INTRODUCTION

Conductive polymers have attracted attention during the last decades because of their versatile promising applications in different fields such as mechanical and optical sensors, actuators, light-emitting diodes, transistors, energy storage, supercapacitors and so on [1, 2]. The polymers are converted to the electrically conductive or doped forms via oxidation or reduction reactions which form delocalized charge carriers. Study on Raman spectroscopy of polypyrrole and its 2,5-\(^{13}\)C-substituted and C-deuterated derivatives by Furukawa [3] showed that the most rings of pyrrole in neutral polypyrrole are in benzoic form while the oxidized polypyrroles (exhibiting high conductivity) are in quinoid form. Polypyrrole has been one of the most studied polymers in the area of conductive polymers because of its environmental stability, biocompatibility, physical and electrical properties [4]. Its properties such as redox activity, ion-exchange and ion discrimination capacities, corrosion protection etc. depended on the synthesis procedure as well as on the nature of dopant, monomer and solvent [5]. Hence, the study of the new approaches to the synthesis and characterization of conductive polymers is still continuing in order to improve their electrical and mechanical properties. Polypyrrole is readily synthesised from a range of aqueous and non-aqueous solvents and it is one of the few electronically conductive polymers that can be prepared in aqueous solutions. It has potential advantages of low cost and low potential oxidation but it suffers from poor processibility and mechanical properties.

In recent years, many efforts have been done to obtain the composite containing polypyrrole and conventional polymers with the aim of increasing their mechanical properties. Till now, some conductive polymer composites with a wide range of interesting mechanical and electrical properties have been reported [6], among them composites comprising rubber or biopolymer as matrix [7, 8].

Although application of biopolymers such as chitosan, as an electrical or optical material has rarely been reported, using of these materials in electrical devices may be promising [9]. Chitosan is a biodegradable, biocompatible, non-toxic and low-cost polymer, which has been used in bio- or medical materials. In this study, we have used chitosan to enhance the mechanical properties of polypyrrole with the aim of producing a new conductive composite. There are a few reports on the preparation of the polypyrrole in the presence of chitosan. Yang et al. [10] used chitosan as stabilizer to prepare hollow nanometer-sized polypyrrole capsules. They observed that in the absence of chitosan the core/shell structure could not form, to their opinion, the chitosan could induce growth of polycationic polypyrrole chains on the AgCl core. In another work [11], it was shown that acetylamino groups of chitosan provided the formation of active sites for grafting of the polypyrrole chains on silica particles and act as a stabilizer of the silica–polypyrrole particles.

They showed that the conductivity of this hybrid varied in the range of 0.28–2.45 S cm\(^{-1}\), while they reported the conductivity of 37.53 S cm\(^{-1}\) for polypyrrole without chitosan in 2% acetic acid.

Since there is no information about the electrochemical preparation of such composite films in the literature, the aim of the present research was the synthesis of chitosan–polypyrrole composite films by potentiostatic method and their characterization.

**EXPERIMENTAL**

**Materials.** Pyrrole monomer provided by Acros Organic. Chitosan was obtained from a local company with 88% degree of deacetylation, and, p-toluene sulfonate (p-TS) was supplied by Fluka. A typical three-electrode electrochemical cell arrangement was used with a saturated calomel electrode (SCE), a carbon rod and an indium-tin oxide (ITO) glass as the reference, counter and working electrode, respectively. The composite films were produced from an aqueous solution containing pyrrole, p-toluene sulfonate dopant and chitosan.

**Methods.** Various amounts of chitosan powder were dissolved in 1% acetic acid solution and various concentrations of chitosan acetate were formed. The prepared chitosan acetate was mixed with polypyrrole and p-TS in 1% acetic acid solution. Electrochemical deposition of polypyrrole and chitosan was performed using a potentiostat (Model: PS 605, USA). All polymers were electrochemically prepared in a solution containing 0.3 M pyrrole (predistilled) and 0.1 M p-TS dopant and various concentrations of chitosan at room temperature for 2 h. For the comparison purpose, the film of chitosan in acetic acid by casting method [13] and polypyrrole film without chitosan were prepared. The anodic potential of the working electrode was measured as +1.2 volt against a saturated calomel electrode (SCE). Usually pyrrole is oxidize at potential range between 0.6 to 1 volt versus SCE [14] but in the presence of chitosan the solution becomes more viscous and at a lower potential, the rate of oxidation and, therefore, polymerization is too slow. Hence a higher potential is needed to overcome the resistance offered by chitosan.

