This article reports synthesis of polypyrrole (PPy) and its composites having various amounts of selenium (Se) in the presence of nitric acid in aqueous medium via chemical oxidative polymerization. Samples were spectroscopically characterized using Fourier transform infrared spectroscopy, ultraviolet-visible spectroscopy, and atomic absorption spectroscopy. Although morphology of the samples was examined by using scanning electron microscopy (SEM), their thermal properties were studied via differential scanning calorimetry (DSC). The alternating current (ac) conductivity and dielectric properties were investigated as a function of temperature. Variation of adsorption free energy obtained from Langmuir adsorption isotherm showed that metal cations were physically adsorbed onto the polymer surface. SEM images showed that filling process significantly changes the morphology of PPy. DSC results indicated that cold crystallization temperature ($T_{cc}$) of unfilled PPy decreases with increasing filling level. Dielectric measurements showed that relaxation times for PPy and its composites have decreased linearly with increasing temperature. The conductivity of the PPy, when filled with 1 g of Se, increased ~ four times at room temperature for 1 kHz.

**INTRODUCTION**

Conducting polymers have widely been studied in the last two decades due to their potential applications as chemical sensors, electrochemical super capacitors, electrochromic devices, photovoltaics, light-emitting diodes, optical computers, and batteries [1–12]. In recent years, extensive research has been performed on creating conducting polymer matrix composites with the aim of improving physical and structural properties of conducting polymers [2, 3, 7, 9, 12, 13]. One such class of these, attracting a special attention is to create composites which contain inorganic materials which are usually metals or metal salts filled into the conducting polymers via various methods [7, 12–18]. Experimental parameters such as polymerization method, type of the oxidant, and temperature used during preparation of polymeric composites seemed to be of crucial importance in terms of their physical and structural properties. Physical and chemical properties of these inorganic materials should also be well known as these would also play an important role in choosing the most appropriate preparation method for composites.

In this study, polypyrrole/selenium (PPy/Se) composites with various amounts of Se; PPy being a polymeric matrix and Se metal as an inorganic material were prepared. PPy is one of the most extensively studied conducting polymers due to its high electrical conductivity and chemical stability and as well as its easy preparation through chemical and electrochemical oxidation of pyrrole in the organic solvents and in aqueous medium [4, 8, 11, 19–25]. Chemical polymerization is the preferred method in this study as it gives us a much better control over the mass content when compared to the electrochemical method. Se, which was used as a filler, does also have important applications in areas such as photocells, current convertors, diodes, production cameras, and glass industry as reported in [26–28]. Shumaila et al. [27] and Bormashenko et al. [28] studied Se filled polyaniline, where they showed that polymer containing Se can have superconductive features.

The main reason for choosing this type of composite stemmed from not only the fact that electrical and structural properties of PPy/Se composites have not previously been reported in the literature but also whether it would be possible to use better electrical properties exhibited by...
Se through a composite created with a highly conducting polymer.

Samples were characterized by using Fourier transform infrared spectroscopy (FTIR) and ultraviolet-visible spectroscopy (UV-vis). Atomic absorption spectroscopy (AAS) was used to determine the interaction mechanisms between the polymer and metal cations by measuring the quantity of Se remained in the filtrate after polymerization. Surface morphologies were investigated with the help of scanning electron microscopy (SEM) and thermal properties were studied with differential scanning calorimetry (DSC). Finally, temperature and frequency-dependent dielectric measurements are reported.

EXPERIMENTAL

Materials

Pyrrole, ammonium peroxydisulphate ((NH₄)₂S₂O₈), nitric acid (HNO₃) (65 wt%) were supplied by Merck (Germany). Metallic Se powder was supplied by BDH Chemicals (England). These materials were used without any preprocessing.

Synthesis of PPy

A total of 5 mL (72 mmol) pyrrole was added into 0.7 M 100 mL HNO₃ and stirred. Then, 2.5 M 20 mL (NH₄)₂S₂O₈ was added into the above solution as an oxidant and stirred at 5°C for 5 h. The precipitate obtained after polymerization was filtered by using a coarse filter paper and washed with deionized water (3 × 100 mL). The black colored PPy powder was obtained after vacuum drying at 60°C for 24 h.

Filling Process

A total of 0.2 g metallic Se powder was dissolved in 5 mL concentrated HNO₃ resulting in an orangey/yellowish colored solution. This mixture was added into 95 mL distilled water and stirred thoroughly. A total of 5 mL (72 mmol) pyrrole was added into the final solution and stirred again. A total of 2.5 M 20 mL (NH₄)₂S₂O₈ was then added into the above solution as an oxidant and stirred at 5°C for 5 h. After filtration, washing and drying processes as mentioned above, 0.2 g (4.13 wt%) Se filled PPy samples were obtained. The same procedure was repeated for 0.4, 0.6, 0.8, and 1 g Se filling levels corresponding to Se weight percentages of 8.27, 12.41, 16.55, and 20.68, respectively.

