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STUDIES OF CONDUCTING POLYPYRROLE THIN FILMS

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ABSTRACT

Polypyrrole thin films were prepared by solvent evaporation method. The thermal analysis (TG/DTG) was carried out on NETZSCH - Geratebau GmbH Thermal Analyser (Model - STA 409 C), at RSIC, Chennai. The conducting polypyrrole thin film samples S1, S5, S8, S10, S12, S15 and S20 in powder form were used. The weights of sample were 19.660; 22.570; 20.460; 20.640; 21.190; 22.670 and 20.650, respectively. The temperature range was 30 to 500ºC with heating rate of 10 K/min. The atmosphere used was nitrogen. TG curves of 1, 5, 8,10,12,15 and 20 wt % of pyrrole thin films which are scanned in the temperature 293 to 1173 K. The data obtained from TG and DTG curves.

Key words: Polypyrrole, Thin film, Thermogravimetric analysis (TG and DTG).

INTRODUCTION

The conducting polymers are not stable at temperature much above 100-200ºC. Polypyrrole, for example, losses conductivity with heating to around 200ºC, then decomposes without significant softening or melting. Several of these polymers have a similar decomposition pattern. The method was used to evaluate kinetic data from TG. The differential method using Freeman-Carroll equation: Differential method based on the rate of weight loss versus temperature data. Free-man *et al* (1958) have devised a method to calculate the thermal parameters using thermo-gravimetric data.

The Freeman-Carroll equation was used in the form -

$$\frac{\Delta \log dw/dt}{\Delta \log w_T} = \left\{ \left[(-E/2.303)\Delta(T^{-1})\right]/(\Delta \log w_T) \right\} + n$$

Where E is the activation energy in J mol^{-1} of the term w_T and T can be directly obtained from the TG traces. By drawing tangents, the temperature slopes, dw/dt were converted into time slope, dw/dt, using the relation,

$$\frac{dw}{dt} = \left(\frac{dw}{dt}\right)\left(\frac{dT}{dt}\right) = \left(\frac{dw}{dT}\right)\Phi$$

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$\left(\frac{\Delta(T^{-1})}{\Delta \log w_T}\right) versus \left(\frac{\Delta(dw/dt)}{\Delta \log w_T}\right)$ was drawn and found to be linear from which the order of reaction and activation energy were obtained from the intercept and slope respectively. The order of reaction (n) was found unity. The usual first order rate law expression, (dx/dt) = k (a -x) can be put in the following form using the w and w_T

$$(dw/dt) = k\, w_T$$

Combining this with Arrhenius equation, i.e. k = Z exp (- E / RT), we get

$$\log[(dw/dt)/w_T] = \left(\frac{-E}{2.303RT}\right) + \log Z$$

A plot of the left hand side against (T^{-1}) was found to be linear, from the slope of which W was calculated. Z was calculated from the intercept and entropy of activation ΔS* was obtain from the equation,

$$Z = \left(\frac{kTs}{h}\right)\exp\left(\frac{\Delta S^*}{R}\right)$$

EXPERIMENTAL

The thermal analysis (TG/DTG) was carried out on NETZSCH - Geratebau GmbH Thermal Analyser (Model - STA 409 C), at RSIC, Chennai. The conducting polypyrrole thin film samples S1, S5, S8, S10, S12, S15 and S20 in powder form were used. The weights of sample were 19.660; 22.570; 20.460; 20.640; 21.190; 22.670 and 20.650, respectively. The temperature ranges was 30 to 500ºC with heating rate of 10 K/min. The atmosphere used was nitrogen.

RESULTS AND DISCUSSION

Fig, 1 shows TG curves of 1, 5, 8, 10, 12, 15 and 20 wt. % of pyrrole thin films which are scanned in the temperature 293 to 1173 K. The data obtained from TG and DTG curves is reported in Table 1 from the spectra it is observed that the films are thermally stable up 340^0C.The decomposition of the film occurs between the temperature ranges 593 to 733 K The thermal decomposition of pyrrole films as observed from Fig. 1. Occurs in single stage for 1, 5, 8, 10, 12, 15 and 20-wt. % of pyrrole films. The transition was due to the evaporation of residual solvents and moisture. This step reveals that the polypyrrole films retain the solvents and environmental moistures in large amount. The percentage of residue after decomposition in all the films is in the range of 4.13 to 17.06 %.