**Polymer characterization.** The samples peeled up from the ITO glass easily and their thicknesses were measured by micrometer at room temperature. The thicknesses of the films were in the range from 0.03 to 0.137 mm. The conducting polymer composite films were characterized by conductivity measurement, Fourier Transform Infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), Atomic force microscopy (AFM), X-ray diffraction (XRD) and dynamic mechanical analysis (DMA). The electrical conductivity was measured at room temperature by the standard four probe technique using a JANDEL Resistivity Test Unit. The FT-IR spectra of the samples were recorded by Perkin Elmer Fourier Transform Infrared spectrophotometer (model 1725X) using KBr disc. SEM studies of the films were performed using a Jeol scanning electron microscope (Model 1455 LEO). Samples for SEM observation were mounted on aluminum stubs using double sided tape and vacuum coated with polaron SC500 sputter coater. Topography was measured by using an atomic force microscopy (Quesant Instrument Corporation, Q-Scope 250) operating in contact mode, with a commercial Si3N4 cantilever. X-ray diffraction scans were taken on a Philip PanAnalytical PW-3040 MPD wide-angle diffractometer and the dynamic mechanical analysis was done by using Perkin Elmer (Pyris Diamond) DMA. The storage modulus of the composite films were measured in the temperature range from 25 to 250°C with a heating rate of 2°C per minute and at a frequency of 1 Hz.

**RESULTS AND DISCUSSION**

**Electrical conductivity of the composite films.** Standard four-point probe technique was used for measuring the electrical d.c. conductivity of the prepared composite films at room temperature. Composite films were prepared in 40 × 20 mm in dimension with a thickness ranging from 0.033 to 0.068 mm. The electrical conductivity, \(\sigma\), (S cm\(^{-1}\)) was calculated by Ohm’s law, Eq. (1):

\[
\sigma = \frac{\ln 2 I}{\pi V t},
\]

where \(V\) is voltage (volt), \(I\) the current (ampere), \(t\) the thickness (centimeter) of the sample, respectively.

Each composition of polypyrrole–chitosan composite film was prepared five times (five films) and for each film, the electrical conductivity was measured by taking the average value of several reading at various points of the film. Subsequently, average value of the conductivity was taken from the five films. The standard deviation data were in the region of 1.7 to 8.2 and it is shown as error bar on the diagram of conductivity. The conductivity of all the composite films was measured at the both electrode and solution side. Its value obtained from both sides of the films was almost the same confirming the homogeneous film formation. The electrical conductivity of the composite films as a function of chitosan concentration is shown in Fig. 1.

The electrical conductivity increased from 33.5 to 69.1 S cm\(^{-1}\) with an increase in chitosan concentration from 0.1 to 0.7% (w/v). This can be due to the formation of more polarons, which are responsible for electrical conduction in polypyrrole composite. It has been already proved by means of electron spin resonance that the electronic conductivity in conductive polymer is due to the presence of polaron as species with spin and bipolarons as spinless species at different oxidation level [15]. Since the electrical conductivity increases as the conjugation length of the polymer enhances [16], it may be supposed that the addition of
chitosan can increase the conjugation length. This has been confirmed by the results obtained from FT-IR.

In addition, according to the literatures [17, 18], conductivity increases with the increase in chain length of dopant. It has been shown that bulky doping counterions cannot move easily out of/into the film and the conductivity of these films are larger than those doped with small counterions. Below it will be discussed that there is some interaction between p-TS and chitosan providing the higher conductivity for composite film.

At chitosan concentrations higher than 0.7% (w/v) the rate of oxidation and polymerization is very low and the amount of deposited polymer decreases which leads to low conductivity and thickness (table). These results have also been confirmed by conjugation chain length measurements, which were based on the work of Tian and Zerbi [19]. They demonstrated by theoretical calculations that the intensity of the antisymmetric ring stretching mode at 1535 cm−1 (C=C stretching) decreases and the intensity of the symmetric mode at 1450 cm−1 (C–N stretching) increases with the increase in conjugation chain length. In other words, the ratio of integrated absorption band intensity of C=C stretching (benzoic form) to the integrated absorption band intensity of the C–N stretching is inversely proportional to the extent of derelocalization. In our study, benzoic form of C=C stretching and C–N stretching appeared at 1552 and 1450 cm−1, respectively. The band ratio ($I_{C=C}/I_{C–N}$) of composite films with different concentration of chitosan is shown in table. It can be seen that with the increase of chitosan amount and the conductivity of the composite the value of $I_{C=C}/I_{C–N}$ decreased indicating the increase in conjugation length. Further increase of chitosan content results in the rise of the value of $I_{C=C}/I_{C–N}$, probably due to decrease of the conjugation length.

