



# STRUCTURAL AND THERMAL PROPERTIES OF PPy-PEO COMPOSITE FILMS

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## ABSTRACT

Polypyrrole (PPy) - Polyethylene oxide (PEO) composite thin films were synthesized by chemical oxidative polymerization method with the solution of ferric chloride ( $\text{FeCl}_3$ ) oxidant in methanol. The composite films were synthesized with various weight percentages of pyrrole, and characterized by transference number, scanning electron microscopy, thermogravimetry (TGA) & differential thermal analysis. The transference numbers for the PPy-PEO films were determined by dc polarization technique. The values of transference number are found to be in the range of 0.39-0.82. This shows the mixed mode conduction (i.e ionic as well as electronic). SEM images show polycrystalline behavior. In which the randomly distributed tiny clusters having size less than 100 nm and voids are observed. Thermal analysis of the samples is carried out in the temperature range 0 to 600 °C at the heating rate of 10<sup>0</sup>C/min in inert gas atmosphere. TG/DTA data shows that, there are three degradation steps. Initial weight loss is due to absorbed moisture in the samples. Further weight loss may attribute to a structural decomposition and weight loss observed in third step is due to phase formation or crystallization.

**Keywords:** PPy-PEO composites, SEM, Transference number, TG/DTA

## 1. Introduction

Conducting polymers such as polyacetylene, polythiophene, polypyrrole, etc., have been the subject of research over the past few years for their inherently conducting properties [1-4]. Among these polymers polypyrrole has been

studied the most in detail since it is stable in air as compared to polyacetylene which makes it easy to handle under normal laboratory conditions [5, 6]. 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 dopants [7-13] or preparing composites of polypyrrole with other insulating polymers having desirable mechanical properties [14-16]. 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 polymerization [17]. The advantage of chemical synthesis is that it offers mass production at a reasonable cost. In the present study, the Polypyrrole-Polyethylene oxide (PPy-PEO) composites were prepared by chemical oxidative polymerization method and characterized by transference number, scanning electron microscopy, thermogravimetry (TGA) & differential thermal analysis.

## 2. Experimental

### 2.1 Synthesis of PPy-PEO composites

The PPy-PEO composites were prepared by chemical oxidative polymerization by using  $\text{FeCl}_3$  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-  $\text{FeCl}_3$  solution was homogenized by constant magnetic bar stirring. In this case the wt% of PEO and that of  $\text{FeCl}_3$  was kept constant. Then monomer pyrrole was added dropwise to the homogeneous solution of PEO- $\text{FeCl}_3$ . 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. Prepared polymer composites were characterized by SEM and TG/DTA.

## 2.2 SEM characterization

The morphology of the PPy- PEO polymer composites was observed by scanning electron microscopy (SEM) using JSM-7600F microscope at RSIC, Indian Institute of Technology, Powai, Mumbai.

## 2.3 TG/DTA characterization

Thermal analysis is the determination of change in weight and energy in the form of heat as the material is being cooled or heated at a constant rate. The samples were analyzed by Perkin Elmer, USA, Model –Diamond TG/DTA. All thermal reactions of the dried powder were carried out in a static system by simultaneous thermo-gravimetric (TG) and differential thermal analysis (DTA) at the rate of  $10^\circ\text{C}/\text{min}$  from room temperature to  $500^\circ\text{C}$  in inert gas atmosphere.

## 2.4 Transference number measurement

The transference number gives quantitative information of the extent of ionic and electronic contribution to the total conductivity. The ionic/electronic transference number can be defined as:

$$t_{\text{ion}} = \sigma_{\text{ion}} / \sigma_{\text{T}} = I_{\text{ion}} / I_{\text{T}} \quad (1)$$

$$t_{\text{e}} = \sigma_{\text{e}} / \sigma_{\text{T}} = I_{\text{e}} / I_{\text{T}} \quad (2)$$

Where,  $\sigma_{\text{ion}} / \sigma_{\text{e}}$  and  $I_{\text{ion}} / I_{\text{e}}$  are the conductivity and current contribution due to ions / electrons respectively.

The ionic / electronic transference number was measured by using dc polarization technique [18] in which a PPy-PEO film is sandwiched between blocking (Graphite) and non-blocking (Silver) electrodes. A constant dc voltage (1V) is applied across the sample and the resultant current (pA) was recorded as a function of time.