Table 1: Thermal parameters from TG curve

S. No.	PPY sample wt. %	Initial wt. (mg)	Stability temp. (K)	Peak transition temp. (K) from DTG	Temperature range of maxi. wt. loss (K)	Loss of wt. %	Residue %
1	1	19.66	612	689.1	613-733	80	13.75
2	5	22.57	612	687.7	613-713	75	15
3	8	20.46	612	685.3	613-703	76.83	15
4	10	20.64	612	684.8	613-713	73.08	17.06
5	12	21.19	592	682.8	593-723	90	7.32
6	15	22.67	612	686.2	613-703	87.57	40.13
7	20	20.65	592	684.6	593-713	82.66	7.32

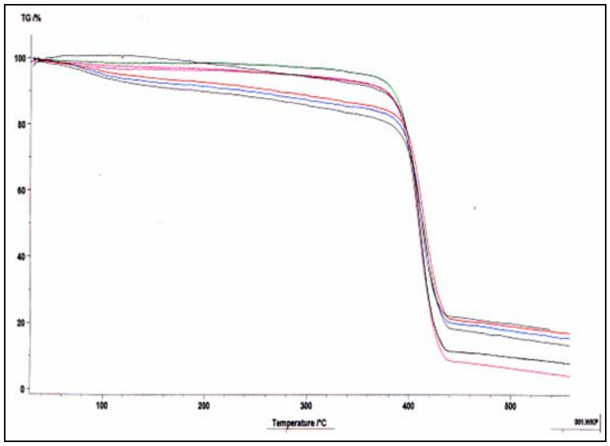

Fig. 1: TG curves of 1, 5, 8, 10, 12, 15 and 20, wt. % of pyrrole

In studying decomposition kinetic; and thermal parameters have been calculated using Freeman-Carroll equation for which the thermo gravimetric curves are used for computation of parameters. The various parameters are reported in the Table 2.

Table 2: Kinetic parameters using Freemann-Carroll equation

S. No.	PPY Sample wt. %	Thermal parameters from Freemann Corroll-equation	
1	1	Activation energy JKmole^{-1}	665.4
		Entropy (ΔS*) JK^{-1} mole^{-1}	105.0
2	5	Activation energy JKmole^{-1}	7682.9
		Entropy (ΔS*) JK^{-1} mole^{-1}	94.6
3	8	Activation energy JKmole^{-1}	2117.2
		Entropy (ΔS*) JK^{-1} mole^{-1}	99.8
4	10	Activation energy JKmole^{-1}	1728.8
		Entropy (ΔS*) JK^{-1} mole^{-1}	99.5
5	12	Activation energy JKmole^{-1}	1526.3
		Entropy (ΔS*) JK^{-1} mole^{-1}	111.0
6	15	Activation energy JKmole^{-1}	1842.8
		Entropy (ΔS*) JK^{-1} mole^{-1}	100.0
7	20	Activation energy JKmole^{-1}	1857.7
		Entropy (ΔS*) JK^{-1} mole^{-1}	98.5

The Arrhenius type plots using Freeman- Carroll equation are shown in Fig. 2. The values of kinetic parameters are well in agreement with the value reported by Vatsala et al (1986). From the result of PPY composites good thermal stability is observed (Wen et al, 2001). TG analysis of polypyrrole film shows that transition of thermal decomposition for complete thermal decomposition of the film (1 to 15 wt. %), a temperature above 1173 K is required. Thermal kinetic parameters like an activation energy, entropy and frequency factor using Freeman- Carroll equation has been calculated (Uyar et al, 2001). A weak interaction between the dopant and polymer chain showed evaporation of the dopant and peak due to the classical fragmentation pattern should appear in the pyrolysis mass spectra. It has been proposed that the undoped polypyrrole exist in the aromatic form where as the doped polypyrrole exist in the quinonld form (Kikuchi et al, 1992, Forsyth et al., 1994). The methods of kinetic analysis of thermo gravimetric data are divided in to five categories to facilitate discussion and comparison; these are (Flymn et al., 1966).