**IR SPECTROSCOPY**

The IR spectrum of chitosan showed a strong –OH stretching absorption band around 3436 cm−1 and the aliphatic C–H stretching at 2920 cm−1. The peak at 1654 cm−1 represents acetylated amino group of chitin, which indicates that the sample is not fully deacetylated. The peak at 1382 cm−1 shows the C–O stretching of primary alcoholic group (–CH2–OH). The absorption band around 1030 cm−1 represents the primary amino group (–NH2) at C2 position of glucosamine [20]. The absorption band at 1560 cm−1 showed bending vibrations of NH3+ [9]. When chitosan is dissolved in acetic acid a salt or chitosan acetate is formed, which causes the shift of the bands [21].

The infrared absorption spectra of the composite film, polypyrrole, p-TS and chitosan acetate are shown in Fig. 3. The composite film prepared from

![Fig. 1. Electrical conductivity of conductive polymer composite films versus chitosan concentration.](image1)

![Fig. 2. The FT-IR spectrum of chitosan and chitosan acetate.](image2)

<table>
<thead>
<tr>
<th>Chitosan, % w/v</th>
<th>Thickness, mm</th>
<th>Intensity ratio $I_{C=C}/I_{C–N}$</th>
<th>Conductivity, S cm−1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (PPy)</td>
<td>0.068</td>
<td>0.67</td>
<td>35.2</td>
</tr>
<tr>
<td>0.3</td>
<td>0.062</td>
<td>0.53</td>
<td>39.3</td>
</tr>
<tr>
<td>0.5</td>
<td>0.055</td>
<td>0.49</td>
<td>49.4</td>
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<tr>
<td>0.7</td>
<td>0.050</td>
<td>0.46</td>
<td>69.1</td>
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<tr>
<td>0.9</td>
<td>0.040</td>
<td>0.62</td>
<td>42.1</td>
</tr>
<tr>
<td>1.1</td>
<td>0.033</td>
<td>0.70</td>
<td>33.2</td>
</tr>
</tbody>
</table>

0% of chitosan represents the PPy film without CHI.
solution contains 0.3 M pyrrole, 0.1 M $p$-TS and 0.7% chitosan at 1.2 volt (vs. SCE). The characteristic peaks of polypyrrole at 3443 cm$^{-1}$ (N–H), 1634 cm$^{-1}$ (C=C quinoid form), 1546 cm$^{-1}$ (C=C benzoic form), 1452 cm$^{-1}$ (C–N stretching), 1168 cm$^{-1}$ (S=O) and 1034 cm$^{-1}$ (S–C), confirm the formation of polypyrrole doped with $p$-TS. All of characteristics peaks for chitosan (1654, 1382, 1030 cm$^{-1}$) have overlapped with the characteristic peaks of polypyrrole. These overlapping caused band broadening in this area.

In the spectrum of the composite film (Fig. 3) the broad band at 3448 cm$^{-1}$ shows N–H stretching of pyrrole and O–H stretching of chitosan. The shift of the band at 1168 cm$^{-1}$ corresponding to S–O stretching in polypyrrole to the 1174 cm$^{-1}$ in the polymer composite as well as the shift of the peak at 1654 cm$^{-1}$ which is due to acetylated amino group (C=O) in chitosan to 1733 cm$^{-1}$ in polymer composite confirms interaction between polypyrrole and chitosan in the composite formed.

The region of C–H out-of-plane deformation vibrations of the ring at 908, 762, 670 cm$^{-1}$ are slightly influenced by the presence of chitosan in the samples. The band of C–H and N–H in-plane deformation vibration located at 1034 cm$^{-1}$ and the band of the C–C out-of-plane ring deformation vibration at 966 cm$^{-1}$ are observed at the same position in the spectra of polymer composite.

The coexistence of vibrational bands attributable to both benzoic (1552 cm$^{-1}$) and quinoid forms (1636 cm$^{-1}$) confirms the presence of two different structures in the composite films. It is observed that the intensity of C=C bond at 1552 cm$^{-1}$ (benzoic form) and 1636 cm$^{-1}$ (quinoid form) in composite film are lower and higher than those in polypyrrole film, respectively. This is evidence toward the formation of polaron and bipolaron, which are responsible for conductivity in the composite structure. These results are in a good agreement with reported previously [3, 22].

Based on the results obtained we propose the structure of polypyrrole–chitosan composite film presented on Fig. 4. As was mentioned above, the conductivity of the composite film increased in the presence of a certain amount of chitosan which could be due to the possible interaction of $p$-TS with chitosan. This interaction may cause a prolongation of the chain for $p$-TS and hence an increase of the conductivity for composite film.

