



CHARACTERIZATION OF POLYPYRROLE BASED POLYVINYL CHLORIDE THIN FILM COMPOSITES

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ABSTRACT

The present study reveals with study of structural and thermal properties of polypyrrole filled PVC thin films composites. Conducting polymer composites have attracted considerable interest in recent years because of their numeric applications in variety of electric and electronic devices. Polypyrrole has been regarded as one of the most studied conducting polymer because of its physical and electrical properties that have led to several applications such as solid state devices and electronics. The X-RD diffractogram reveals the amorphous nature of the films. Thermal stability of Polypyrrole filled PVC was investigated by TGA/DSC. It is evident from the results that PPy filled polyblends are more stable.

Keywords: TSDC, Thermoelectrets, Polypyrrole, TGA/DSC

Introduction

In recent years, polypyrrole is popular in research and has been focus of many studies over other conducting polymers because of its high chemical and air stability and ease of preparation [1]. The typical polypyrrole, which is insoluble and infusible, exhibits poor process ability and lacks essential mechanical properties. Efforts to overcome these drawbacks have led to numerous researchers on the synthesis of polypyrrole. Among them, a significant strategy to approach high electrical conductivity is preparing blends or composites of polypyrrole polymers with other insulating polymers (Kassim 2004) [1]. The combination of conventional polymers with conductive polymers or fillers is an important alternative to obtain new polymeric materials with design properties. The combination of conventional

polymers with conductive polymers or fillers is an important alternative to obtain new polymeric materials with design properties. In such blends, the insulating polymer provides good mechanical properties and process ability while the conducting polymer would provide electrical conductivity.

Conducting polymer composites containing polymer materials incorporated conductive filler have recently been subject of intensive studies. Taking this view into consideration thin films of PPy filled PVC were prepared. The present study discusses the electrical and thermal properties in PPy filled PVC

Experimental

Polypyrrole was synthesized by chemical oxidative method from pyrrole monomer using ammonium per sulfate as oxidant and p-Toluene sulphonic acid as a dopant. Aqueous solution of pyrrole 0.5 ml in 7.5 ml water was added instantly to a solution of ammonium per sulphate (150 mg) and p-toluene sulphonic acid (500mg). After 5 minutes the product was recovered by filtration, washed with water and dried at 700 c for 12 hours [2].

Preparation of sample:

In the present study PPy acts as an additive. For composite samples of PPy filled PVC 0.5 weight percent PPy doped PVC, 0.995 gm. of PVC was dissolved in 15 ml of THF then 0.005 gm. of PPy was added. After stirring the solution for specific hours the film were prepared by pouring the solution on a clean optically plane glass plate. This glass plate was kept over a pool of mercury to ensure uniform thickness. After complete evaporation of solvent the film was detached from glass surface [3].

Thickness measurement:

The thickness of the sample was measured by the compound microscope in conjunction with an oculometer having a least count of 15.38 μm similar to method reported by Sangawar (2007). The thickness of the sample was kept constant throughout the work and is of the order of 46.14 μm .

Electrode coating:

The electrode coating on the film of measured thickness was done by using quick drying and highly conducting silver paint supplied by Eltecks Corporation, Bangalore. A mask of circular aperture of 2.5 cm diameter was used while coating, to ensure uniformity in the size of the coated silver electrode.

Structural characterization

For structural characterization the X-ray diffractograms of PPy filled PVC films were obtained on XRD-PKL 1729 Phillips Bulk XRD (Figure1). The X-ray diffractograms of all the samples ensures the amorphous nature. To confirm the presence of different functional groups in the prepared samples, the study of infrared spectroscopy of all samples was done on Perkin-Elmer Spectrometer. The thermogravimetry analysis of polymer composites was carried out on TGA Perkin-Elmer Diamond TGDTA

Results & Discussion**XRD ANALYSIS**

Figure 1 shows X-ray diffraction pattern (2 θ versus intensity) polypyrrole filled PVC thin films. The diffraction pattern shows big humps at low diffraction angles, which confirms the amorphous nature of polymer composites [10]. Fig. 1 and 2 are the diffractograms for 0.5 and 7 wt% of PPy added PVC thin films respectively. A big hump (broad peak) is observed at angle 2 θ = 120 and 150 for 0.5 wt. % and 7 wt % PPy/PVC composites.