Measurements

Samples were characterized by FTIR (Shimadzu FTIR 8201 spectrophotometer) between 4000–400 cm⁻¹ and UV-vis (Agilent UV-vis spectrometer) between 200–1000 nm. Thermal properties were determined by DSC (Perkin Elmer DSC 4000) at 10°C min⁻¹ heating rate between 0°C and 400°C. Morphologies of the samples were examined by SEM-EDX (JOEL 50 A) micrographs taken at 10 kV. Se quantities remained in the filtrates after polymerization were determined by AAS (Perkin Elmer AA-Analyst 800).

For the dielectric measurements, pellets with 13 mm diameter were prepared by applying a pressure of 10 tonnes using a hydraulic press. Each of the pellets weighted ~0.1 g, and their thickness varied between 0.41 and 0.47 mm. Both sides of the samples were coated with aluminum to be used as electrodes by using a vacuum coating system (Univex 300). Dielectric measurements were performed by an LCR meter (AGILENT 4284A) between 100 Hz and 1 MHz frequency at a temperature range of 300–400 K under vacuum (10⁻³ Torr). The temperature was controlled by using a temperature controller (OXFORD-ITC 502).

The real (‘ε’ and imaginary (‘ε’’) parts of the complex dielectric constant (‘ε’) were calculated from the measured capacitance (Cₑ) and dielectric loss factor (tan δ) values through equations ε’ = Cₑd/ε₀A and ε’’ = ε’ tan δ. The alternating current (ac) conductivity (σₑ) was calculated from σₑ = ω Cₑd tan δ/A, where d is the sample thickness, A is the electrode area, ω is the angular frequency, and ε₀ is the dielectric permittivity under vacuum (8.85 × 10⁻¹² F m⁻¹).

RESULTS AND DISCUSSION

Characterization

A black colored PPy powder form was obtained after oxidation of pyrrole with (NH₄)₂S₂O₈ in diluted (0.7 M) aqueous HNO₃ solution (Scheme 1).

Characteristic peaks of PPy can clearly be seen in all FTIR spectra given in Fig. 1. KBr sample discs were used in the measurements. For the unfilled PPy, the peaks at 1552 and 1471 cm⁻¹ are related with C—C and C—N stretching vibrations, respectively [1–3, 6, 8–10, 21, 25]. The broad region at about 3400 cm⁻¹ refers to N—H stretching [1–3, 21, 23]. The peak at 1384 cm⁻¹ is related with C—N asymmetric vibration while the peak at 1047 cm⁻¹ is related with C—H deformation and N—H stretching vibration [2, 5, 8–11, 14]. It is observed from the spectra of PPy/Se composites that the peaks of unfilled PPy at 1047, 1471, and 1552 cm⁻¹ have shifted to 1050, 1473, and 1560 cm⁻¹ for 1 g filling level,
respectively, due to the deformation which may have been caused by interaction between Se and the polymer.

Characteristic absorption bands of unfilled PPy were also seen in UV-vis spectra (please see Supporting Information). The peak at 239 nm is due to \( \pi-\pi^* \) transition in PPy, while the peak at 486 nm is due to the transition from valance band to antibonding polaron state [11, 18]. The peaks observed at 588 and 657 nm are related with \( n-\pi^* \) transition and polaron, respectively [19, 20].

**AAS**

The quantity of metal cations adsorbed onto the PPy surface was measured by AAS to obtain the optimum adsorption isotherm. It was determined that the ions adsorbed onto the polymer surface were in accordance with Langmuir adsorption isotherm;

\[
\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \quad (1)
\]

where \( C \) is the concentration of metal cations (mol dm\(^{-3}\)) and \( K_{\text{ads}} \) is the adsorption equilibrium constant. One should note that \( \theta \) is the fraction of Se absorbed onto the polymer surface as determined from \( \theta = (C_0 - C)/C_0 \), where \( C_0 \) is the initial concentration of Se in the polymerization process and \( C \) is the concentration of Se in the filtrate after polymerization [7]. \( C/\theta \) \( C \) variation obtained from Eq. 1 is given in Fig. 2. By using the slope of the isotherm curve shown in Fig. 2, \( K_{\text{ads}} \) constant was determined which, when subsequently placed into Eq. 2, the adsorption free energy change, \( \Delta G_{\text{ads}}^0 \), was found to be \(-14.82 \) kJ mol\(^{-1}\);

\[
K_{\text{ads}} = \frac{1}{55.5} \exp(\Delta G_{\text{ads}}^0 / RT) \quad (2)
\]

where \( R \) is the universal gas constant, \( T \) is the thermodynamic temperature, and the constant value of 55.5 is the concentration of water in the solution (mol dm\(^{-3}\)). The \( \Delta G_{\text{ads}}^0 \) values between 20 and 0 kJ mol\(^{-1}\) indicate that the cations are adsorbed onto the polymer surface physically through electrostatic interactions [7]. This interaction mechanism is given in Scheme 2. Selenious acid (H\(_2\)SeO\(_3\)) is the result of interactions between concentrated nitric acid and metallic Se [29]. This acid causes protonation of N atoms in the polymer chain yielding quaternary ammonium salts and selenite anions (SeO\(_3\)^{2-}\).

