

Synthesis and characterization of conductive polypyrrole filled PVC: PMMA composites

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Abstract: *The present study reveals with study of electrical, thermal and optical band gap of polypyrrole filled PVC: PMMA thin films thermoelectrets. 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 polymers because of its physical and electrical properties that have led to several applications such as solid-state devices and electronics. The electrical conductivity of polypyrrole filled PVC: PMMA thermoelectrets have been studied. Electret effects in polymers can be produced by orientation of dipoles and /or trapping of charge carriers injected from electrodes as well as generated in the bulk of polymers. It has been shown by thermally stimulated discharge conductivity technique (TSDC) that the characteristics of electrets are very sensitive to the structure of electret forming materials. In this respect TSDC study of composite is likely to yield information about the extent of mixing between the components. Electrets prepared by composites have better charge storage capacity than the individual polymers. Measurements of TSD conductivity have been carried out at different polarizing fields. It has been observed that the conductivity of polypyrrole filled PVC: PMMA composite have been increased with increase in percentage of polypyrrole. The X-RD diffractogram reveals the amorphous nature of the films. The thermograms are plotted between $\log \sigma$ and temperature ($103/T$). From the analysis of the absorption spectra the band gap of polypyrrole filled PVC: PMMA composite have been found to be lie in the range 1.8 eV to 3.3 eV. Thermal stability of Polypyrrole filled PVC: PMMA was investigated by TGA/DSC. It is evident from the results that PPy filled polyblends are more stable*

Key Word: *TSDC, Thermoelectrets, Optical band gap, Polypyrrole, TGA/DSC.*

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I. Introduction

Polypyrrole is an intrinsic conducting polymer which can be made to have conductivities up to 1000 S-cm⁻¹ rendering its versatile applications in batteries, electronic devices, functional electrodes, electro chromic devices, optical switching devices, sensors, micro actuators, anti-electrostatic coatings and biomedical [1-4]. 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 [5]. 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 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). The combination of conventional polymers with conductive polymers or fillers is an important alternative to obtain new polymeric materials with designed properties. In such blends, the insulating polymer provides good mechanical properties and processability while the conducting polymer would provide electrical conductivity. In addition, through blending, the brittleness and lack of processability that are the main drawbacks hindering conducting polymers better utilization could be overcome by new polymeric materials with improved processability, flexibility and controllable conductivity [6]. There is increasing interest in the development of conductive polymer composites due to their excellent electric properties [7-10]. However, the conductive mechanism of conductive polymer/inorganic composites is not well understood and challenge to optimize the proportion of conductive polymer for achieving better efficiencies still remains.[11]

The present study discusses the electrical, thermal and optical properties in PPy filled PVC: PMMA thin film thermoelectrets. Since PVC is proton donor and PMMA is proton acceptor selected as a basic polymeric material. The choice of these polymers is considered for the donor acceptor capabilities. The conducting polymer, polypyrrole is added into these polymers to identify electrical conduction. In number of applications band study is essential, for light emitting diode, transparency in the visible region combined with high electrical conductivity [12, 13]. Shaktawat et al (2007) have studied the electrical conductivity and band gap determination of polypyrrole doped with different acids [14]. In present work, typical conductive theories of

polymer composites such a Percolation theory was used to study the insulator to conductor transition and percolation network formation using randomly oriented anisotropic fillers in disordered mixture [15]

II. Material And Methods

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 [16].

Preparation of sample:

Polymethyl methacrylate was supplied by Dental Products India Ltd. (Mumbai). Polyvinyl chloride supplied by Reliance Industries (Mumbai). Pyrrole monomer (Emerck Germany) was supplied by G. Kuntal & Company (Mumbai).

In the present study PPy acts as an additive. To prepare the samples containing the two polymers and additives the following procedure is adapted. For the composite sample of 1 weight percent 0.78 gm of PVC and 0.19 gm of PMMA was dissolved in 30ml of THF and 0.01 gm of PPy was then added in the solution which was kept at 343 K for 12 hrs with continuous stirring for uniform dispersion. After stirring the solution for specific hours, the film was 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. The whole assembly was placed in a dust free chamber. After complete evaporation of solvent, the film was detached from glass surface [17].