## 3. Results and discussion

### 3.1 SEM analysis

Fig. 1 shows the morphology of PPy-PEO composites of different wt % of Pyrrole. The SEM pictures show crystalline behavior. In which the randomly distributed tiny clusters having size less than 100 nm and voids are observed. Crystals of micrometer size of pyrrole are created. Alongwith the microcracks, fibres are also seen. The large number of non-uniform voids, bigger and flat patches also seen in the micrograph. The morphology of the composite films is strongly dependent on the Py/ $\text{FeCl}_3$  weight ratio that was used in the chemical polymerization and also on the preparation method. This may be due to solvent polarity [19]

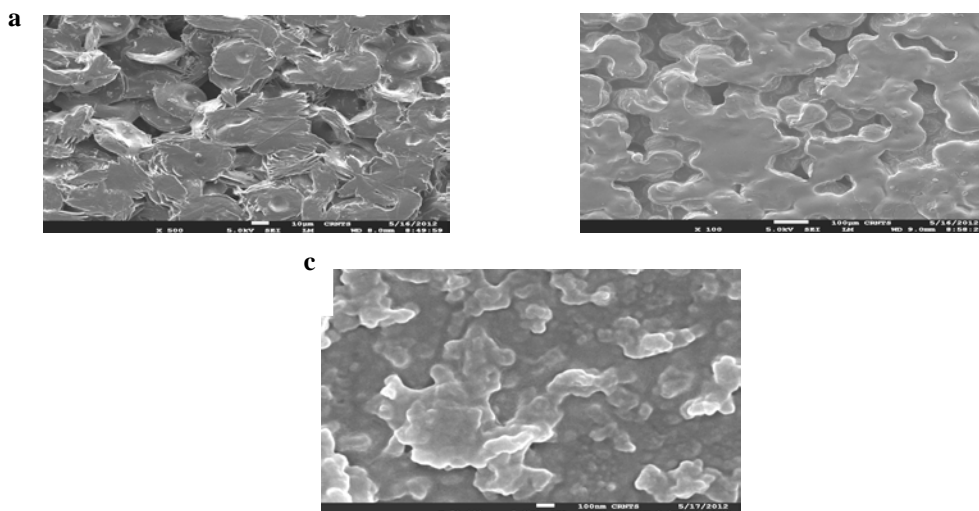
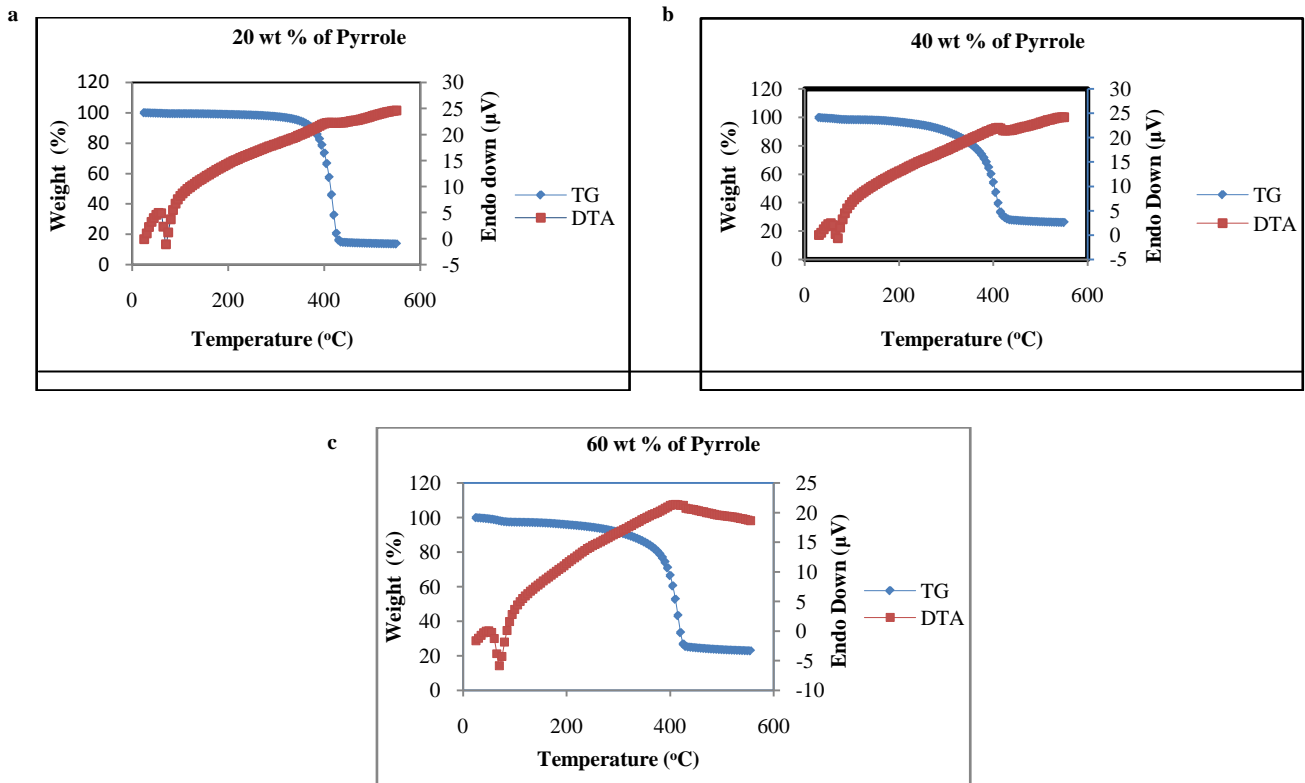


