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Characterization of Electro Active Polymer Composite Films Based on Gelatin and Poly 2-(3-thienyl)-ethoxy-4-butylsulfonate (PTEBS)

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ABSTRACT

Composites of gelatin and polythiophene sodium poly 2-(3-thienyl)-ethoxy-4-butylsulfonate (PTEBS) were prepared by solution casting. PTEBS content in the composites were in the range of (wt.%) 0.01-0.08%. The surface morphology of the composite films was investigated by means of a scanning electron microscope (SEM). The electrical conductivity of the composites has been found to show Ohmic behavior while the dielectric characteristics show normal characteristics. The light-harvesting ability of the composite films was investigated by UV-Visible spectroscopy. Throughout the investigation it has been observed that the electrical and dielectric properties, and light harvesting efficiency of the composite films improved significantly with the incorporation of PTEBS to the pure gelatin.

Keywords: *Gelatin, PTEBS, surface morphology, electrical conductivity, electrical impedance, dielectric constant, optical properties.*

1. INTRODUCTION

The growing demand for cost-effective approach to develop raw materials for energy storage devices or organic electronics utilizing biopolymers is an important scientific and technological concern. Electro active Polymers based on biopolymers have received much attention from academics and industries because of their potential applications such as sensor, actuators, biosensor, solar materials and components in high-energy batteries [1-3]. For example biopolymers like chitin, cellulose, starch that have a wide range of applications, functioning as energy storage, [4] transport, signalling, and structural components. However, the study on the electrical and optical properties of biopolymers like gelatin has found very scant attention.

Even though all the polymers are not electrically conductive, however most of them shear some intrinsic electrical properties. Their flexibility in design and compatibility with a wide range of substrates and cost-effectiveness make them appealing for use in low-cost, flexible solar cells. One way to make organic material more conductive is to add impurity atoms that donate mobile charges to their molecular host [5]. Another approach is to mix two chosen molecules carefully that exchange charge with each other and together form a crystalline, conducting solid known as charge-transfer salt [5]. This research works gives a new insight in the development of electro active composite films based gelatin and PTEBS.

Gelatin is a biopolymer. It is a well-characterized protein fragment obtained by partial degradation of water insoluble collagen fiber [6] and it is relatively low cost [7]. Gelatin is a denatured collagen, undergoes thermo reversible gelation in hydrogen-bond friendly environment, when the protein concentration is higher than typically 2-3% (w/v). Many efforts have been devoted in the past to study the kinetics of gelation mechanism of this protein [7-13]. Considering the fact that this is one of the most abundantly found proteins in mammals, the importance of such studies can be hardly stressed. Gelatin, as any protein, is an optically active material in both the random coil and helical states. However, due to coherent long-range chiral ordering, helical domains rotate the plane of light polarization much more strongly than the individual chiral amino acids in the coil state. Thus, the coherent optical activity gives a direct indication of the fraction of the monomers in helical states [14].

In the work described in this paper, we have utilized the unique properties of a water-soluble, light-absorbing polythiophene polymer to fabricate electro active composite films. The idea is to take advantage of the properties of conjugated polymers (flexible, tenable, and easy to process) and incorporate the additional benefits of water solubility to have good compatibility with gelatine. In addition, the anionic side chain containing secondary amine in gelatin can promote good compatibility with PTEBS (Figures 1a and 1b). It is important to mention here that the benefits of using water as the solvent are numerous. Solvent evaporation rates have been shown to have a strong influence on film morphology and device performance [15-16] and the evaporation of water can be carefully controlled using heat. Because water is a part of the fabrication process, devices made from this polymer can show improved stability under atmospheric conditions.