Thickness measurement:

The thickness of the sample was measured by the compound microscope in conjunction with an occulometer 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 . [17].

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 PMMA: PVC films were obtained on XRD-PKL 1729 Phillips Bulk XRD (Figure1). The X-ray diffractograms of all the samples ensures the amorphous nature. The presence of PPy in PMMA was confirmed by SEM of the sample taken on Jeol JSM 6380A (fig. 2).

Measurement of thermally stimulated discharge conductivity (TSDC):

Thermo electrets preparation: Experimental sample was sandwiched between two brass electrodes of the sample holder. The metal polymer metal (M-P-M) system so formed was placed inside the furnace. The M-P-M system was heated at a nearly uniform rate up to a polarizing temperature $T_p=343$ K and was kept constant for 30 minutes. Different polarizing fields (E_p), 4kV/cm, 8kV/cm, 12kV/cm and 16kV/cm were applied using a stabilized D.C. voltage source for 1 hour keeping the field on. The sample was slowly cooled to room temperature under continuing electric stresses. Total time of polarization was adjusted to be 2.5 h in each case. After polarization, the field was removed and the sample was short circuited for 20 minutes in order to remove stray charges if any. Thus, thermoelectres were prepared by simultaneous application of heat and different polarizing fields [18].

After the electret formation the M-P-M assembly was placed in a controlled temperature furnace supplied by Pushpa Scientific, Hyderabad. The sample was thermally discharged at a uniform rate of 2 K/min and the corresponding was measured in the temperature region 313-403K. The transmission spectra of Polypyrrole filled PVC: PMMA recorded in the region of wavelength 200-700 nm on Hitachi-330UV-VIS spectrophotometer at room temperature as shown in fig. 6

III. Result

Figure 1 shows X-ray diffraction pattern (2θ versus intensity) polypyrrole filled PVC: PMMA thin films. The diffraction pattern shows big humps at low diffraction angles, which confirms the amorphous nature of polymer composites [19].

Fig. 2 shows SEM micrographs of PPy filled polypyrrole. The scanning electron microscopy shows the non-uniform distribution of polypyrrole in PMMA: PVC polyblend. The PPy particles are distributed in the polyblend which confirms the presence of polypyrrole in the polyblend.

Fig. 3 and 4 shows the thermograms for the thermoelectrets of unfilled and PPy filled PMMA: PVC for different polarizing fields (4, 8, 12 and 16 kV/cm) in the temperature range 313-403 K. The conductivity increases with increasing temperature by an equation

$$\sigma = \sigma_0 \exp(-E_a/KT)$$

Where σ_0 is pre exponential factor, E_a activation energy of conduction and K is the Boltzman's Constant and T is the thermodynamic temperature.

PVC and PMMA are amorphous polymers but have different electrical conductivities. Patil et al (2001) reported thermally stimulated depolarization current (TSDC) characteristics in configuration of PVC: PMMA bands of different weight percent composition ratio PVC: PMMA (100:0), (90:10), (95:5) and (80:20) as a function of polarizing field and temperature. The better results are obtained for 80:20 weight percent compositions [20]. Therefore, in the present study this composition has been selected. The aim of the study is to observe the effect on conductivity of PVC: PMMA blend when PPy added in different weight percent and along with the effect of polarizing field (4, 8, 12, and 16 kV/cm).

Electrical conductivity of PPy involves movement of positively charged carriers or electrons along polymer chain and hopping of these carriers between polymeric chains. Polyvinyl chloride is proton donor and polymethyl methacrylate is proton acceptor. The charge transfer occurs due to increase in electro positivity. The degeneracy of the ground state has an important effect on the nature of charge species. Polypyrrole is nondegenerate ground state polymer. On addition of polypyrrole the polymer chain gets ionized and this ionization process creates polarons having half spin. At low doping level these polarons are carriers of electricity. Increased polarons result in large probability of interaction which in turn results to form bipolaron. Bipolarons are doubly charged but spinless. A single bipolaron is more stable than double polarons. The relatively high conductivity of polymers probably results from motion of spinless bipolarons. It is also evident that the conductivity also increases with the polarizing field [20-21].

