Study of Thermal Decomposition of Polystyrene Using Viscometric Analysis and Assessment of Its Reaction Rate Models

Dr. Aniruddh Singh[1], Arun Maurya[2] and **Rohit Patel[3]**
[1]Department of Applied Science and Humanities,
[2]Department of Electrical and Electronics Engineering, [3]Department of Civil Engineering
Ajay Kumar Garg Engineering College, 27 Kmstone, NH-24, Adhyatmic Nagar, Ghaziabad 201009 UP India
ani_rud_dh@hotmail.com

Abstract -- **Kinetics of thermal decomposition of polystyrene atatic was studied by non isothermal analysis. Method of determination of molecular mass with the help of solution viscometry at different stages of the reaction was applied to determine the extent of the reaction. Activation energy was determined using a model independent isoconversional method. The reaction model was determined from value of activation energy thus established and utilization of non-isothermal data without taking recourse to curve fitting.**

Keywords: Thermal Decomposition, Viscometric Analysis, Mark Houwink Sakurada relation, Isoconversional method

I. INTRODUCTION

SOLUTION viscometry is a standard technique to study the molecular mass of a given polymer sample. The method is extensively used in polymer science to physically characterize the sample and determine its physio-chemical properties as function of molecular weight. The analysis is also important when critical tailoring of properties is required for a specific market application. The determination of the molecular mass of the polymer for a thermally treated sample is based upon the famous Mark Houwink Sakurada relation which relates the intrinsic viscosity of the dilute solution of the polymer with its viscosity averaged molecular mass [1]:

$$[\eta] = K[M_V]^a \tag{1}$$

where $[\eta]$ is the intrinsic viscosity of the polymer solution, and $[M_v]$ is the viscosity averaged molecular mass of the polymer. K and a are the Mark Houwink co-efficients which are dependent on the combination of solute and solvent being used and also temperature. The values of these coefficients are tabulated at various places [2].

The study of decomposition of polymers with the help of viscometry is a valid approach and had been employed earlier at various places such as study of ultrasonic degradation of superabsorbent hydrogels [3]. The decomposition of polymers is a process slightly different from the decomposition of simple solids. In ordinary solids, a small number of elements compose the molecule of the solid. When such a solid decomposes, it usually converts in to molecules of lower molecular mass, some of which are gaseous in nature. Thus the loss of such volatile molecules results in considerable decrease in the mass of the reactant in the sample and thus is amenable to gravimetric analysis.

In case of polymers which are macromolecules of a very large molecular mass, the process of chain scission in the middle of the polymer chain results in decomposition without any mass loss of the sample. On the other hand, two broken chains can join together and form a larger chain. On an average, these two competitive processes nullify each other and the number of polymer chains may not change substantially. The reduction in the average molecular mass of the sample is then seen as a result of breaking off of monomer units from the end of the chain and escaping the reaction area in gaseous form. Thus the average molecular mass as determined by solution viscometry is a good indicator of the extent of the reaction and is comparable with other thermo-gravimetric methods.

In this technique with the use of the Mark Houwink equation, the average molecular mass of the that sample can be determined directly which undergoes decomposition over a period of time or as a function of temperature. The limitation imposed by the thermogravimetric method for the determination of the kinetic triplet, which is that the decomposition process must be non isothermal and the sample is heated at a constant rate[4], is not applicable in present method and this method is open to both isothermal and non isothermal studies.

II. KINETIC MODELING-THEORETICAL BACKGROUND

The basic rate equation is given by:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{2}$$

where α represents the extent of reaction, t is the time, $k(T)$ is the temperature-dependent rate constant which is of the Arrhenius type, $f(\alpha)$ represents a particular reaction model. Several reaction models have been suggested [5] depending upon the physical conditions and are tabulated in Table 1. The temperature dependence of the rate constant is expressed by the following equation:

$$k = A exp(-\frac{E}{k_B T})$$ (3)

where A and E are the pre exponential factor and the activation energy. The three parameters ($A, E, f(\alpha)$) constitute the kinetic triplet which determine the overall kinetics of the reaction. The aim of the present study is to find out these three parameters for thermal decomposition of polystyrene.

Several methodologies have been proposed to extract these parameters from the kinetic data. They fall under two broad categories: Isoconversional and model fitting methods. Although it has been reported in literature that isoconversional method is free from the ambiguity that model fitting method produces [6], it has been stressed upon that the complete information about the reaction should also include the reaction model that is being followed by the reaction [5]. In this work, a novel method is proposed which disposes of the inherent ambiguity of curve fitting and produces the most accurate kinetic triplet unambiguously.