The diffractograms show big hump representing amorphous nature of the entire sample. However slight changes are observed i.e. shift in the peak position, broadening of the peak and decrease in height of the peak.

These results can be explained as follows.

Polymers form ordered structures that are unlike the perfect crystal formed by atomic and molecular solids due to

- Constraints imposed to covalent interchain bonding
- Van der Waals or hydrogen bonding interchain interactions and
- The large configuration space i.e. large entropy of a flexible polymer chain.

Polymers form structures that are often partially crystalline and partially amorphous (Bower D I, 2002). [4]

There are two broad types of polymer crystal structure, depending on the persistence length of the chains (1) Lamellae formed by stiffer polymers, this is commonly accepted crystal model for conjugated polymers and (2) Fringed mucelles, typically formed by very flexible polymers such as polystyrene, polyethylene, polyvinyl chloride etc. Both polymer systems show both crystalline and amorphous regions (Kohlman R S, 1998) [5].

Polymers are subject to lattice distortions of the first and second kind. Lattice distortions of the first kind (Lamella) are random deviations from the ideal lattice points just due to thermal vibrations. For this reason, they are often called "Frozen in thermal displacements". Distortion of this type is very common.

Distortions of the second kind (Fringed mucelles) are also called paracrystalline distortions. Paracrystals have no long range order. They have lattice spacing that has some variation from cell to cell. This types of disorder is characterized by $g = \Delta d/d$

Where, d is lattice spacing. The effect of this type of disorder is both a decrease in intensity, I with diffraction order, h and an increase in the width,

goes as $\Delta d = 120$ and 150 for 0.5 wt. % and 7 wt %

$$I = \exp(-2\pi^2 g^2 m^2)$$

& If the width is defined as

$$\delta b = \frac{\int (I(b) - I_0) db}{I_{\max}}$$

Where, b is equal to $1/d$ & I_0 is the background, then the width goes as

$$\delta b = \frac{(\pi gh)^2}{d}$$

This type of disorder is responsible for the fact that polymer crystals are typically very small. The small size of the crystals results in increase in the width of the peaks and a decrease in the height but these do not change with peak order. The height of diffraction peak with size L goes as L^2 & the width is characterized by the Scherer equation.

$$\delta b = \frac{1}{L}$$

The total effect of the microparacrystals on the width of the diffraction peaks.