The activation energy values are calculated from the slope of thermograms. It is observed that the value of activation energy decreases with increase in concentration of PPy in PVC: PMMA and is found to be 0.61eV. This is in good agreement with the reported order of magnitudes (S. H. Deshmukh et al 2005) [22].

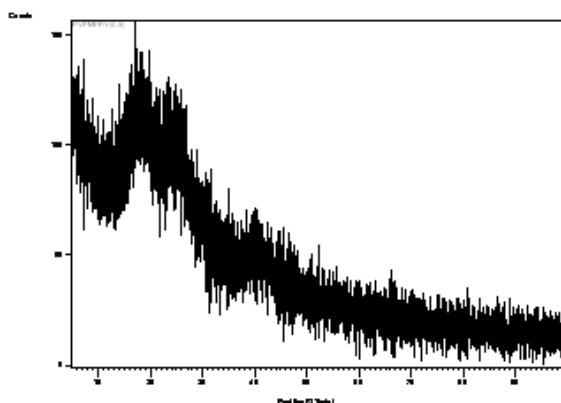


Figure 1 X-ray diffraction pattern for 0.5 wt% PPy filled PVC: PMMA thin films.

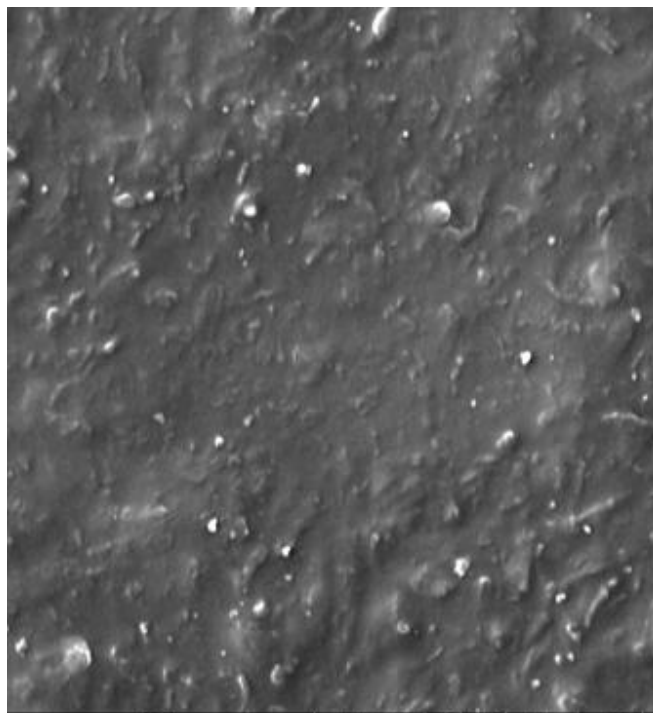


Figure 2 SEM micrograph of PPy filled PMMA: PVC thin films.