The parameter α which is the extent of the reaction is determined by the following equation:

$$\alpha = \frac{m_o - m_t}{m_o - m_f}$$ (4)

where m_t is the mass of the sample at particular temperature. m_o and m_f are the initial and final masses of the reaction respectively.

Integrating equation (2) one gets:

$$g(\alpha) = \int_0^\alpha [f(\alpha)]^{-1} d\alpha = k(T)t$$ (5)

Substituting for $k(T)$ from equation (3) and taking the log one gets:

$$\ln(t) = \frac{E}{RT} - \ln\left(\frac{g(\alpha)}{A}\right)$$ (6)

For a constant value of α, one can find out the activation energy E by the slope of log t versus $[T]^{-1}$ plot. This method was proposed by Kujirai and Akahira [4] and they were the first to propose the isoconversional method of kinetic evaluation.

TABLE 1 -- SOLID-STATE RATE AND INTEGRAL EXPRESSIONS FOR DIFFERENT REACTION MODELS

| Sl. No.	Model	Differential form $f(\alpha) = \frac{1}{k}\frac{d\alpha}{dt}$	Integral form $g(\alpha) = kt$
1. Nucleation models(1 to 6)	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
2.	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
3.	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
4.	Avrami-Erofeyev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
5.	Avrami-Erofeyev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
6.	Avrami-Erofeyev	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
7. Geometrical Contraction Models (7 to 8)	Contracting Area	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
8.	Contracting Volume	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
9.Diffusion models (9 to 12)	1D diffusion	$1/(2\alpha)$	α^2
10.	2 D diffusion	$-[\frac{1}{\ln(1-\alpha)}]$	$(1-\alpha)\ln(1-\alpha) + \alpha$
11.	3 D diffusion-Jander	$[3(1-\alpha)^{\frac{2}{3}}]/[2(1-(1-\alpha)^{\frac{1}{3}})]$	$(1-(1-\alpha)^{1/3})^2$
12.	Ginstling-Brounshtein	$3/[2((1-\alpha)^{-\frac{1}{3}}-1)]$	$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}$
13 Reaction order models (13 to 16)	Zero order	1	α
14.	First order	$(1-\alpha)$	$-\ln(1-\alpha)$
15.	Second order	$(1-\alpha)^2$	$[\frac{1}{1-\alpha}]-1$
16.	Third order	$(1-\alpha)^3$	$(\frac{1}{2})[(1-\alpha)^{-2}-1]$
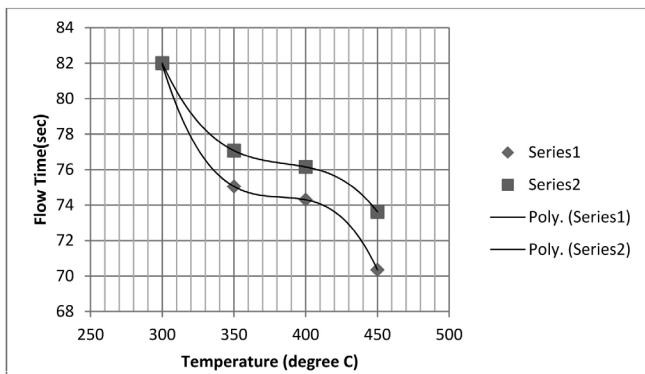
Figure 1. Flow time (*y*-axis) vs Temperature (*x*-axis) plot. Series 1 curve is for 20 min thermal treatment and Series 2 curve is for 10 min thermal treatment. Curve fitting done by a polynomial of order 6.

Figure 2. Flow time (*y*-axis) vs Temperature (*x*-axis) plot. Series 1 curve is for 20 min thermal treatment and Series 2 curve is for 10 min thermal treatment. Curve fitting done by a polynomial of order 2.
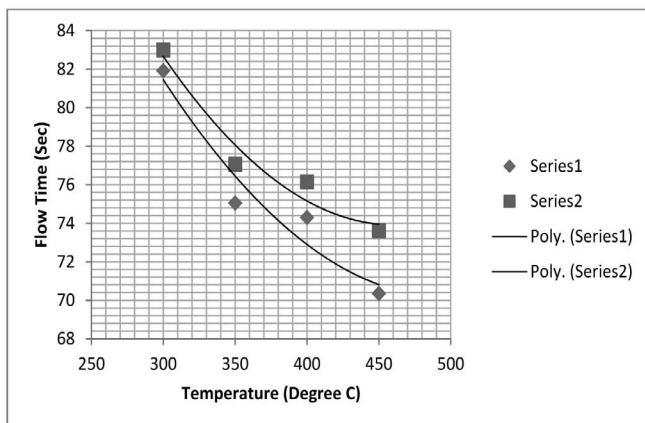
III. EXPERIMENTAL: VISCOMETRIC EVALUATION OF THE EXTENT OF REACTION A.

