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Thermal Dependant Study of Polythiophene Composite Thin Films doped with Bromine

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ABSTRACT
Synthesis of polymer composites poly (vinyl acetate) (PVAc) and polythiopene (PTh) was done by chemical oxidative method using ferric chloride oxidant in methanol. Thin films with PTh-PVAc polymer composite were prepared for Pure, 3.5, 5.5 and 10.4 wt % of Bromine as a dopant.The variation of glass transition temperature with Bromine concentration is studied. The degradation of samples and its effect on the nature of samples is noted. Various parameters such as enthalpy , glass transition temp.etc. are noted.
Keywords: Poly (vinyl acetate) (PVAc), Polythiophene (PTh), enthalpy, glass transition temp.

1. Introduction

By introducing appropriate dopants and altering their structure, polymers can display semiconducting, metallic, or even superconducting properties due to changes in their conduction mechanism. This possibility has fueled the idea that polymers could eventually rival conventional materials in specific applications. For example, conducting polymers have been used for antistatic coatings [1], in the formation of Schottky barriers, and as components in solar cells [2,3]. Additionally, they have been employed as photoelectrodes in photochemical cells [4]. This paper focuses on the heating effects caused by various transducers on the conducting material.

2. Sampple Praparation

Thin solid films of PTh-PVAc doped with Bromine (3.5, 5.5, and 10.4 wt %) were synthesized by chemical oxidative polymerization method in order to study the thermal dependant study of Polythiophene thin films doped with Bromine.

Thermal Gravimetry / Differential Scanning Calorimetry is useful for the determination of changes in weight in relation to change in temperature [5], determination of glass transition temperature etc. TGA/DSC for all the samples of PTh-PVAc composites doped with Bromine was obtained from department of Material Engineering, VNIT, Nagpur and SAIF/CRNTS, IIT, Mumbai. In TGA/DSC temperature is maintained upto 973K. The TGA/DSC of the samples was carried out on instrument from Dupont, U.S.A. and heating rate of the sample was 10^{o}C/min.

3. Result And Discussion

The existence of a single glass transition temperature (Tg) in the amorphous state of the samples indicates the miscibility of two polymers [6-9]. Fig 1 shows the TG curves of pure PTh-PVAc film and Bromine doped films in the temperature range 273 to 923 K.The figure 1 shows that the thin film lost 91.36 to 97.15 % of its weight when it was heated up to 900 K. This indicates that 91.36 to 97.15 % of the sample consists of polymers and softeners. The residual 2.47 to 7.91 % considered to be account for metallic compounds added as sulphides and dopants [10-11].

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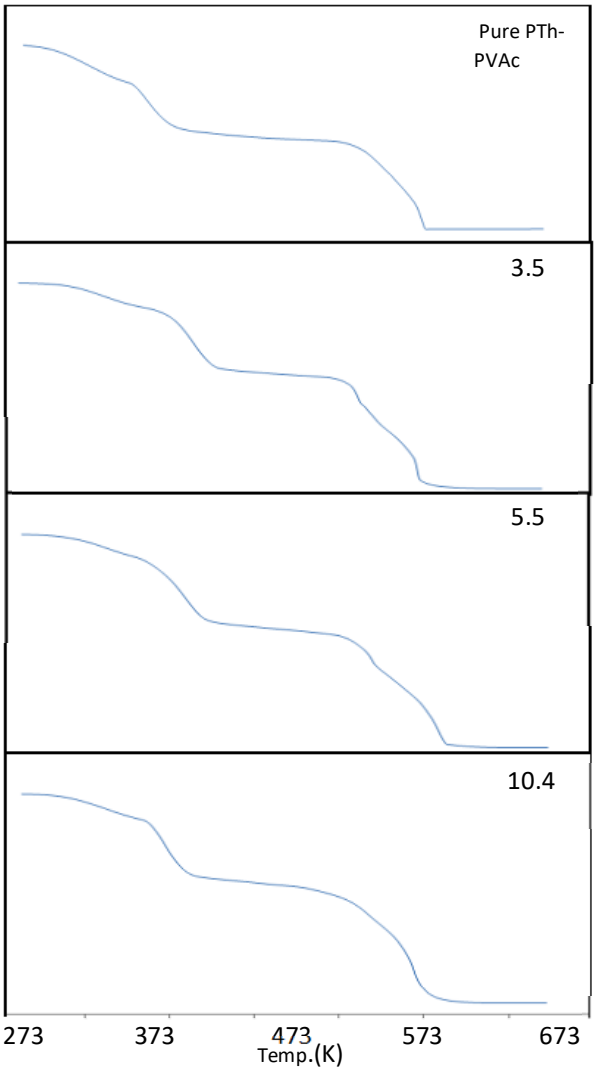