**SEM**

Figure 3 shows the surface and side view micrographs of PPy and PPy/Se pellets. In the micrograph of unfilled PPy, a nonhomogeneous granular structure is observed (Fig. 3a, surface view). In the regions where the particle sizes are small (~0.5 \( \mu \)m), the spaces between the particles are also narrow, whereas in the regions where the particle sizes are larger (~1 \( \mu \)m), the spaces are getting wider. Although micrographs of 0.6 g Se composite exhibited a structure similar to the unfilled PPy, the particle size distribution is relatively narrow (between 0.3 and 0.6 \( \mu \)m; Fig. 3b, surface view). In comparison with the first two samples, particle size distribution of 1 g Se composite seemed to be between 0.4 and 0.8 \( \mu \)m; a slight

![FIG. 1. FTIR absorbance spectra of PPy and its composites.](image1)

![FIG. 2. Langmuirs' adsorption plots of the \( C/\theta \) versus \( C \).](image2)

![SCHEME 2. Possible PPy/Se interaction.](image3)
increase, when compared with the above samples (Fig. 3c, surface view). The bonding at 1 g filling level between the particles also became weaker in the regions where the particle sizes were quite large (~5 μm).

In terms of the effect of the filling process on the electrical conductivity, SEM images from the fracture surfaces (side view) can provide more information. A homogeneous particle size distribution (between 0.2 and 0.4 μm) with stronger inter-particle bonding seem to be a main feature of the unfilled PPy (Fig. 3a, side view). Even though, a homogeneous size distribution is also observed for 0.6 g composite, larger structures (between 2 and 5 μm) seem to exist in some regions (Fig. 3b, side view). Rather different structures seem to appear for 1 g of Se composite in comparison with the other samples (Fig. 3c, side view). A wider particle size distribution between 0.2 and 7 μm and much weaker inter-particle bonding appear to be a prominent feature of this filling level, which may have an adverse effect on the electrical conductivity.

DSC

Two endothermic and one exothermic peaks are observed in the DSC thermograms of PPy and its composites (Fig. 4a).

These endothermic peaks (seen at about 100°C and 280°C) which are not observable in the second cycle heating for the unfilled PPy (Fig. 4b) are generally attributed to the loss of moisture and degradation temperature (Td) [2, 17, 23, 25]. Slight shifts in the endothermic peaks for the composites may be due to small differences in the quantity of moisture content and/or solvent origin molecules.

The exothermic peak observed around 225°C for unfilled PPy is related to cold crystallization temperature (Tcc) [25], and it is significantly lower for the composites (between 180°C and 200°C). This can be due to the fact that selenite anions are increasing the free volume providing an easier movement for polymer chains.

Dielectric Measurements

Dielectric behavior is generally characterized by the change in real (ε′) and imaginary (ε″) parts of the complex dielectric constant, depending on frequency and temperature. The real and imaginary parts are related with the storage and loss of energy under an external field [7, 13]. Shifting to higher temperature values seen in the ε′ − log f and ε″ − log f variations of the unfilled PPy is a characteristic property of polymers (Fig. 5).

Higher dielectric constant observed at low frequencies is due to the time-temperature equivalency in dielectric
relaxation behaviors of polymers [7, 13, 16, 27]. The decrease in the real part observed at higher frequencies (Fig. 5a) clearly shows that dipolar polarizable units are affected by the frequency, and this leads to a relaxation process (Fig. 5b).

When the effect of filling process on the real part was analyzed, similar behavior was observed over the entire frequency region (Fig. 6). The real part exhibits a sudden decrease when the amount of Se reaches a certain value. This can be attributed to the difficult orientation of the polarizable dipoles due to an increase in the filling level, therefore leading to a decrease in the total dipole moment. The temperature seems to be another factor especially at relatively lower frequencies (Fig. 6a). Higher values of the real part show that the dipoles can be orientated more easily at 1 kHz.