Figures 1 and 2 show the flow time of the solution of polystyrene samples made by dissolving 1 gm polystyrene in 100 ml benzene. Prior to dissolution, the polystyrene sample is thermally treated in a muffle furnace for temperatures ranging from 300° C to 450° C for 10 min and 20 min. Solution is passed through an Ubbelohde viscometer with capillary diameter of 0.63 mm purchased from SI Analytics Germany and flow time is noted by SI Analytic automatic viscosity measurement comprising of Xylem Analytic Viscoclock which measures the flow time with an accuracy of 0.1%. The capillary was kept in a Syskin Thermostat viscobath at 30° C.

The intrinsic viscosity of the solution is calculated from a single concentration by the Solomon-Ciuta equation [7] given by:

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - ln(\eta_r)}}{c} \tag{7}$$

where

$$\eta_{sp} = \frac{t - t_0}{t_0} \tag{8}$$

and

$$\eta_r = \frac{t}{t_o} \tag{9}$$

where *t* is the time of flow of the solvent, t_o is the time of flow of the pure solvent and *c* is the concentration. From the value of intrinsic viscosity calculated with the help of equation (7), one can calculate the molecular mass at a given temperature by using Mark Houwink Sakurada equation (Equation (1)). The experiment is done at 30^0 C and the value of Mark Houwink parameters are obtained from literature [2]. The extent of reaction α is defined by the following equation.

$$\alpha = \frac{M_0 - M_t}{M_0 - M_\infty} \tag{10}$$

Here M_0 is the mass of the polymer at the start of the reaction, M_t is the mass at time *t* and M_∞ is the final mass which in our case is zero at the end of the decomposition. The value of [η] and α are tabulated for 3 different temperatures using the values of flow time from figure 2.

TABLE 2 -- INTRINSIC VISCOSITY [H] (ml/gm) AND EXTENT OF REACTION A FOR DIFFERENT TEMPERATURES FOR SERIES 1

Temperature (°C)	Flow Time (Sec)	Intrinsic viscosity [η] (ml/gm)	Extent of reaction α
330	78.2	12.369	0.401
380	74.4	7.252	0.722
420	72.0	5.656	0.806

Calculations: Activation energy for the given decomposition reaction was calculated by a model free method. The reaction was studied at different temperatures by giving heat treatment for two different durations. The temperatures for the two treatments were noted for a given flow time. Since the two temperatures obtained for a single flow time imply that the decomposition is same at the two temperatures, the method employed is an isoconversional method. From equation (3) and (5) we get:

$$g(\alpha) = Aexp\left(\frac{-E}{k_B T_1}\right) t_1 = Aexp\left(\frac{-E}{k_B T_2}\right) t_2 \tag{11}$$

where T_1 is the treatment temperature of the sample at a given α treated for time t_1 and T_2 is the treatment temperature for the same α treated for time t_2. From equation (11)

$$exp\left(\frac{-E}{k_B}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right) = \frac{t_2}{t_1} \tag{12}$$

Since $t_1 = 20$ min and $t_2 = 10$ min, we get after taking the log on both sides:

$$\left(\frac{E}{k_B}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right) = \ln 2 \qquad (13)$$

Below we have tabulated the temperature for the two series of measurements at three different flow times.

TABLE 3 -- FLOW TIME VS TEMPERATURE FOR SERIES 1 AND 2 OF FIG.2.

Flow Time(sec)	T_1 (°C)	T_2 (°C)	Activation Energy (J)
78	333	350	2.123×10^{-19}
76	355	380	1.568×10^{-19}
74.4	370	410	1.049×10^{-19}

From the table, it is clear that activation energy is not constant and is varying with the extent of conversion of the polymer during decomposition. This clearly indicates that more than one mutually competitive models of reaction kinetics are operational in the given process. Although it can also be seen that the variation in the activation energy is not enormously large and thus the method gives a reliable estimate of the activation energy.

To obtain the best model we consider the average value of the activation energy. The value of g(α) for different models given in table 1 are calculated for values of α tabulated in table 1. These values are compared with values calculated from right hand side of equation (5). From equation (5)

$$\frac{g(\alpha_1)}{g(\alpha_2)} = \frac{\exp(\frac{-E}{k_B T_1})}{\exp(\frac{-E}{k_B T_2})} \qquad (14)$$

The model for which the above equation holds with greatest accuracy is taken as the best model for the reaction. In the table 4 given below the values of $g(\alpha_1)/g(\alpha_2)$ for models given in table 1 are calculated for temperatures 330°C and 380°C for values of α taken from table 2.