Fig. 1 – SEM pictures of (a) 20; (b) 40; (c) 60 wt % of pyrrole.

### 3.2 TG/DTA analysis

Figs 2 (a) to (c) shows TG and DTA curves for samples of 20, 40 and 60 wt % of pyrrole.

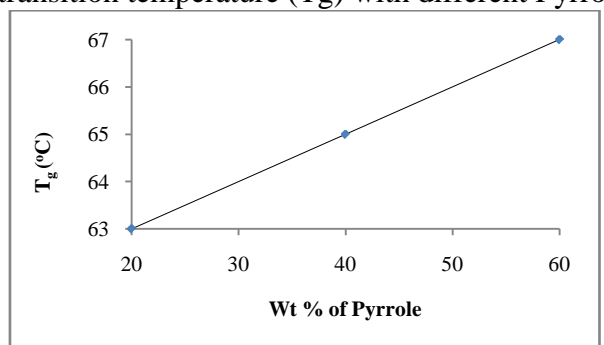


**Fig. 2 – TG/DTA curve of (a) 20; (b) 40; (c) 60 wt % of pyrrole.**

From TG and DTA curves it is observed that:

- In fig. 2(a), horizontal portion from 25 to 300 °C indicates the region where there is no weight loss also the horizontal portion from 60 to 250 °C in figs. 2(b) and (c) indicates the region where there is no weight loss. In this temperature region, the compound is stable. This is an indication of stable physical properties of the compound.
- The weight loss at 60 °C is about 1 %, which is due to loss of water molecules and moisture and an endothermic dip at about 60 °C is observed on DTA curve.
- In fig. 2(a), above 300 °C a continuous weight loss about 60 % is observed upto 430 °C. Similarly in figs. 2(b) and (c) a continuous weight loss about 60 % in the temperature range 250 to 430 °C is observed. This indicates that compound is not stable in this temperature range. This may be due to structural decomposition.
- At the end i.e. at 500 °C, the total loss is nearly 86 % for 20 wt % of pyrrole sample. For 40 and 60 wt % of pyrrole samples the total loss is nearly found to be 75 %.

The variation of glass transition temperature ( $T_g$ ) with different Pyrrole wt % is shown in fig. 3.



