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Thermal characterization of urea phthalic acid material with thermal kinetic calculations

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Abstract---Urea Phthalic acid crystalline material was grown by slow evaporation method. The material was studied by Coats – Redfern method to calculate the thermal kinetic parameters. By analyzing the results, the nature of decomposition reaction of Urea Phthalic acid was investigated. The calculated values of thermal parameters indicate that the material is suitable for device fabrication applications.

Keywords---thermal characterization, urea phthalic acid, thermal kinetic calculations.

Introduction

Many functional materials were synthesized and characterized for their industrial applications [1-3]. By combining Urea with Phthalic acid, a novel Urea Phthalic acid crystal has been grown. The grown crystals were characterized with several techniques such as powder XRD analysis, FT-IR spectroscopic analysis to recognize the functional groups, UV-Vis spectroscopic analysis to detect the transmission of incident light in the visible region, dielectric studies to analyze

electrical properties and mechanical studies by Vickers microhardness tester to understand hardness of the material and reported by K. Sathishkumar et al [4]. Thermal characterization by TGA/DSC analysis, hardness studies by analyzing various parameters such as Vickers microhardness number, work hardening coefficient, yield strength, stiffness constant, brittleness index, standard hardness and fracture toughness as well as dielectric studies by varying applied frequency at different temperatures, the change in dielectric constant, dielectric loss and ac conductivity of Urea Phthalic acid (UPA) was analyzed and reported by M. Suresh Kumar et al [5]. For device fabrication applications, the materials used should possess more thermal stability [6-7]. Consequently, thermal characterization with the calculation of thermal kinetic parameters namely activation energy, activation entropy, activation enthalpy and Gibbs free energy change in decomposition are necessary to understand about the thermal stability and nature of decomposition reaction of a material. In this article, the above thermal kinetic parameters have been computed by Coats – Redfern method and the results were analyzed for UPA material.

Experimental Procedure

Crystal Growth

To grow crystals of UPA, solution growth method with slow evaporation technique was used. Urea was mixed with phthalic acid in the stoichiometric ratio of 1:1 and dissolved in doubly distilled water and the solution was stirred well for 5 hours using a magnetic stirrer. Then the saturated solution has been filtered and kept at constant temperature bath for slow evaporation of water from the solution. UPA seed crystals have been attained from the mother solution after 3 weeks and the grown crystals were recrystallized to get optically good quality crystals.

Results and Discussion

Coats – Redfern method

The TGA /DSC study was carried out using NETZSCH TG - DSC from 30°C to 800°C in the nitrogen atmosphere at the heating rate of 10°C per minute. The initial mass of sample UPA taken for this experiment is 8.506 mg. The melting point of UPA is 490 K. From the TGA study, it was found that 34% of mass loss between 465 K and 484 K and 60% of mass loss from 498 K to 507 K for UPA material. These two ranges of decomposition were taken for the thermal kinetic calculations. The data used for these calculations was taken from Thermogravimetric Analysis (TGA) of UPA.

Coats – Redfern method is an integral method used to calculate kinetic parameters such as activation energy, enthalpy of activation, entropy of activation and Gibbs free energy change of decomposition of UPA. The kinetic parameters of thermal degradation process can be determined by the following relation for theoretical values of order of reaction, $n = 0, 1/2$ and $2/3$ except for $n=1$ [8].

$$\log_{10} \left[\frac{\{1-(1-\alpha)^{1-n}\}}{T^2(1-n)} \right] = \left[\log_{10} \left\{ \left(\frac{AR}{\beta E} \right) \left(1 - \frac{2RT}{E} \right) \right\} - \left(\frac{E}{2.303 RT} \right) \right] \quad (1)$$

For $n=1$, the following modified equation was used.

$$\log_{10} \left[\frac{-\log_{10}(1-\alpha)}{T^2} \right] = \left[\log_{10} \left\{ \left(\frac{AR}{\beta E} \right) \left(1 - \frac{2RT}{E} \right) \right\} - \left(\frac{E}{2.303 RT} \right) \right] \quad (2)$$

Where, α is the fraction of decomposed material, A is pre-exponential frequency factor, R is the gas constant, β is the heating rate in K/minute, E is the activation energy and T is the temperature in K.

The equation for α is given by

$$\alpha = \frac{(W_o - W_t)}{(W_o - W_f)} \quad (3)$$

Where, W_o is the initial mass of the sample at the starting temperature, W_t is the mass of the sample at temperature T and W_f is the final mass of the sample at which the mass loss is approximately unchanged [9]. The correct value of n can be obtained by the best linear curve drawn between $(1/T)$ and $\log_{10} \left[\frac{\{1-(1-\alpha)^{1-n}\}}{T^2(1-n)} \right]$ for the values of n except $n=1$ and drawn between $(1/T)$ and $\log_{10} \left[\frac{-\log_{10}(1-\alpha)}{T^2} \right]$ for $n=1$. The graphs were plotted for the two ranges of temperatures and are shown in figures 1 and 2.