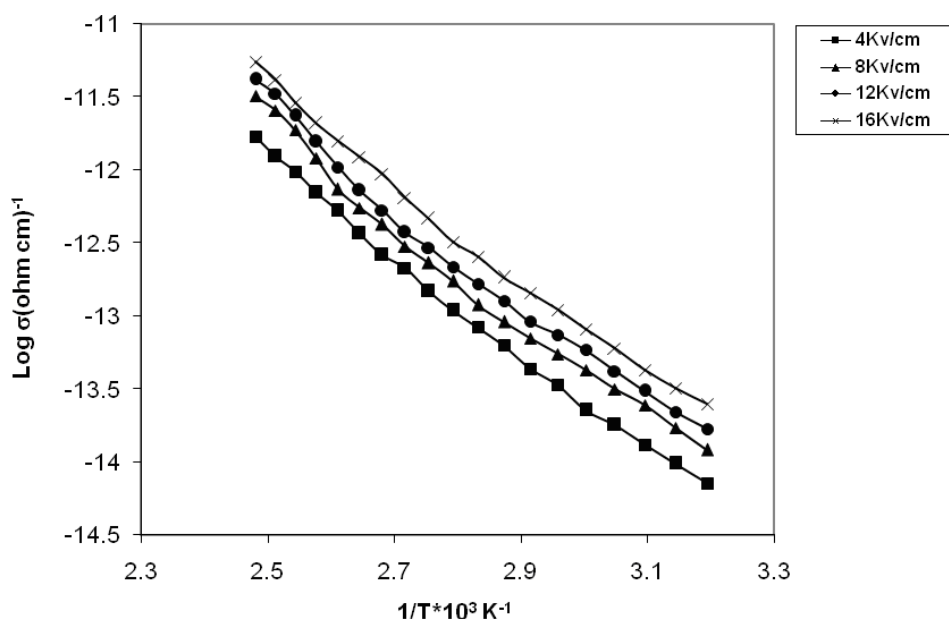


Figure 3 Thermograms of unfilled PVC: PMMA

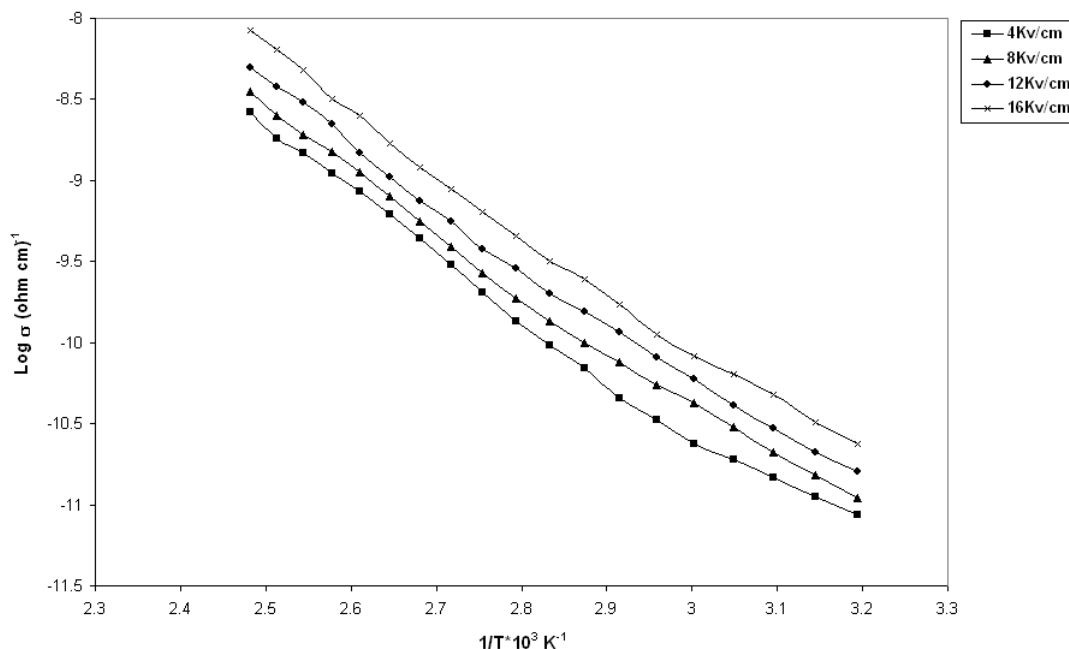


Figure 4 Thermograms of 7% PPy filled PVC: PMMA

Figure 5. Plot of electrical conductivity versus wt% of PPy in PMMA: PVC thin films at room temperature.