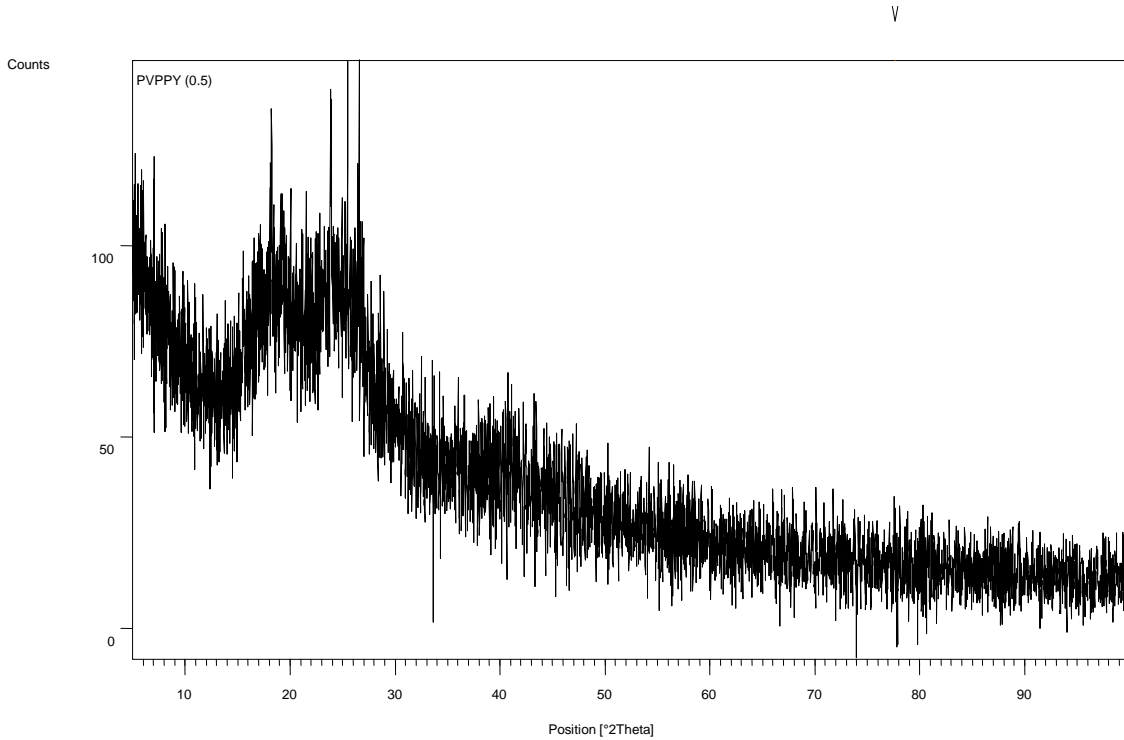


FIGURE 1 X-RD pattern for 0.5 wt.% PPy filled in PVC thin film

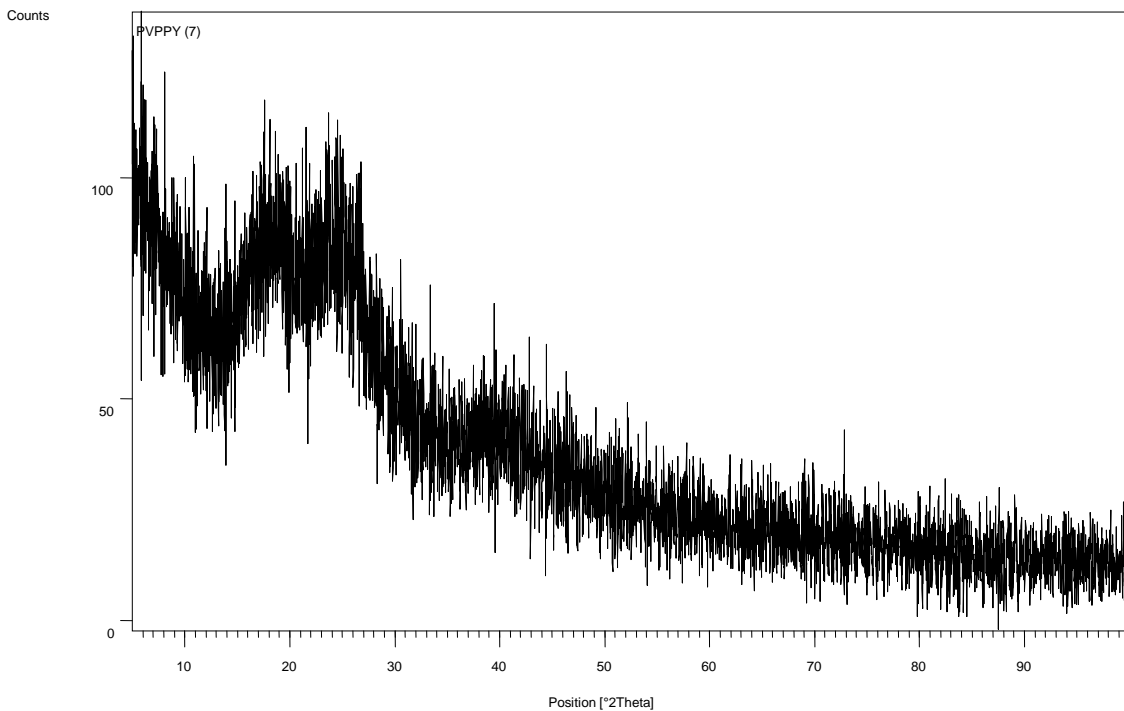


FIGURE 2 X-RD pattern for 7 wt% PPy filled in PVC thin film

THERMOGRAVIMETRY ANALYSIS

Thermal behavior of a sample is its property against time or temperature while temperature of the sample in specified atmosphere is programmed. At sufficiently low temperature rise, each polymer eventually obtains an adequate thermal energy to enable its chains to move freely and behaves like a viscous liquid. TGA/DTA was carried out at temperature range

33°C to 462°C with heating rate of 10°C/min under nitrogen atmosphere. The TGA was conducted in order to assess the effect of different weight percent of polypyrrole on the thermal properties of the composites. Figures 3 and 4 are thermograms for 0.5 and 7 wt % of PPy added PVC composite thin films respectively.