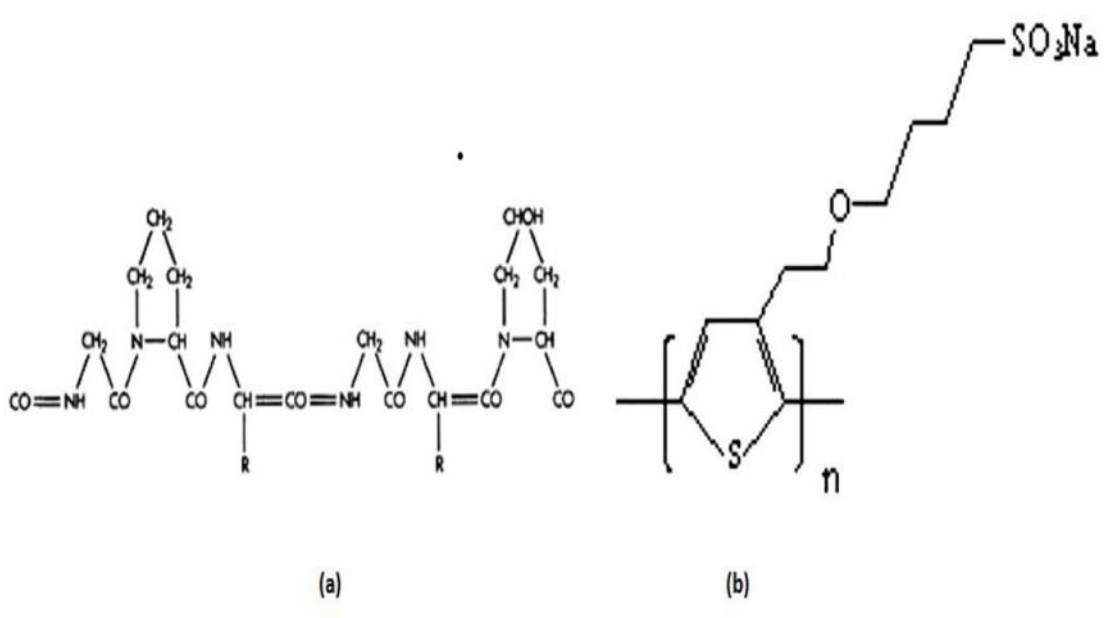

Fig 1: Chemical structure of (a) gelatin and (b) PTEBS.

PTEBS is widely known as a water-soluble thiophene polymer. Water-soluble thiophene polymers have received much attention in the past ten years because of their potential applications in biosensors, chemical sensors, and opto-electronic devices. American Dye Source, Inc. is now offering a new water-soluble thiophene polymer, sodium poly 2-(3-thienyl) ethoxy-4-butylsulfonate (PTEBS, Catalogue No.ADS2000P) for such applications. This polymer exhibits orange color in basic solutions, dark green in acidic solutions and has π electron, which can contribute to electrical conductivity [17-18]. In addition the obvious environmental benefits, using water as the solvent offers other potential advantages. A primary advantage of this water-soluble polymer is its tune ability. Acidic solutions of PTEBS develop a new absorption band in the near-IR and films made from the self-acid form of the polymer show the same optical characteristics [19]. PTEBS has widely been used in organic photovoltaics because of its high absorbance and effective charge transfer rate [17].

This work discusses the preparation and characterization of an electro active composite based on gelatin and PTEBS with an aim to investigate its applicability in organic photovoltaic. The goal of adding PTEBS into gelatin is to enhance the absorbance of UV radiation of gelatin surface. The electrical and optical properties of the composite films have been studied and the influence of PTEBS on overall electrical and optical properties of the films has been discussed. Thermo-mechanical and morphology of the films have also been discussed.

2. EXPERIMENTAL DETAILS

Sodium poly 2-(3-thienyl) ethoxy-4-butylsulfonate (PTEBS) has been used as received from American Dye Source Inc. USA while the gelatin (type-B) was supplied by Global Capsule Ltd. Bangladesh. The composites of gelatin/PTEBS were prepared by solution casting. Gelatin granules and PTEBS powder were blended in different weight ratio (0.0005/5, 0.001/80, 0.002/5 and 0.003/5, 0.004/5 PTEBS/gelatin) in deionized water at room temperature overnight for complete dissolution and mixing of both components. Blended solution was cast on silicon paper and dried under vacuum over P_2O_5 at room temperature for one week. The thicknesses of the films were in the range of500±40 µm. For SEM measurements, samples were mounted with carbon tape on aluminum stubs and then sputter coated with gold to make them conductive prior to SEM observation. The surface morphology of the gelatin/PTEBS composite films was investigated by scanning electron microscope (SEM, model XL 30, Philips, The Netherlands). The electrical properties (conductivity, dielectric constant, dielectric loss, capacitance) of the composites sample were measured by Hewlett Packard impedance analyzer (HP 4291A) in the frequency range of 1 kHz to 13MHz at room temperature. In order to make electrical contact the samples were cut into square shape (area 1 cm^2 and thickness of 0.5 mm) and both sides were coated with silver paste. Two thin copper wires of 100-micron diameter are connected on both side of these samples and another edge of the wires were connected with the impedance analyzer. The dielectric constant of the samples were calculated by capacitance using the relation, $\pounds = C/C_o$, where C is the capacitance of the samples and C_o is the capacitance of vacuum. The current-voltage measurements were performed by Agilent 4263B LCR meter. Glass point and linear coefficient of thermal expansion were measured for all the materials using thermo-mechanical analyzer (TMA) Liensis 200 with a precision of ± 3°C in the

