



Synthesis and Characterization of Conducting Polymer Composite Films: Polypyrrole and Polyethylene Oxide

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Abstract

Polypyrrole (PPy) - Polyethylene oxide (PEO) composite thin films were synthesized by chemical oxidative polymerization method with ferric chloride (FeCl_3) as oxidant in methanol solvent. The composite films were synthesized with various weight percentages of pyrrole, and characterized by FT-IR spectroscopy, conductivity measurement. The FT-IR result shows the successful incorporation of PEG into the PPy structure forming PPy-PEG composite films. The dc electrical conductivity of the films, at 318K, first increases with wt% of pyrrole and attains the maximum value ($\sigma = 2.55 \times 10^{-8} \text{ S/cm}$) at 40 wt% of pyrrole. However, further increase in wt% of pyrrole, decreases the conductivity of the films. Temperature dependence of dc electrical conductivity showed that PPy-PEO composites with different pyrrole wt% samples follow Arrhenius law. The linear nature was observed because of charge carriers created and their increased mobility.

Keywords: PPy-PEO composites, FTIR, Conductivity.

Introduction

Conducting polymers are being most popular due to its interesting conducting properties, light weight and good environmental stability. Conducting polymers (a novel class of materials) that are being evaluated for application in charge storage devices (batteries, capacitors), electromagnetic screens, sensors, membranes, corrosion protective coatings¹. Among the conjugated polymers, polypyrrole (PPy) is the most representative one for its easy polymerization and wide application in gas sensors, electrochromic devices and batteries. However, the typical polypyrrole, which is insoluble and infusible, exhibits poor processability and lacks essential mechanical properties. Efforts to overcome these drawbacks have led to numerous researches on the synthesis of polypyrrole. Among them a significant strategy to approach both high electrical conductivity and desirable mechanical properties is through the use of bulky organic sulfonate dopants²⁻⁸ or preparing composites of polypyrrole with other insulating polymers having desirable mechanical properties⁹⁻¹¹. In other words, a combination of a conventional polymer with conductive polymer allows the creation of new polymeric materials with specific electrical properties.

Conducting polymers can be prepared by using either chemical or electrochemical polymerization¹². The advantage of chemical synthesis is that it offers mass production at a reasonable cost. On the other hand, electrochemical method involves the direct formation of conducting polymers with better control of polymer film thickness and morphology, which are suitable for use in electronic devices.

The present paper focuses on the synthesis of PPy-PEO films by oxidative (chemical) polymerization and characterization of composite films by FT-IR spectroscopy, conductivity measurement.

Materials and Methods

Chemicals used: Anhydrous Ferric chloride (FeCl_3) (AR-grade), methanol from M/S E. Merck (India), pyrrole from Sisco (India) (AR-grade), PEO from Across Organic (USA) are obtained and used in the present study.

Synthesis of PPy-PEO composites: The PPy-PEO composites were prepared by chemical oxidative polymerization by using FeCl_3 as oxidant in methanol solvent. Firstly, PEO dissolved in methanol. This solution was kept in test tube for 12 h. A suitable amount of oxidizing agent (0.2M) was added to the solution. PEO- FeCl_3 solution was homogenized by constant magnetic bar stirring. In this case the wt% of PEO and that of FeCl_3 was kept constant. Then monomer pyrrole was added dropwise to the homogeneous solution of PEO- FeCl_3 . To study the effect of monomer loading, films of different wt% of pyrrole were synthesized. This mixture was constantly stirred for 3-4 h, a dark black homogeneous solution was obtained which was then poured on chemically cleaned polypropylene plane dish to prepare the films of composite. After evaporation of solvent the thin films were formed.

FTIR spectroscopy: The FTIR spectrum of all composite films were recorded on SHIMADZU - FTIR Spectrophotometer at room temperature in the wavelength range 4000 to 500 cm^{-1} and

4 cm^{-1} band resolution was used for structural analysis. Polymers were dispersed in potassium bromide (KBr) and compressed into pellets.

DC conductivity measurement: The dc electrical conductivity of the samples was measured by two-probe method, in which resistance of the sample was measured. A dc regulated power supply and a pico ammeter with resolution of 1 pA is used for measurement. The composite film was sandwiched between two conducting electrodes and then placed in a muffle furnace. Temperature of the furnace was increased from room temperature 303 to 338 K.

Results and Discussion

FTIR Analysis: The Fourier transform infrared spectra of 20, 40 and 60 wt % of pyrrole samples (i.e. PPy-PEO composite films) were recorded in the range 4000-500 cm^{-1} and are shown in Figure-1. The bands at 1261, 1092 cm^{-1} (20 wt % Py), 1246, 1099 cm^{-1} (40 wt % Py) and 1261, 1094 cm^{-1} (60 wt % Py) may corresponds to =C-H bonds in plane vibration. The broad band at 1024 cm^{-1} (20 wt % Py), 1018 cm^{-1} (40 wt % Py) is assigned for N-C stretching¹³ that was found at 1018 cm^{-1} in 60 wt % Py. The broad band at 908 cm^{-1} in 20 and 60 wt % Py may be assigned to di-substituted pyrrole rings. The same assignment was found at 964 cm^{-1} in 40 wt % Py.