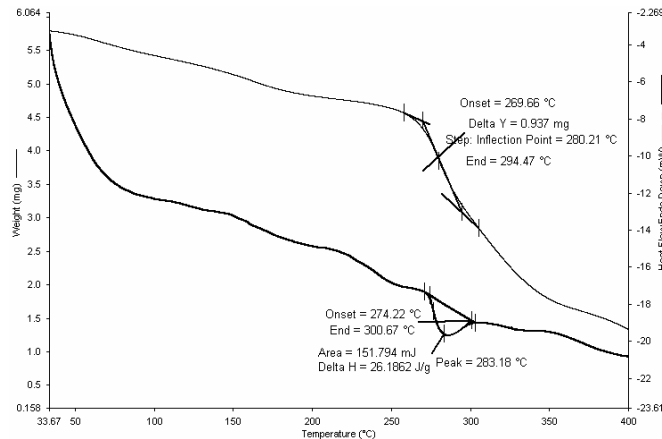


Figure 3 TGA/DSC curves for 0.5 wt% PPy filled PVC thin films

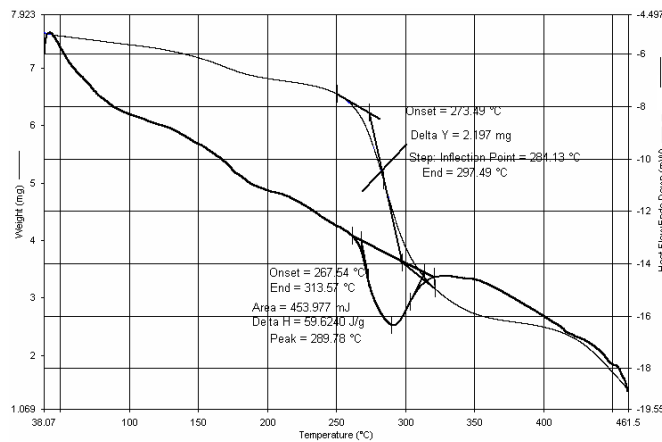


Figure 4 TGA/DSC curves for 7 wt% PPy filled PVC thin films

Thermal behavior of a sample is its property against time or temperature while temperature of the sample in specified atmosphere is programmed. At sufficiently low temperature rise, each polymer eventually obtains an adequate thermal energy to enable its chains to move freely and behaves like a viscous liquid. TGA/DTA was carried out at temperature range 33°C to 462°C with heating rate of 10°C/min under nitrogen atmosphere. The TGA was conducted in order to assess the effect of different weight percent of polypyrrole on the thermal properties of the composites.

From the DSC curves, three major transitions corresponding to glass transition temperature, melting temperature and vaporization temperature were observed for different concentration of PPy. In present study we have not focused on vaporization temperature since almost all polymers will thermally degrade before they vaporize [6]. The endothermic peak and the broad peaks on DSC curves corresponds to melting temperature and glass transition temperature [19]. The corresponding melting temperatures for 0.5wt% and 7wt% PPy concentrations are 283.180 C and 289.780C. The glass transition temperature increases from

99 to 1000 C. From the data it is apparent that the thermal degradation began to occur only after the materials have absorbed certain amount of heat energy (ΔH values). The heat initiated the degradation process and breaking down of molecular chain ruptures [7].

From the TGA data it is observed that the weight loss of polypyrrole filled composites decreases and the thermal degradation temperature increases with increase in concentration of polypyrrole in the polymers. The TGA/DSC analysis for polypyrrole filled composites shows that the glass transition temperature slightly decreases with increase in concentration of filler. This shows that polypyrrole filled PVC polyblends are more stable.

Conclusion

The TGA/DSC analysis shows that the films are thermally more stable. It can be concluded that the wt. % of conductive fractions, temperature, charge mobility and the conductivity behavior of the films are in tight interaction with each other. The addition of conductive fillers in the

insulating polymers could lead to innovation in synthetic method for better conducting films.

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