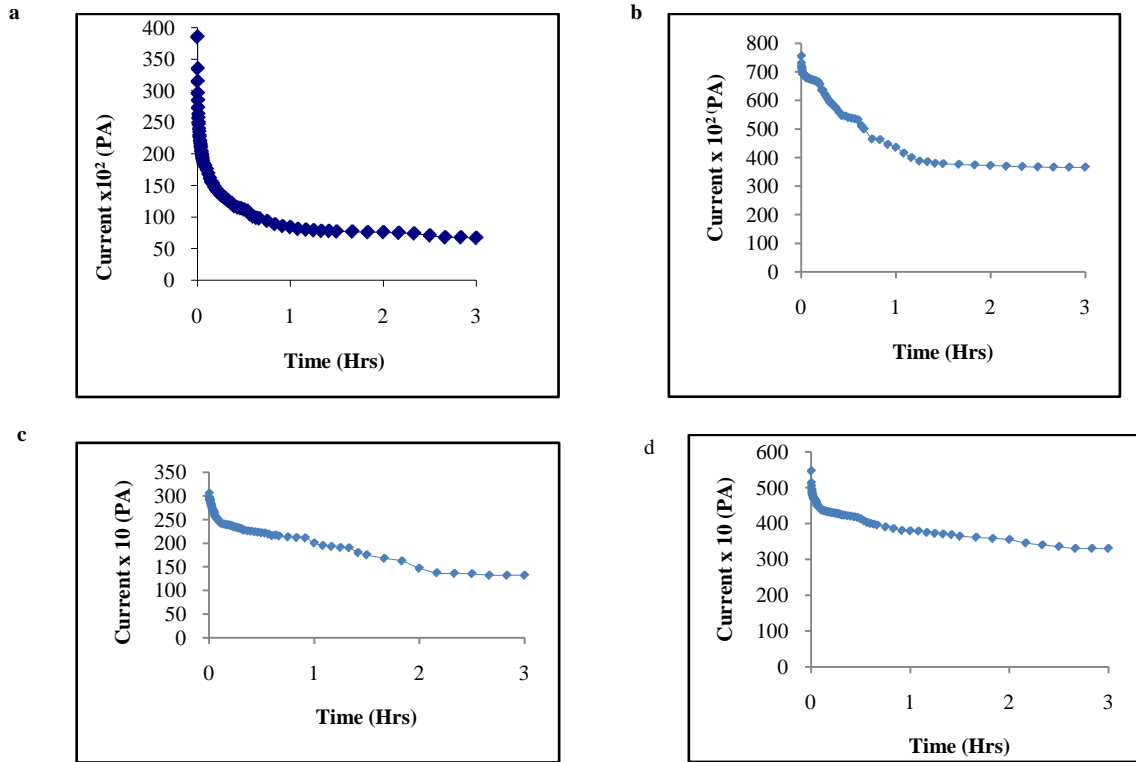
**Fig. 3 – Variation of  $T_g$  with pyrrole wt %.**

The composites with an initial particle loading of 20, 40, 60 wt % of Pyrrole, show shift in T<sub>g</sub> towards higher temperature as shown in fig. 3. The increase in glass transition of PPy in the composites with the higher particle loading may be due to the thermal stability. Increase in the glass transition temperature in the composites may have two probabilities: One may be the attainment of the longer chain length due to the

addition of oxide and other may be due to weak interactions of PPy and oxide in the more ordered system of the composite.

**3.3 Transference number measurement**

The current versus time plot of the PPy-PEO films with different pyrrole wt % are shown in figs 4 (a to d).



**Fig. 4– Current versus time plot (a) 20; (b) 40; (c) 60 (d) 80 wt % of pyrrole.**

The high current has been observed at initial time period and it starts decreasing with time and then the total current becomes nearly constant. All the samples show the same trend.

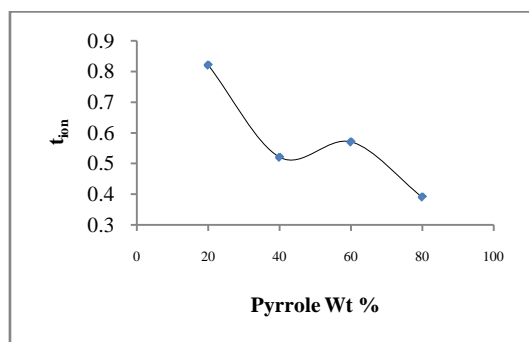
The final residual current is mainly due to electrons / holes. The ionic transference number is calculated separately from the polarization current versus time plots using equation 2.

The calculated transference numbers for different pyrrole wt% are shown in table 1:

**Table 1 - Transference number for different pyrrole wt%..**

| S.No. | Pyrrole (wt %) | Ionic transference number (t <sub>ion</sub> ) |
|-------|----------------|---|
| 1     | 20             | 0.82  |
| 2     | 40             | 0.52  |
| 3     | 60             | 0.57  |
| 4     | 80             | 0.39  |

The variation of transference number with pyrrole wt % is shown in fig.5:



**Fig. 5 - Variation of transference number with pyrrole wt%.**

The values of transference number are found to be in the range of 0.39-0.82. This shows the mixed mode conduction (i.e ionic as well as electronic) is possible, but the ionic contribution is more as compared to the electronic contribution except 80 wt% pyrrole sample.

#### 4. Conclusion

PPy-PEO polymer composites were prepared successfully by *insitu* chemical oxidative polymerization of pyrrole. SEM micrograph shows the polycrystalline morphology. TG/DTA data shows that, there are three degradation steps. Initial weight loss is due to absorbed moisture in the samples. Further weight loss may attribute to a structural decomposition and weight loss observed in third step is due to phase formation or crystallization. Samples are not thermally stable at higher temperatures. But the weight loss observed in samples for different compositions suggests the presence of interaction between the polymers. Transference number was found to be in the range of 0.39-0.82. This shows the ionic conduction except 80 wt% pyrrole sample.

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