The absorbance spectra have been normalized to the CH_2 symmetric stretching feature at 2851 cm^{-1} . The sharp band at 1148 cm^{-1} (20 wt % Py), 1165 cm^{-1} (40 wt % Py) and 1161 cm^{-1} (60 wt % Py) corresponds to C-O symmetric Stretching of PEG.

The FT-IR spectra of the PPy-PEG composite films reveal the peaks associated with pure PPy and the polyethylene glycol peaks. The strong absorption at 2920 cm^{-1} , 1250 cm^{-1} , 1018 cm^{-1} and 964 cm^{-1} are characteristic peaks of PPy. The spectra also show the characteristic PEG absorption at 1150 cm^{-1} due to C-O. The FT-IR result reveals the successful incorporation of PEG into the PPy structure forming PPy-PEG composite films¹⁴.

DC Conductivity: Variation of electrical conductivity with pyrrole wt % at constant temperature 318 K is as shown in Figure-2.

It is observed that initially as the pyrrole wt % increases conductivity also increases and becomes maximum 2.55×10^{-8} S/cm for 40 wt % of pyrrole.

Further increase in pyrrole wt % decreases the conductivity of samples. This may be due to the lack of conjugation. Overloading of monomer concentration may disturb the conjugation character, which plays an important role in conduction.

The temperature dependence of conductivity for different wt % of pyrrole is shown in Figure-3.

From this plot it is observed that as the temperature increases conductivity also increases, as the temperature increases mobility of charge carriers increases and it hops among the conducting domains. Also for lower wt % of Pyrrole requires higher activation energy (excitation energy) to hop, so the resistance rises and conductivity decreases.

It is clearly observed from the graph that as wt % of Pyrrole increases, the curve shifted upwards, indicates the increase in conductivity. All the curves are linear. It is observed that, in common with other amorphous semiconductors or polymers the temperature dependence of conductivity obey Arrhenius relation^{15,16}. Nature of graph follows famous Arrhenius law. The slope of Arrhenius curve decreases suggesting that the activation energy for conduction decreases as the PPy content increases in the composite i.e. at this concentration electron requires very less activation energy to transport from one conducting particle to another.

The activation energy for conduction is calculated from the plot of $\log \sigma$ versus $1/T$, and it is found to be temperature independent. For different pyrrole wt %, activation energy and pre-exponential factor are reported in Table-1.

Table-1
Arrhenius fitting parameters for different pyrrole wt %

Pyrrole wt %	Activation energy E_a (eV)	Pre-exponential factor σ_0 (S/cm)
20	0.39	1.92×10^5
40	0.37	1.05×10^6
60	0.70	1.24×10^{16}
80	0.42	2.99×10^7

Conclusion

The PPy-PEO composites were synthesized by chemical oxidative polymerization method with the solution of ferric chloride (FeCl_3) oxidant in methanol. The Fourier transforms infrared spectra of different wt % of pyrrole samples were recorded in the range 4000-500 cm^{-1} . The polymerization of Py monomer was confirmed from FT-IR analysis. The FT-IR analysis showed the PPy synthesized by chemical polymerization method obtained as Cl⁻ doped. The FT-IR result shows the successful incorporation of PEG into the PPy structure forming PPy-PEG composite films. Temperature dependence of dc electrical conductivity showed that PPy-PEO composites with different pyrrole wt% samples follow Arrhenius law. It was observed that initially as the pyrrole wt % increases conductivity also increases and becomes maximum 2.55×10^{-8} S/cm for 40 wt % of pyrrole.