The value of the right hand side of equation (14) for average of the activation energy values given in table 3 and for temperatures $T_1 = 330$°C and $T_2 = 380$° C is calculated to be equal to 0.2515.

TABLE 4 -- VALUES OF $g(\alpha_1)/g(\alpha_2)$ FOR VALUES Of α TAKEN FROM TABLE 2 FOR MODELS OF TABLE 1

Model Number	$g(\alpha_1)/g(\alpha_2)$
1	0.7452
2	0.8219
3	0.8632
4	0.6327
5	0.7370
6	0.7954
7	0.4781
8	0.4557
9	0.3084
10	0.2567
11	0.2043
12	0.2378
13	0.5554
14	0.4003
15	0.2577
16	0.1496

The values given in the second column of table 4 are compared with the value calculated using the right hand side of equation (14). It is found that only two models, model 10 which is the 2 D diffusion model and model 15 which is the second order reaction model come close to value calculated by right hand side of equation (14).

IV. DISCUSSION AND CONCLUSION

It has been found from the above study that a 2 D diffusion model gives best comparison with the values calculated from the data. The 2D diffusion model is applicable when the reacting particle is a solid cylinder and diffusion occurs in the radial direction across a cylindrical shell. The group of polymer chains thus acts as a reacting cylinder and the 2D reaction model appears to be applicable in the given condition. The second order reaction model also appears to fit in as number of reaction sites exposed to the reaction conditions are proportional to the surface area. In order based reactions which are applicable under homogeneous reaction environment, the rate is proportional to the concentration raised to a particular power. If the volume occupied by the reactants is proportional to the cube of concentration then the surface area exposed to the reaction is proportional to its square and the second order reaction becomes a possibility.

The advantage of the methodology followed in this study is that the determination of the activation energy occurs before the model is fixed. Thus in this type of study, the activation energy is not model dependent and is determined by isoconversional technique. Also the model of the reaction is not fixed by varying the values of the activation energy and preexponential factor and finding the best fit. This type of method which is usually followed gives ambiguity in the fixing of models as several models give comparable statistical results. In our method, the model is fixed unambiguously from a single value of activation energy calculated from isoconversional method.

REFERENCES

[1] F.W. Billmeyer, *Textbook of Polymer Science*, Wiley Edition, pp. 209-210.

[2] Appendix I - Springer Link link.springer.com/content/pdf/bbm%3A978-3-662-03910-6%2F1.pdf

[3] Rajabali Ebrahimi, Giti Tarhande, and Saeed Rafiei "The Study of Ultrasonic Degradation of Superabsorbent Hydrogels", *Organic Chemistry International*, Article ID 343768, 2012.

[4] Sergey Vyazovkin and Charles A. Wight , "Isothermal and non-isothermal kinetics of thermally stimulated reactions of solids", *International Reviews in Physical Chemistry*, vol.17, no.3, pp. 407- 433, 1998.

[5] Ammar Khawam and Douglas R. Flanagan, "Solid-State Kinetic Models: Basics and Mathematical Fundamentals", *J. Phys. Chem. B*, vol. 110 (35), pp. 17315-17328, 2006.

[6] S. Vyazovkin Chapter 4: "Modern isoconversional kinetics", pp. 131-172 in: *The Handbook of Thermal Analysis & Calorimetry*, vol.6: Recent Advances, Techniques and Applications, 2nd ed.", Eds. S. Vyazovkin, N. Koga and C. Schick, Elsevier, p. 842, 2018.

[7] Werner-Michael Kulicke and Christian Clasen, *Viscosimetry of Polymers and Polyelectrolytes*, ISBN 3-540-40760-X Springer-Verlag.

Dr. Aniruddh Singh is PhD in nuclear physics from Jamia Millia Islamia, New Delhi. He has done his post graduation from IIT Kanpur and graduation from Delhi University. Possesses teaching experience of over 14 years. Published several papers in reputed national and international journals.

Arun Kumar Maurya student in Department of Electrical and Electronics Engineering, Ajay Kumar Garg Engineering College (2016-2020 batch) completed 12th standard from Jainarayan Inter College, Bareilly. Involved in many projects at AKGEC like AICTE, Smart India Hackathon, KPIT Sparkle and University projects. Recently published a research paper on "An evolutionary optimization based fuzzy-PID controller design". His key interest areas include Power Systems, Signals and Systems, Polymer Synthesis and Electrical Machines.

Rohit Patel completed 12th from St. Mary's Inter College, Mauranipur, Jhansi district, UP. Involved in many projects at AKGEC like AICTE, Smart India Hackathon, KPIT Sparkle and University projects. Recently won the National Level Technical Paper Presentation 'Scrolls'. His key Interest areas include Environmental Research, Road Construction, Polymer Synthesis and Structure Designing.