temperature range of 60–220°C.UV-Vis spectra of the composites were recorded using a T-60A spectrophotometer UV-Visible spectrophotometer (PG electronics UK) in the wavelength range of 200 to 700 nm. In order to measure the mechanical properties of the composites, the blend samples were dried at room temperature in a vacuum oven for 24 hours. Mechanical tests were performed by Instron Dynamometer (model 1011, UK) at room temperature at a cross-head rate of 10 mm/min (nominal strain rate of 0.1 min^{-1}) on test pieces of 80 mm length (distance between grips of about 40 mm) and 10 mm width. The thickness of the specimen was 500±40 µm. ASTM D882 was followed for the tensile test and five replicates were tested for each sample to obtain the optimum results.

3. RESULTS AND DISCUSSION

3.1 Surface Morphology of the Gelatin/PTEBS Composites

The morphologies of pure gelatin film and gelatin/PTEBS composite film containing 0.06% PTEBS are shown in Figures 2. From scanning electron

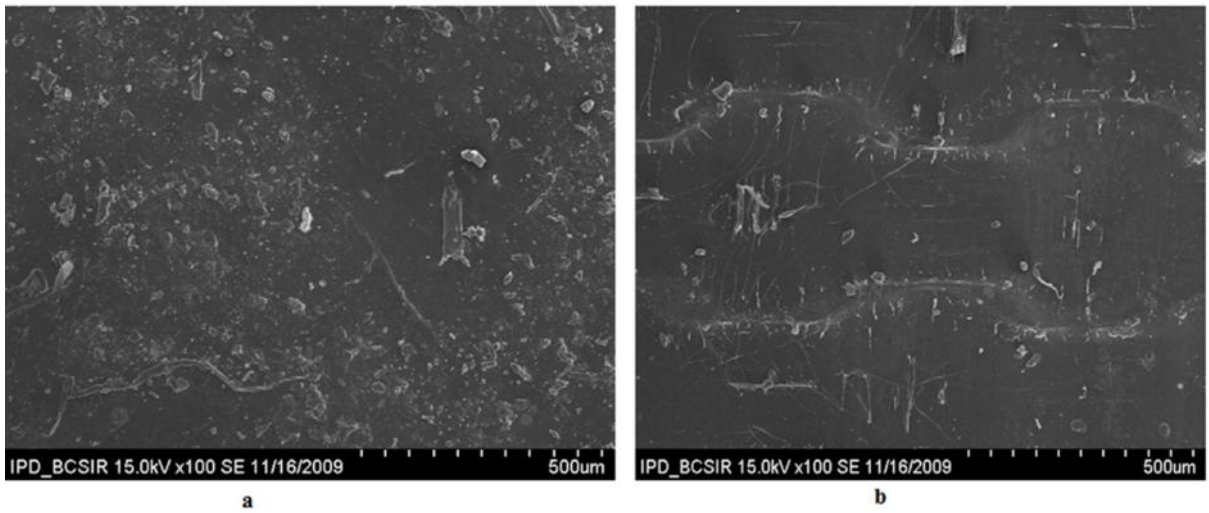

Fig 2: Scanning Electron Micrograph of (a) Pure Gelatin, (b) Gelatin with 0.06% PTEBS.

micrograph of pure gelatin (a), it is obvious that the surface is rough and uneven. However, the surface of pure gelatin membrane is also porous. But after the inclusion of 0.06% PTEBS has made the surface smooth due to better cross linking between pure gelatin and PTEBS.