Fig.1 TGA Curve

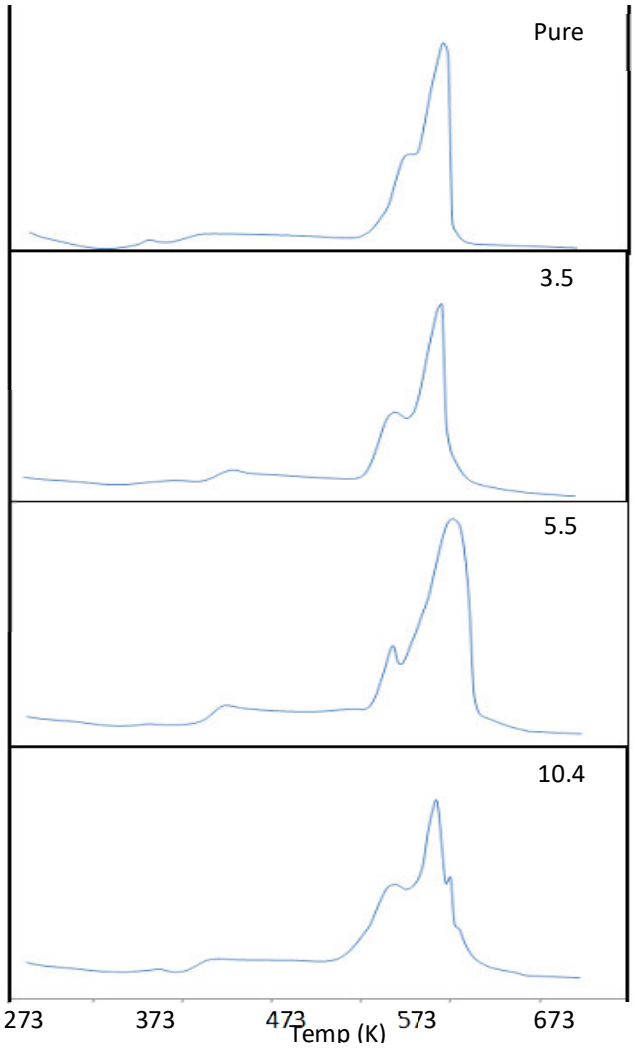

Fig 2 DSC Curve

The fig.1 shows three step degradation in the curve [10-11]. The first step degradation occurs in the temperature range 293 to 438 K and the weight loss in this temperature range is small i.e. 9.71 to 19.91 %, which is due to the moisture content in the sample. The second step degradation occurs in the temperature range 425 to 655 K and the weight loss is 26.63 to 33.33 %. In third step degradation the weight loss is observed to be higher than the first two steps. The third step is observed in the temperature range 526 to 798 K and the weight loss is in the range 44.82 to 56.45 %. Weight loss in each step and total weight loss for different wt % of Bromine are tabulated in table 1.

Table 1: Weight loss in each step for PTh-PVAc film doped with Bromine

Sr. No.	Composition Bromine wt %	Weight loss (%)				
		Step1 293 to 438 K	Step 2 425 to 655 K	Step 3 526 to 798K	Total Weight loss (%)	Residue (%)
1	Pure PTh-PVAc	19.91	26.63	44.82	91.36	7.91
2	3.5	10.45	31.77	52.97	95.19	4.45
3	5.5	9.71	33.33	54.11	97.15	2.47

4	10.4	11.44	27.04	56.45	94.92	4.95

The figure 2 shows DSC curve for pure PTh-PVAc film and Bromine doped films. The first exothermic peak represents the glass transition temperature which varies in the range 374 to 400 K. The glass transition temperature [12] gives the softening temperature of the sample. The TG curve is analogous to the DSC curves [13] as the variation in TG curve will give the simultaneous variation in DSC curves that can be seen from the figures 1 and 2. The various parameters such as glass transition temperature, peak height, onset temperature, peak temperature and end temperature from DSC curves are tabulated in the table 2

Table 2: Thermodynamic Parameter from DSC Curve for PTh-PVAc films doped with Bromine

Composition Bromine (wt %)	Glass Transition temperature (Tg) (K)	Crystallization exothermic peak			
		Onset Temp.(K)	Peak Temp.(K)	End Temp.(K)	Peak Height (μV)
Pure PTh-PVAc	374	420	431	449	5.01
3.5	398	466	487	508	-4.45
5.5	400	437	486	510	-14.47
10.4	386	446	472	509	-7.02

4. Conclusion

It is observed that all the samples with different wt % of Bromine give the degradation in the range 91 to 95 % when heated up to 923 K. The glass transition temperature is also noted for all the samples which found in the range 374 to 400 K [12-13]. It is observed that the glass transition temperature decreases with increasing content of Iodine as well as Fe. This means addition of Iodine or Fe relieves the structure of polymer composites and it becomes soft. Also the enthalpy of the composites decreases with increasing content of Bromine.

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