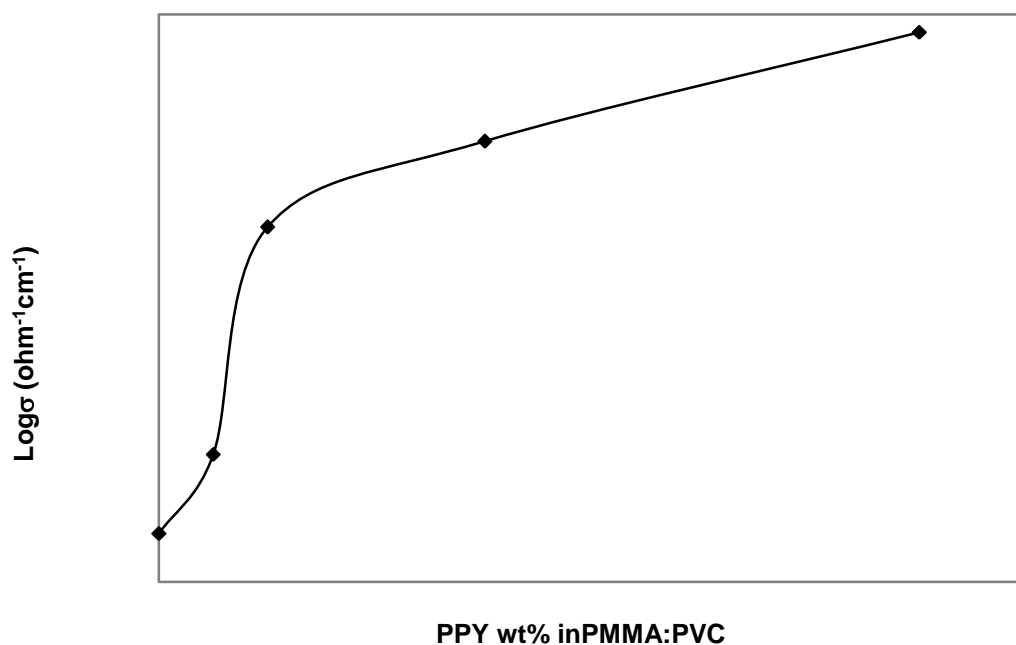


Figure 5 Plot of electrical conductivity versus wt% of polypyrrole

It can be noted that the room temperature electrical conductivity depends strongly on the fraction of polypyrrole in the blends. The conductivities of these blends increase with increasing content of conductive polypyrrole showing the conductive fractions dependence of the conductivity. The enhancement of conductivity of the blend films with increasing polypyrrole loading is owing to the conductive paths formation through the blends [23]. The reason behind electrical conductivity of polymer composite is the percolation theory. At percolation threshold, the conductivity of polymer composite is of the several order of magnitude. This shows that percolation threshold is the minimum concentration of filler, which results in continuous conductive path ways throughout the polymer matrix. Beyond this point the conductivity of polymer composite increases at high magnitude as the filler loading increases [24].

The optical transmission spectra of (1) PVC: PMMA, (2) 0.5 wt% PPY filled PVC: PMMA and (3) 7 wt% PPY filled PVC: PMMA shown in Fig.4. The absorption coefficient was calculated as a function of photon energy from transmission Vs wavelength curve.

The absorption A is defined as

$$A = \alpha hv$$

Where α is the absorption coefficient, h is the Planck's constant and v are the frequency. The absorption coefficient α is directly determined by the relation

$$\alpha = (2.303/d) \log (1/T)$$

Where d is the film thickness and T is the transmittance. The variation in the absorption coefficient with photon energy, hv is given by

$$\alpha hv = \beta [hv/E_g(\text{opt})]^m/hv$$

Where $E_g(\text{opt})$ is the optical band gap energy, β is the temperature dependent and describes the degree of randomness of the material and m is the effective mass (Migahed M.D. 1994) [20]. Fig.5 shows the plot of $(\alpha hv)^{1/2}$ Vs hv. The extrapolation of the straight line to $(\alpha hv)^{1/2}=0$ axis gives the value of band gap energy. From the analysis of these graphs the value of band gap energy for unfilled PVC: PMMA, 0.5wt% polypyrrole filled PVC: PMMA and 7 wt% polypyrrole filled PVC: PMMA comes out as 3.21 eV, 2.5eV and 1.8eV respectively.