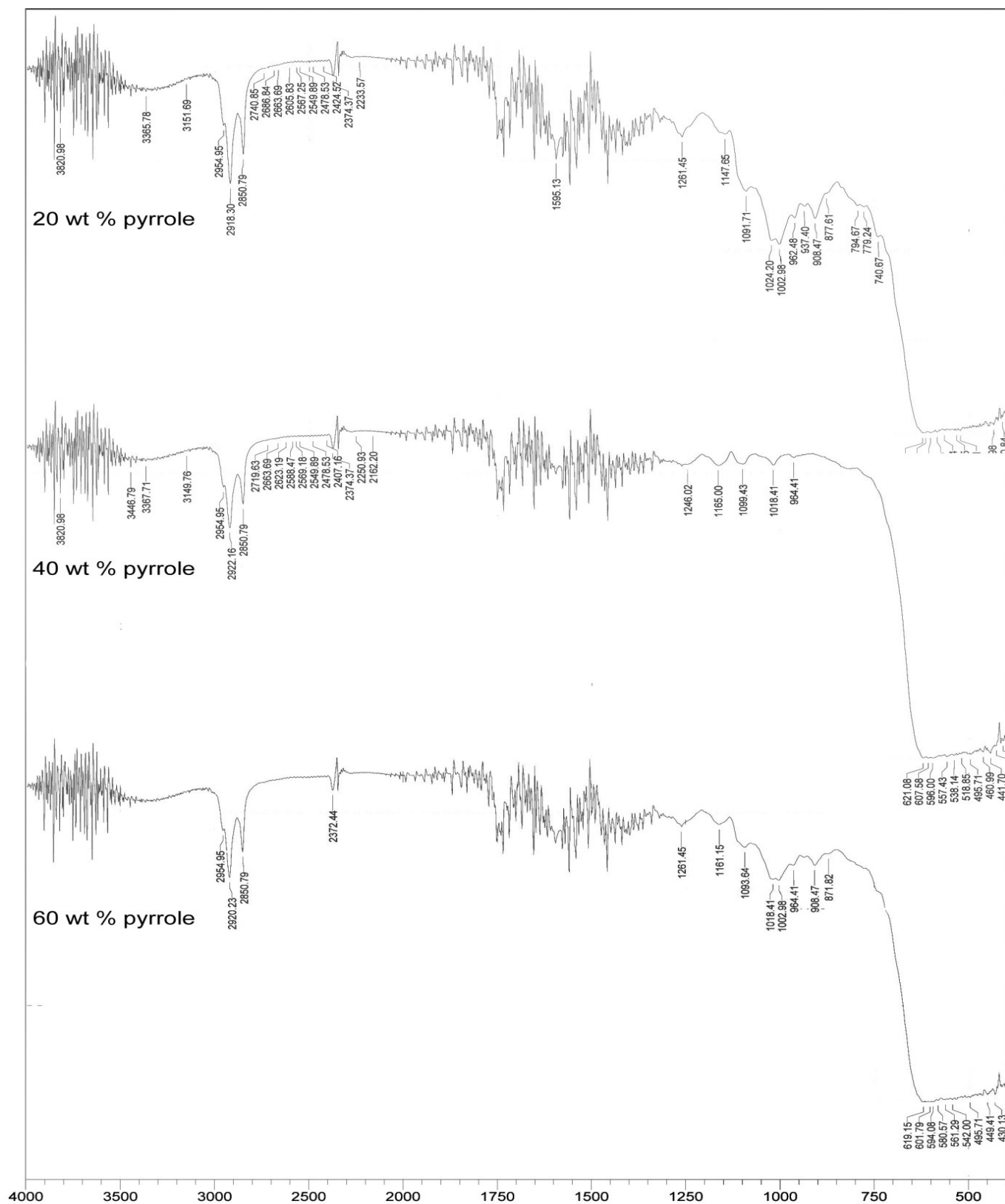


Figure-1
FTIR spectra of 20, 40 and 60 wt % of Pyrrole

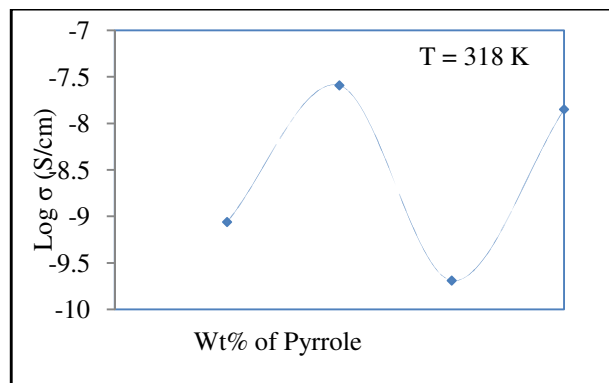


Figure-2

Variation of conductivity with pyrrole wt % at 318 K

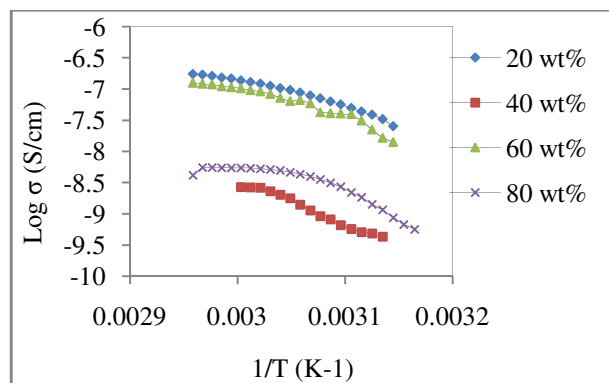


Figure-3

Temperature dependence of conductivity for different wt % of Pyrrole

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