**DYNAMIC MECHANICAL ANALYSIS**

The elastic modulus for chitosan film is more than 1 GPa over the temperature range from 25 to 250°C, more than all of polypyrrole and polymer composite films [13, 23]. Due to high mechanical properties of chitosan, it was expected that this biopolymer can improve mechanical properties of polypyrrole film. Figure 5 shows the changes in the storage modulus ($E'$) of the composite films with the increase in chitosan content over the study temperature range. The polypyrrole film without chitosan had a very low $E'$ value in the measured temperature range; however the storage modulus ($E'$) of the polypyrrole–chitosan composite film rises with increase of chitosan content.

In addition, no changes in storage modulus was found in the range of the glass transition temperature of chitosan ($T_g = 203°C$, [23]) confirming the incorporating chitosan in the polypyrrole structure and formation of the homogeneous composite.
The storage modulus increased with the increase in temperature over the investigated temperature range (25–250°C) for all of the composite films. As reported by Mecerreyesa [24], this could be possibly due to the cross-linked nature of the polypyrrole segments. The damping characteristic (tanδ) of the composite films synthesized from different concentration of chitosan is shown on Fig. 6.

An increase in storage modulus of polypyrrole is associated with a maximum of tan δ at 220°C. This result is consistent with that obtained by Lesueur [25]; this transition could be related to cross-linking effects and dependent on the nature or on the steric hindrance of dopant and is not frequency dependent.

MOLECULAR ORDER
OF THE COMPOSITE FILMS

X-ray diffraction patterns of polypyrrole, chitosan and the polymer composite are presented on Fig. 7.
In the solid state, chitosan is a semicrystalline polymer [27], according to literary data natural chitosan usually presents signals at $2\theta = 10.4$, 19.6 and 21.4°, which correspond to the reflections of the (200), (020) and (220 and 202) planes [28]. The X-ray diffractogram of chitosan used in the present research showed the high degree of the order at $2\theta$ of 10.1°, 19.9° and 26.6°, which disappeared in the diffractogram of the composite. Diffractograms of polypyrrole and polymer composite showed broad scattering peaks at approximately 9°–10° and 26°–27°, which indicates a highly amorphous structure that is similar to those reported in [26]. This confirms the homogeneous composite film formation of polypyrrole in the presence of chitosan.

**MORPHOLOGICAL STUDY OF THE COMPOSITE FILM**

The surface morphology of the composite films was investigated by SEM and AFM. It was found that the electrode side of all of the composite films prepared during 2 h was smoother than that of the solution side. This is possibly due to the fact that polymerization was started on the electrode side and proceeds towards the solution. First, a very thin layer of the composite film is formed on the ITO glass; when the thickness of the film increases the surface becomes more rough and irregular. Finally the polymer can be stripped off the electrode, presenting rough surface in contact with the electrolyte and smooth (brilliant) for that in contact with the electrode. The same observation has been reported by others [29].

In order to investigate the film formation in details, we prepared thin films during 1, 2 and 3 min and studied the surface morphology of these thin films on the ITO glass by means of AFM. As is shown on Fig. 8a, the composite film prepared in 1 min displayed a very uniform and smooth surface. The root mean square value (RMS) of the roughness was measured to be 3.011 nm, average height 35.89 nm indicating deposition of the film in a regular fashion on the substrate. The film prepared in the same conditions during 2 and 3 min, presented a rougher morphology with globules having a higher diameter, producing an increase in roughness (Figs. 8b and 8c). The RMS of the roughness was equal to 6.56 nm and 8.06 nm for the films prepared in 2 and 3 min, respectively.

Figure 9 shows the SEM images of the polypyrrole and composite films prepared from different concentration of chitosan during 2 h. The surface morphology of polypyrrole shows almost all globular morphology with the diameter ranging from 200 to 400 nm (Fig. 9a). The addition of chitosan leads to agglomeration of the resulting polymer (Fig. 9b). The agglomeration becomes more evident with increase of the chitosan concentration from 0.5 to 0.9% (Figs. 9c–9e). The same results have been reported by Zhao [30].

It can be seen that the chitosan concentration strongly affects the morphology of the composite films, which may influence the composite conductivity. No phase separation can be seen on the micrographs of the films.
confirming the homogeneous film formation of polypyrrole with chitosan.

**CONCLUSIONS**

In the present research we reported about the synthesis of conductive polymer composite based on polypyrrole and chitosan by electrochemical method. The FT-IR and the electrical conductivity measurements showed that in the presence of chitosan, the formation of quinoid, polarons and bipolarons increases causing higher electrical conduction of the composite films.

The DMA analysis revealed the enhanced mechanical properties of the composite films. The morphology study revealed the globular morphology for the composite films, and the chitosan may affect the agglomeration of the composite films.

**REFERENCES**

SYNTHESIS AND CHARACTERIZATION OF A NEW CONDUCTING POLYMER