3.2 Electrical Conductivity of Gelatin/PTEBS Composites

Figure 3 shows the effect of PTEBS content (wt%) on AC electrical conductivity of gelatin/PTEBS composites as a function of frequency. From Figure 3, it is found that the conductivity increases with increase in frequencies up to 10MHz. This behavior is acceptable because the AC field is not sufficient to activate the charge carriers and increases their motilities giving an increasing pattern of conductivity up to 10MHz. The deviation from the linearity in the high frequencies may be due to the dispersion of molecules. Generally, the electrical conductivity of the polymer depends on the presence of free ions connected chemically with macromolecule. The molecular chain does not participate in the transfer of electrical charge [20]. Hydrogen bonded polymer usually have higher conductivity with respect to non-hydrogen bonded polymers. Also, the conductivity increases with increasing frequency [21]. The available experimental results on the frequency dependence of AC conductivity have revealed a considerable similarity of behavior for all samples. However, after incorporation of PTEBS in gelatin based films, the conductivity of the films found to be increased. This increase in conductivity might be associated with the charge injection that occurs through the gelatin/PTEBS composite, because of the polyanionic nature of PTEBS. Throughout the observation, it has been found that at 0.06% PTEBS containing gelatin film showed very good level of conductivity in comparison with the other compositions.

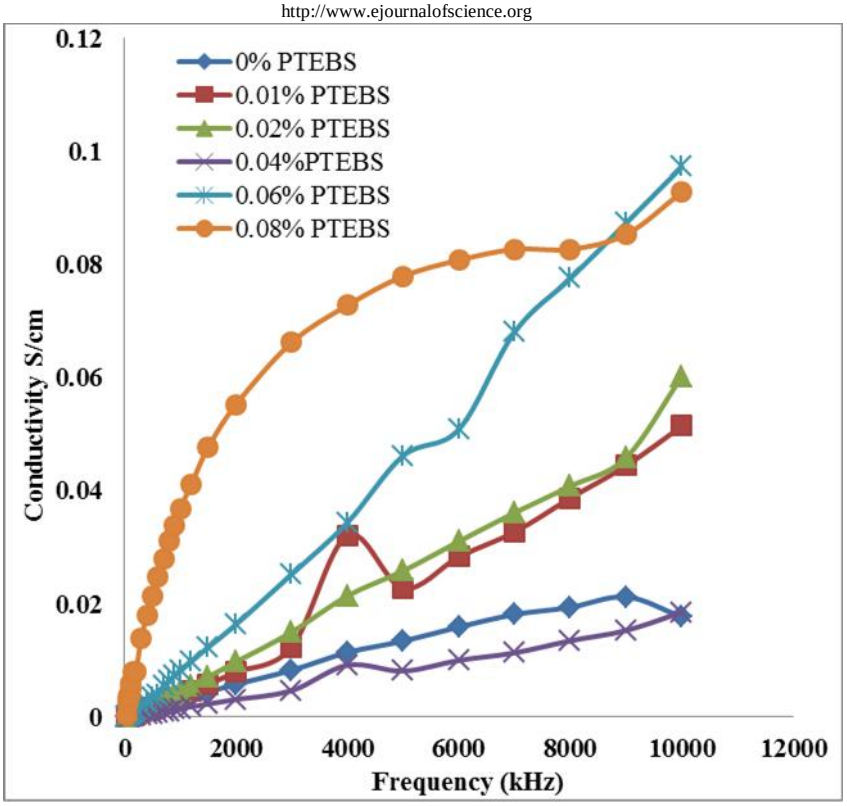

Fig 3: Effect of PTEBS content on conductivity of gelatin/PTEBS composite as a function of frequency.

3.3 Current-Voltage (I-V) Characteristics Gelatin/PTEBS Composites

The I-V characteristics of gelatin / PTEBS composites showed Ohmic behavior, which was observed from the Figure 4. It can be noticed that the current conduction increased rapidly for the sample containing higher percentage of PTEBS (i.e. 0.06% and 0.08% PTEBS). Although the maximum current conduction was observed for the sample containing 0.08% PTEBS, the sample containing 0.06% PTEBS showed a linear trend for the increase in current conduction. Thus, the I-V characteristics of 0.06% PTEBS containing composite film is well fitted to ohms law.

