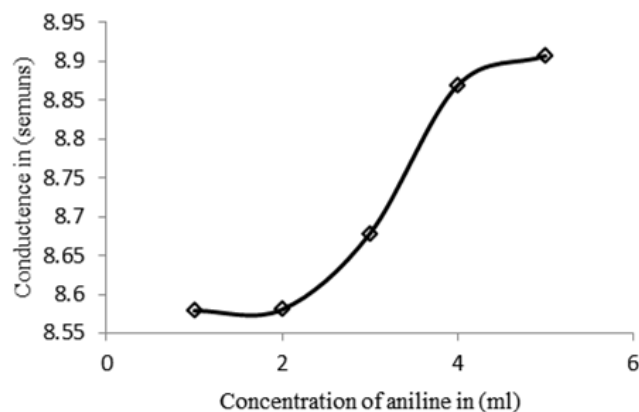


Fig. 5. Variation in conductance of composite sample with concentration of aniline.

Conclusion

Gelatin exhibits high brittleness in solid form, modification in its properties or tailoring it for specific applications was concern of scientists since decades. In this investigation improvement in mechanical properties with enhance in electrical properties have been reported. The crosslinked gelatin/aniline composite shows improved mechanical and electrical properties.

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Author's contributions

Conceived the plan: S. K. Bajpai; Performed the experiments: Ajay S. Utiye; Data analysis: Sanjay Kumar Awasthi, B. Mishra Wrote the paper: Sanjay Kumar Awasthi. Authors have no competing financial interests.

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