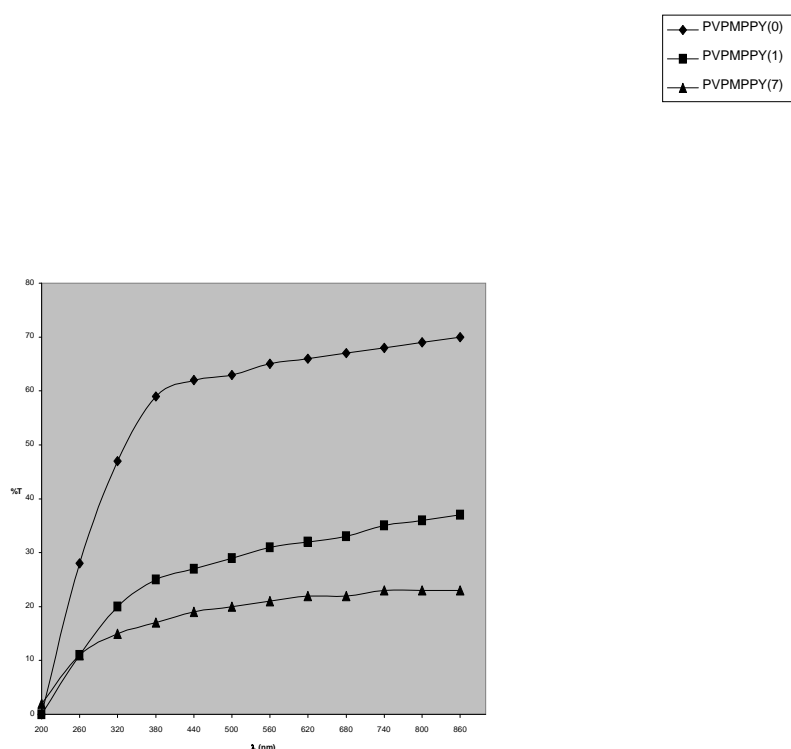


Figure 6 Optical transmission spectra of unfilled PVC: PMMA and PPY filled PVC: PMMA

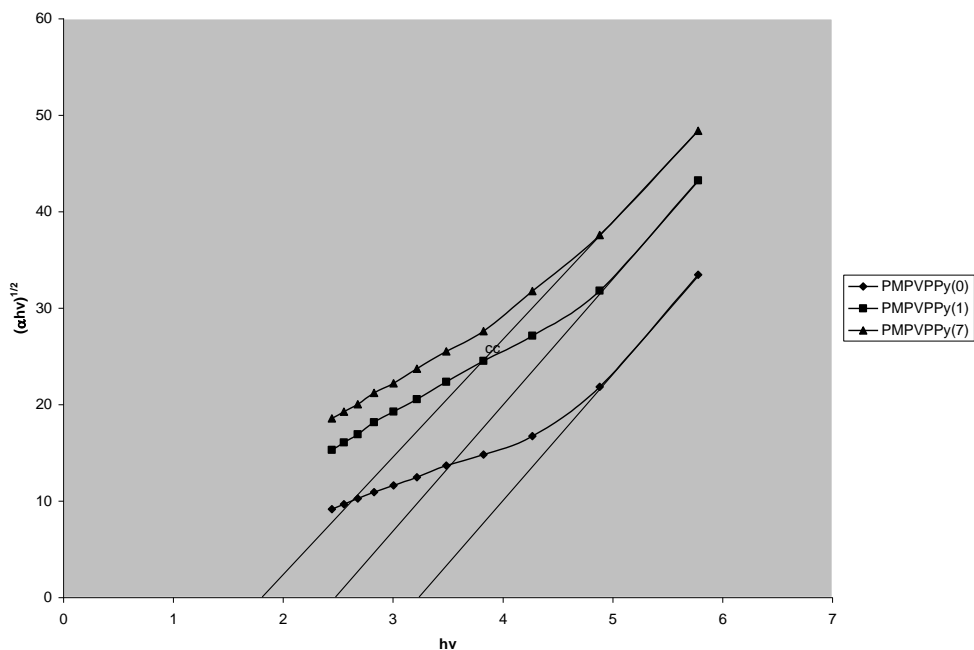


Figure 7 Plots of $(\alpha hv)^{1/2}$ Vs $h\nu$ for unfilled PVC: PMMA and PPY filled PVC: PMMA

The lower values of E_g for higher weight percent addition of polypyrrole may be attributed to the creation of localized states in the band gap as a result of compositional disorder. Also, the increase in the number of unsaturated defects increase the density of localized states in the band structure and consequently leads to decreasing the optical gap [25].