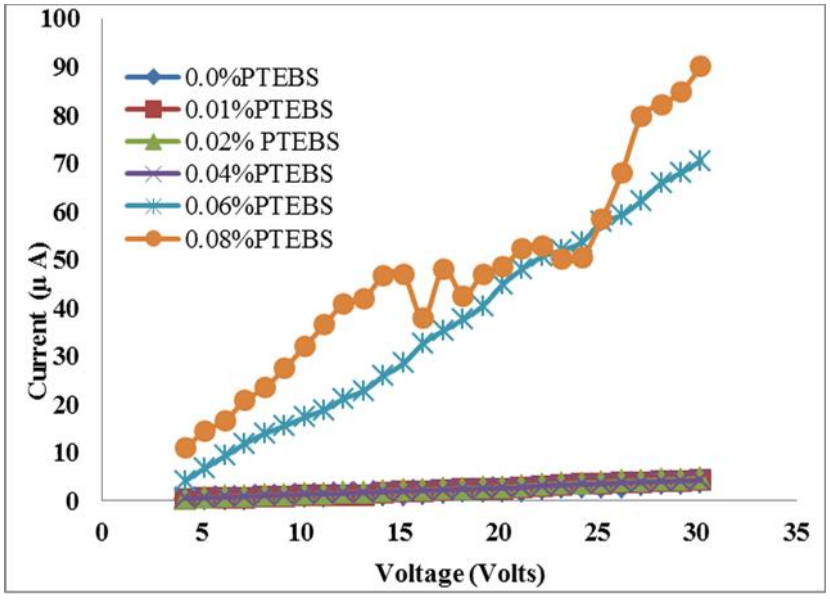

Fig 4: Effect of PTEBS content on current conduction in gelatin/PTEBS composite as a function of voltage.

3.4 Dielectric Properties of gelatin/PTEBS composite

The dielectric constant (έ) showed a decreasing trend with increasing frequency as shown in the Figure 5. This is due to the dielectric dispersion as a result of the lag of the molecules behind the alternation of the electric field which was observed when frequency is less than 10 kHz. Generally, the polarizability (α) increases with the increase of dipolar moment, orientation and reorientation motion which is due to the decrease of έ at higher frequency. The slight decrease of έ after 1000 kHz may be due to the effect of the polymer main chain dynamics, such that molecules bound to the hydrophilic groups of the polypeptide chain (i.e., gelatin) resulting in decrease of the dipolar moment of the side groups [22]. On the other hand, the dependence of dielectric constant (έ) on the frequency was adequately interpreted in terms of an equivalent circuit model [23]. According to this model, the capacitance in series,

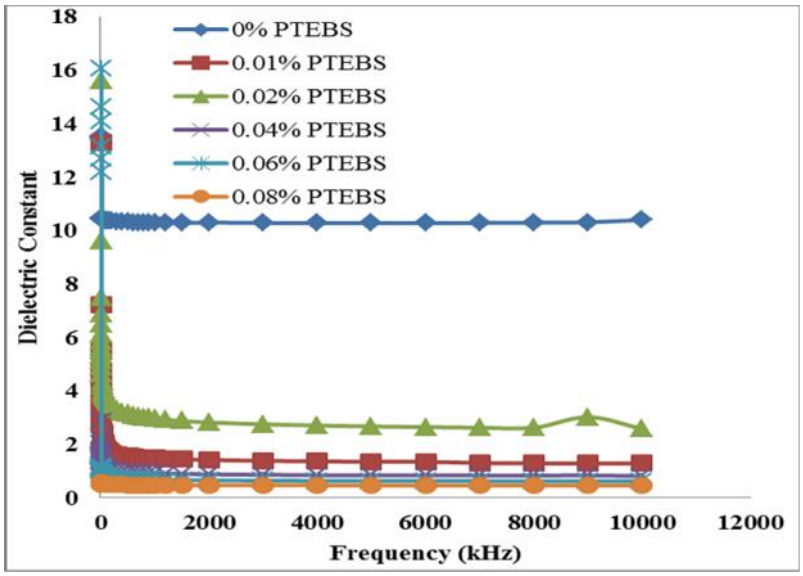

Fig 5: Effect of PTEBS content on the dielectric constant of gelatin/PTEBS composite as a function of frequency (kHz).

Cs depends directly on έ, predicted that Cs should be decreased with the increase in frequency that eventually tends to a constant capacitance at any frequency as is observed in Figure 6. For 0.02% PTEBS containing film the έ is higher than that of the other composition up to 13 kHz. This can be attributed to the strengthening of the intermolecular interaction by hydrogen bonding. The rigidity of the structure formed by intermolecular interaction hydrogen bond will decrease the mobility of molecules and this leading to increase of έ.