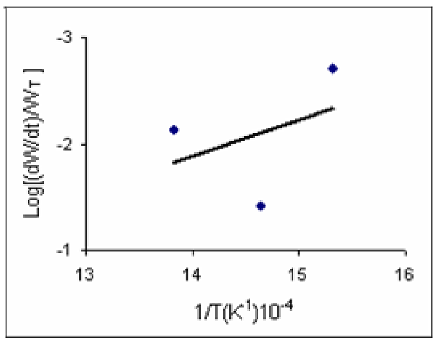

Fig. 2: (a) pyrrole 1 wt. %

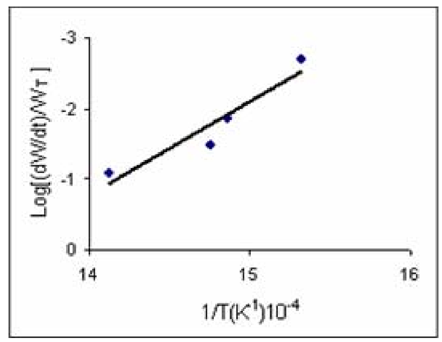

Fig. 2:(b) pyrrole 5 wt. %

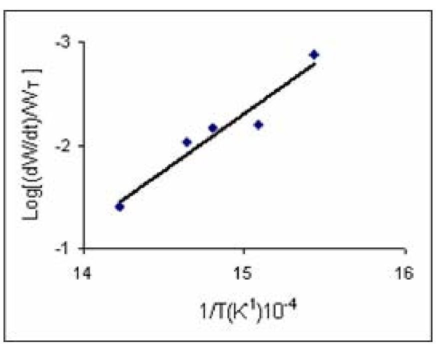

Fig. 2:(c) pyrrole 8 wt. %

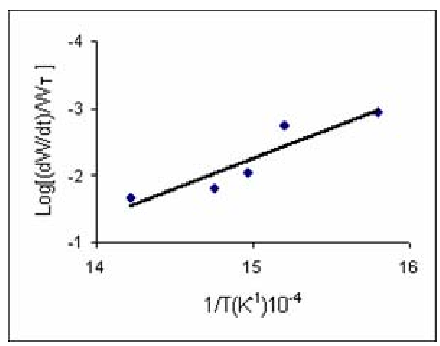

Fig. 2:(d) pyrrole 10 wt. %

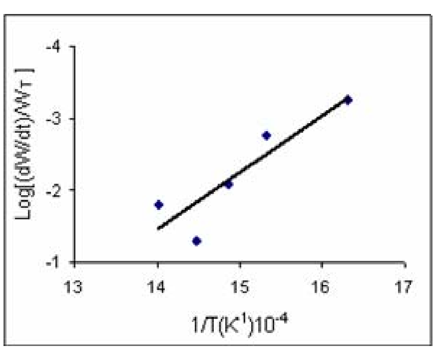

Fig. 2:(e) pyrrole 12 wt. %

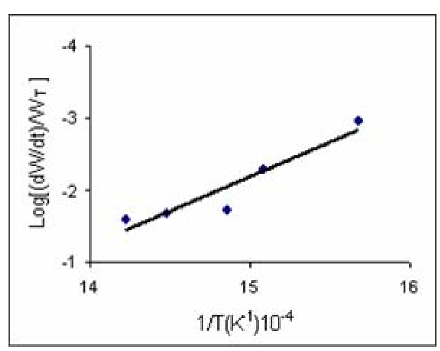

Fig. 2:(f) pyrrole 15 wt. %

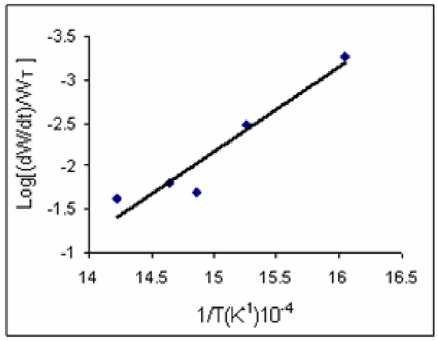

Fig. 2:(g) pyrrole 20 wt. %

(a) "Integral" method utilizing weight loss versus temperature data directly (b) "differential" methods utilizing the rate of weight loss (c) " difference-differential" methods involving differences in rate (d) methods specially applicable to initial rates and (e) nonlinear or cyclic heating rate methods.

Differential method based on the rate of weight of loss versus temperature data has been devised which are much simpler in application. The difference – differential method of Freeman and Carroll and in modification (Anderson et al, 1961) is the most widely used method for the kinetic analysis of thermo gravimetric data. It has been applied both to the investigation of inorganic materials and polymers, (Anderson et al., 1961, Anderson et al, 1962, Coat et al., 1963, Lgarashi et al., 1964, Chatterjee et al., 1965, Kurosu et al, 1995).

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