Figure 8 and 9 shows TGA/DSC curves for unfilled and polypyrrole filled PVC: PMMA

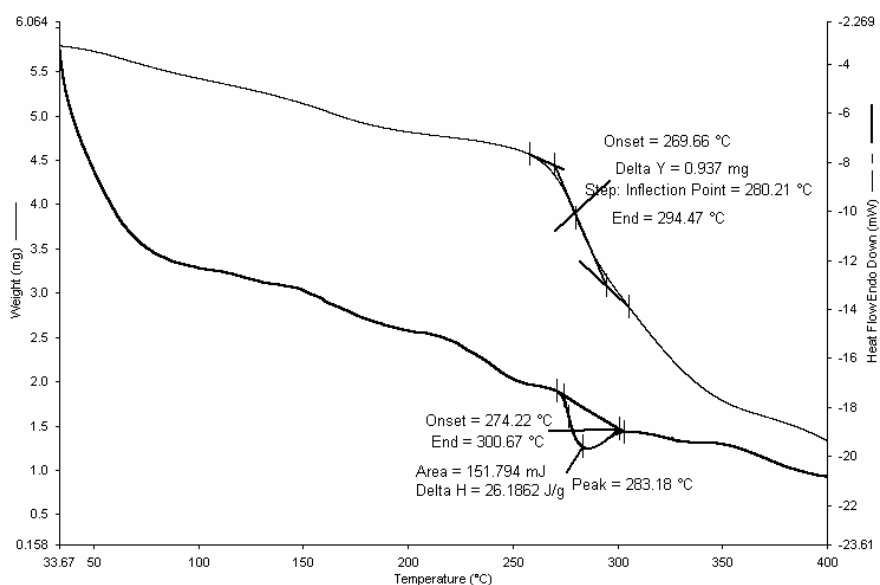


Figure 8 TGA/DSC curves for unfilled PVC: PMMA thin films

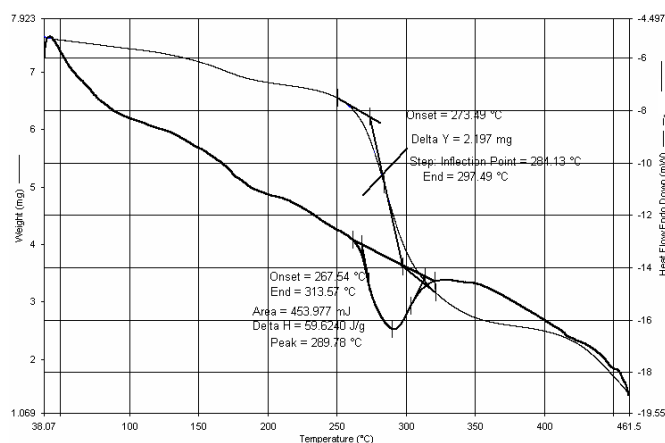


Figure 9 TGA/DSC curves for PPY filled PVC: PMMA Thin films

From the TGA curves it is observed that the onset temperature increases from 269°C to 273°C . The mass loss for 0.5wt% PPy filled PVC: PMMA polyblend starts at 269.66°C and that for 7wt% starts at 273.49°C . It is observed that the mass continues to vary slowly at temperature below 400°C . Above this temperature, this process takes place very rapidly. The mass loss at onset temperature decreases from 16% to 15%.

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 [18]. 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 283.18°C and 289.78°C . The glass transition temperature increases from 99 to 100°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 [26].

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: PMMA polyblends are more stable.

IV. Conclusion

Present study reveals that the temperature, polarizing field and concentration of PPy influences the conductivity of PVC: PMMA blends. The order of D.C. electrical conductivity of unfilled PVC: PMMA was of the order of 10^{-13} ohm $^{-1}$ cm $^{-1}$. After doping of PPy in PVC: PMMA in sufficient quantity it increases to 10^{-7} ohm $^{-1}$ cm $^{-1}$. The increase in conductivity at room temperature is due to the percolation of PPy in the polyblends. The optical band gap energy decreases with increase in percentage of polypyrrole in PVC: PMMA. The optical absorption shows that the polypyrrole filled films have allowed direct transitions. 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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