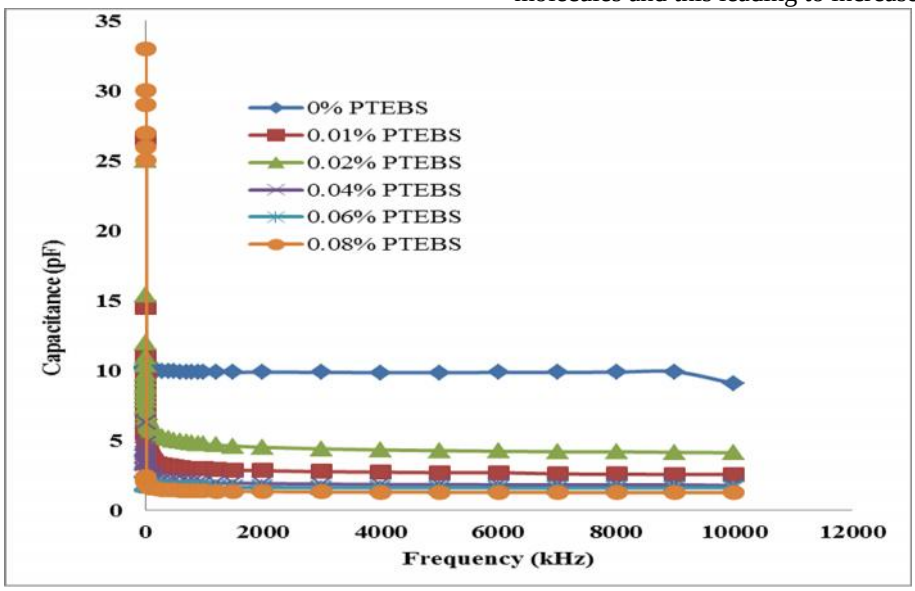

Fig 6: Effect of PTEBS content on the capacitance of gelatin/PTEBS composite as a function of frequency (kHz).

The capacitance started decreasing with the increasing frequency. The increase in capacitance and therefore in the dielectric constant when the frequency was lowered could be attributed to the interfacial polarization caused by space charge and intermediate field distortion. The influence of PTEBS on the capacitance of the dry gelatin film is clear from the Figure 6. It was found that 0.08% PTEBS containing gelatin film has poor level of capacitance and dielectric constant in comparison with the other compositions. This phenomena can be explained as it losses the dielectric behavior and shows semi- conducting property.

3.5 Optical Properties of Gelatin/PTEBS Composites

UV-Visible absorption spectra of gelatin/PTEBS composite films are shown in Figure 7. From this figure it was found that, the absorption spectrum showed a number of absorption bands corresponding to structural groups within the molecule. For pure gelatin, the absorption remained high till 235 nm wavelength but with inclusion of PTEBS, the absorption has shifted to the greater wavelength. The peak and line shape of absorption in the composite