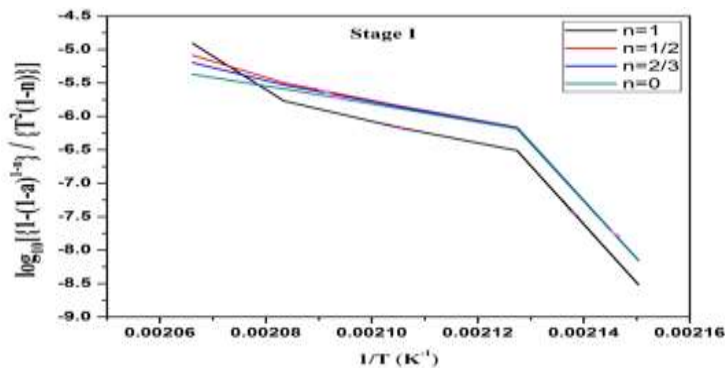


Figure 1: Plot between L.H.S of equation (1) & (2) and $1/T$ for 465 K-484 K

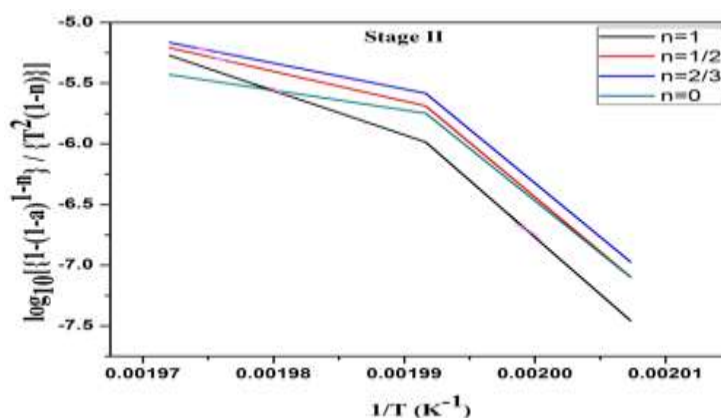


Figure 2: Plot between L.H.S of equation (1) & (2) and $1/T$ for 498 K-507 K

The slope of the linear curve gives the activation energy (E) and the interception gives the pre-exponential frequency factor (A). Both the values were calculated for UPA, which are tabulated. The other kinetic parameters enthalpy of activation (ΔH), entropy of activation (ΔS) and Gibbs free energy change of decomposition (ΔG) were calculated by the following relations [10].

$$\Delta H (\text{KJmol}^{-1}) = E + \Delta nRT$$

(4)

$$\Delta S (\text{JK}^{-1} \text{mol}^{-1}) = 2.303 R \log_{10} \left(\frac{Ah}{KT} \right)$$

(5)

$$\Delta G (\text{KJmol}^{-1}) = \Delta H - T \Delta S$$

(6)

Where, Δn = Number of moles of product – Number of moles of reactant in the reaction, h is Planck's constant and K is Boltzmann constant. The calculated values are tabulated in table 1.

Table 1: Kinetic parameters of UPA

| Range of Temperature | E (kJmol^{-1}) | ΔH (kJmol^{-1}) | ΔS ($\text{JK}^{-1} \text{mol}^{-1}$) | ΔG (kJmol^{-1}) | A (min^{-1}) |
|----------------------|-----------------------------|------------------------------------|---|------------------------------------|---------------------------|
| 465 K-484 K | 765.89 | 769.83 | -61.63 | 799.18 | 5.86×10^9 |
| 498 K-507 K | 683.83 | 688.01 | -61.28 | 718.79 | 6.59×10^9 |

with temperature. The entropy of activation (ΔS) values are negative, which indicate that the activated complex has more ordered structure than the reactants. The positive values of Gibbs free energy change of decomposition (ΔG) show that the dissociation processes are nonspontaneous [11]. The high value of activation energy (E) confirms that high degree of thermal stability and resistance to heat. This leads to the application in improving hardness of the UPA material [12].

Conclusion

The thermal kinetic parameters were calculated by Coats – Redfern method for the UPA material. The results show that the decomposition reaction is rapid and endothermic in nature. It is also found that the process is nonspontaneous and enhanced with temperature. The very high value of activation energy confirmed the material UPA is thermally more stable and UPA offers more resistance to heat. Hence, UPA is suitable for device fabrication applications.

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