To examine the behavior of the temperature dependent relaxation process, $f_{\text{max}}$ values which are locations of peak maxima determined from $\varepsilon''(f)$ variations (Fig. 5b) and $\tau$ relation times were calculated from the equation, $\omega_{\text{max}}\tau = 2\pi f_{\text{max}}\tau = 1$. The effect of the filling process on the relaxation time was also investigated PPy/Se composites using the same procedure as above. The relationship between the relaxation time and temperature is generally analyzed by Arrhenius law:

$$\tau = \tau_0 \exp\left(\frac{E}{k_B T}\right)$$

where $E$ is the activation energy of relaxation process, $\tau_0$ is the pre-exponential factor, $k_B$ is the Boltzmann constant (86.13 $\mu$eV K$^{-1}$), and $T$ is the temperature [15, 16, 30].
The relaxation times decrease linearly with increasing temperature for the PPy, and its composites as seen in Fig. 7. $\tau_0$ and $E$ values calculated for PPy and its composites are given in Table 1, where the activation energy of PPy/0.2 Se composite is lower than the others'. This may indicate that the amount of energy required to orient the polarizable units in this structure is relatively lower. The similar changes are also apparent in $\varepsilon'$ versus filling level as given in Fig. 6. Although the real part increases up to 0.2 g filling level, it decreases significantly for higher filling levels. The easy orientation of the dipoles in the structure of PPy/0.2 Se under an external field also explains the increase in the total dipole moment.

**AC Conductivity**

Conductivity of the PPy and its composites can be seen in Fig. 8 for two frequencies. It increases up to a certain

![Figure 6](image1.png)

**FIG. 6.** Variation of the real part versus filling level for (a) 1 kHz and (b) 1 MHz at different temperatures.

![Figure 7](image2.png)

**FIG. 7.** Arrhenius' plots of In $\tau$ versus 1000 $T^{-1}$ for PPy and its composites.

![Figure 8](image3.png)

**FIG. 8.** Variation of conductivity versus filling level for (a) 1 kHz and (b) 1 MHz at different temperatures.

**Table 1.** Relaxation parameters of PPy and its composites obtained from Arrhenius' plot.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau_0$ (s)</th>
<th>$E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPy</td>
<td>$4.06 \times 10^{-8}$</td>
<td>0.127</td>
</tr>
<tr>
<td>PPy/0.2 Se</td>
<td>$7.02 \times 10^{-7}$</td>
<td>0.017</td>
</tr>
<tr>
<td>PPy/0.4 Se</td>
<td>$3.84 \times 10^{-6}$</td>
<td>0.141</td>
</tr>
<tr>
<td>PPy/0.6 Se</td>
<td>$4.93 \times 10^{-6}$</td>
<td>0.140</td>
</tr>
<tr>
<td>PPy/0.8 Se</td>
<td>$3.47 \times 10^{-6}$</td>
<td>0.121</td>
</tr>
<tr>
<td>PPy/1 Se</td>
<td>$6.88 \times 10^{-7}$</td>
<td>0.113</td>
</tr>
</tbody>
</table>
filling level and then decreases at 1 kHz. When 1 g Se was added into unfilled PPy, its conductivity for 300, 350, and 400 K increased ~4, 4.3, and 2 times, respectively. The increase is much more dramatic for the composite with 0.6 g Se as seen in Fig. 8a. It is seen that conductivity begins to decrease for all temperatures after this filling level.

On the other hand, at 1 MHz, the conductivity of the PPy/Se composite with 1 g Se decreased considerably. In this frequency region, conductivity exhibits a significant decrease after 0.2 g filling. One reason for this decrease could be that the interaction between selenite anions and PPy is relatively weaker at high frequency region, leading to a significant decrease in ionic conductivity. The restriction placed on the mobility of \( \pi \)-electrons due to increasing filling level could be another reason. Furthermore, it is possible to say that charge carriers might be following different length conductivity paths due to different morphological structures that are also apparent in SEM micrographs. It is possible to say that all the filling level dependent fluctuations seen in the conductivity can be due to the reasons mentioned above.

**CONCLUSIONS**

The characteristic peaks of PPy synthesized via a chemical method were observed in the FTIR and UV-vis spectra in all samples. SEM micrographs showed different morphologies between PPy and its composites. Adsorption free energy calculated from the Langmuir isotherm curve indicated a weak electrostatic interaction between polymer and metal cations. Thermal analysis showed that filling process decreases the cold crystallization temperature of PPy.

Relaxation times for PPy and its composites, determined with respect to Arrhenius’ law decreased linearly with increasing temperature. Conductivity of the unfilled PPy was significantly affected by the increase in the temperature at especially high frequencies. It was observed that there is around four times increase in the ac conductivity of PPy at 1 g filling level depending on temperature and frequency.

**ACKNOWLEDGMENTS**

The authors thank Dr. Umit Ay and Prof. Dr. Muzaffer Zeren for helping AAS and SEM measurements, respectively. They also thank Assoc. Prof. Ozcan Gundogdu of Kocaeli University for his invaluable help and advice.

**REFERENCES**