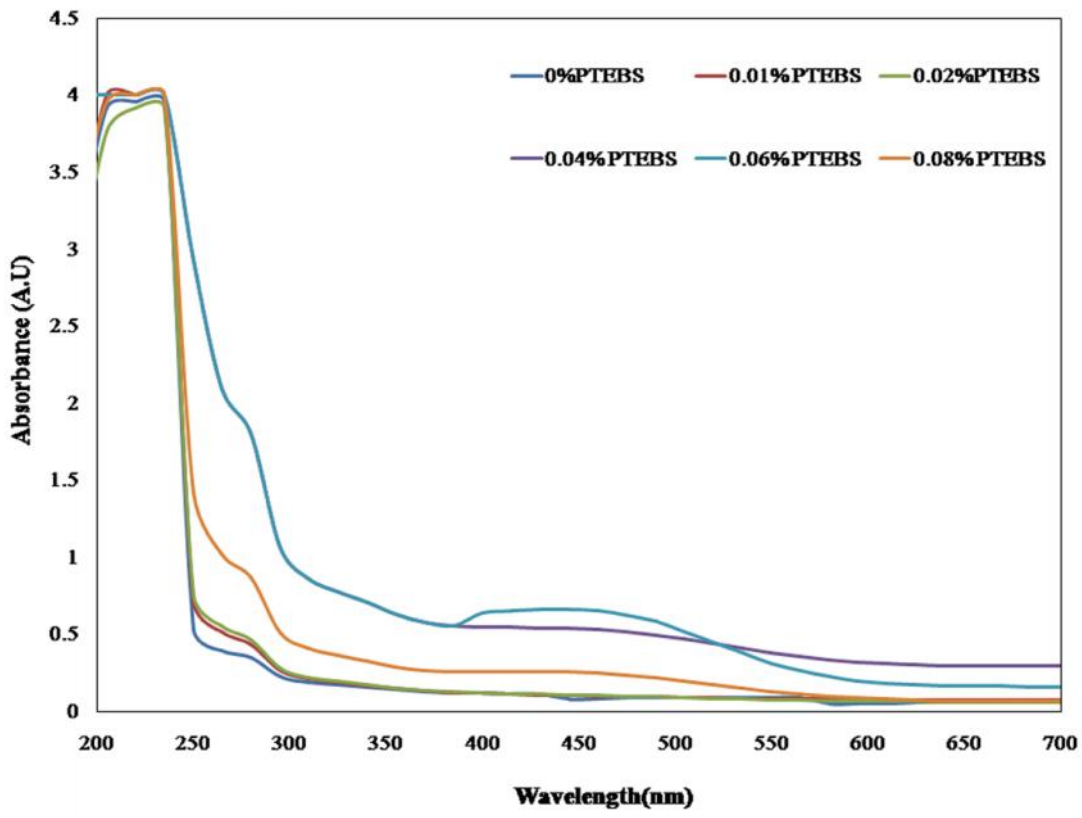

Fig 7: Variation of absorbance with wavelength for pure gelatin and different gelatin/PTEBS composites.

films indicates that it is the superposition of the absorption of gelatin and PTEBS. The red shift in gelatin/PTEBS composite films represents an increase degree of conjugation present in the composite. It is well known that increasing conjugation generally moves the absorption to longer wavelength [24]. The 0.06% PTEBS containing gelatin films showed a wide band of absorption spectra. For pure gelatin the absorption peak appeared at 235 nm. The increasing absorption of the composite films around wavelengths 400 nm implied that absorption is mainly due to the π-π^* absorption of polymer [25].

3.6 Mechanical Properties Gelatin/PTEBS Composites

Figure 8 shows the change in tensile strength with increasing PTEBS content in gelatin/PTEBS composites. From this figure it was found that, any significant change in TS has not been occurred for the blend films containing lower percentage of PTEBS (33-30 MPa). The initial slight drop in tensile strength of the 0.01% to 0.04% PTEBS containing films may be due to the insufficient intermolecular interaction through hydrogen bonding. After that, a sudden increase in tensile strength (50.7 MPa) occurred at 0.06% PTEBS containing films, then the tensile strength of the blend films began decreasing steadily with the increasing percentage of PTEBS in the blend films. This must be due to repulsion between the free electron of the donor PTEBS and the bonding may become weak. Figure 9 represents the effect of PTEBS content on the elongation at break (Eb) of gelatin/PTEBS composites. From this diagram, it was found that the Eb has been decreased continuously with

the addition of PTEBS in the pure gelatin. The Eb value for pure gelatin was 14.76%. After adding PTEBS at different concentrations (0.01-0.06) the Eb value has been found to be decreased from 13.8% to 10.9%. The composites containing 0.06% PTEBS shows an acceptable value of elongation at break (10.9%). However, the 0.08% PTEBS containing gelatin composites became brittle with the lowest elongation at break.

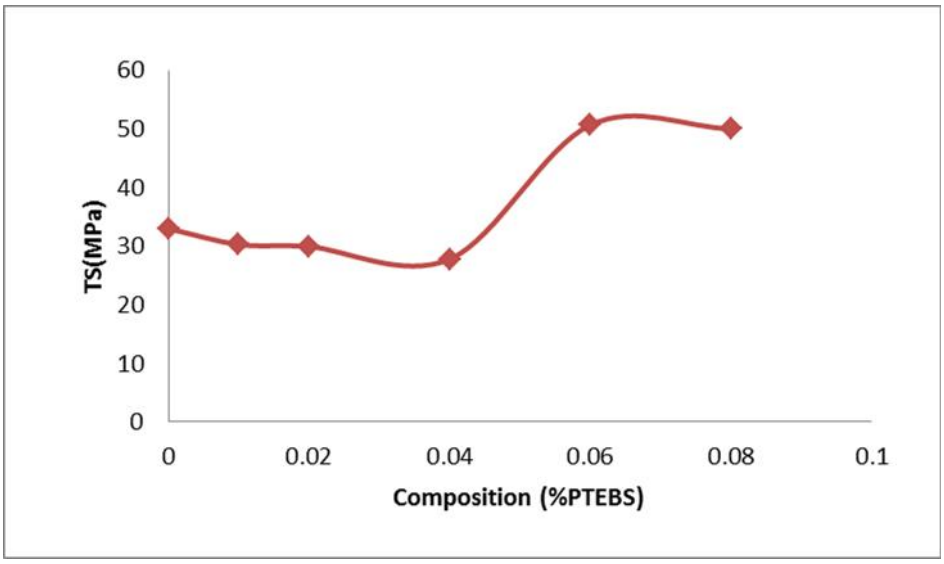

Fig 8: Effect of PTEBS content on the tensile strength of the gelatin/PTEBS blends.

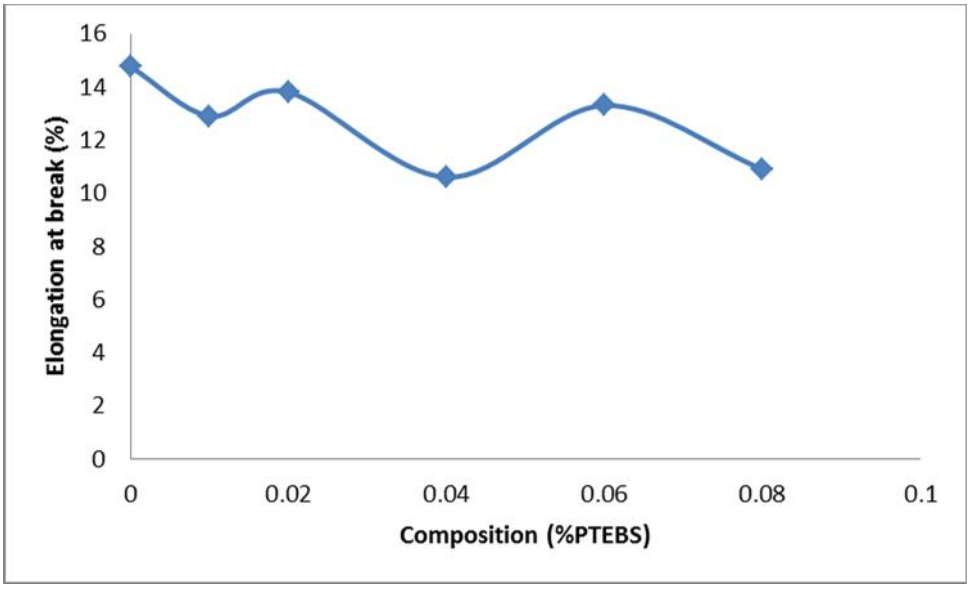

Fig 9: Effect of PTEBS content on the Elongation at break of the gelatin/PTEBS blends.

4. CONCLUSIONS

The gelatin/PTEBS composite films were prepared by solution casting. The electrical, optical thermo-mechanical and morphological properties of the films were characterized. Since the protein and water is poor conductor of electricity, the incorporation of PTEBS has enhanced the conductivity of the composites. From the I-V characteristics it is clearly evident that the contact behavior is ohmic. Electrical properties of the composites were found to be improved due to better conjugation between gelatin and PTEBS. The thermal stability of the films has been improved due to PTEBS content in films. It has been observed that with addition of 0.06% PTEBS to the pure gelatin the tensile strength of gelatin increases by 53.6%. The change in mechanical properties in every blend ratio indicates the intermolecular interaction of PTEBS side chains to gelatin polypeptide side-chains. The SEM study showed the change in the morphological characteristics of composite. Throughout the SEM study, it has been noticed that composite containing 0.06% PTEBS has improved smooth surface structure than other blend ratios. This work has some outstanding results

which are very important in the field of electro active natural polymer; it might have great potential in the field of organic photovoltaics.

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