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Studies on non-isothermal kinetic of solid state decomposition of polymethyl methacrylate

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ABSTRACT

Non-isothermal kinetics of solid-state decomposition of Polymethyl Methacrylate [PMMA Mw: 1.5×10^4] has been investigated under nitrogen atmosphere. Thermal data deduced through simultaneous thermogravimetric-differential thermal analysis -differential thermo gravimetric [TG-DTA-DTG] was used for calculations of thermodynamic parameters through Horowitz-Metzger and coats-Redfern methods along with kinetics and mechanism of degradations. © 2008 Trade Science Inc. - INDIA

INTRODUCTION

The quality control and assessment in the industrial polymers have been found to be tedious and a series of experimental techniques were developed since past few decades^[1-2]. Among such techniques, thermo analytical methods has emerged as a rapid and cost effective substitute over other analytical methods with reproducible results^[3-4]. Most of the modern chemical and metallurgical industries employ process involving solid-state gas-solid interface reactions. A detailed knowledge of the thermodynamics, kinetics and reaction mechanisms of these thermally induced processes is of immense help to optimize and control the operating parameters leading to design of proper process equipment. Thermal analysis techniques like thermogravimetry (TG), differential thermal analysis (DTA) etc, where the property of a substance measured, as a function of temperature is extremely useful in this context^[5]. In addition, if real time analysis of the product gases evolved during a ther-

mally induced reaction will greatly enhance the possibility of correctly interpreting the kinetic data and arriving at most appropriate mechanism governing the process. Thus, knowledge of single particle kinetics becomes a pre-requisite for studying interface transport phenomena between moving gas stream and porous of solid materials^[6]. Such single particle kinetics can be easily studied through simultaneous TG-DTA-DTG. The technique TG-DTA-DTG is frequently used as a means of assessing the thermal stability and conveniently provide valuable information about kinetics and thermodynamics of the solid state decompositions of polymers and related heat resistant materials^[5,6].

MATERIALS AND METHODS

PMMA with molecular mass (PMMA Mw: 1.5×10^4) was synthesized through AIBN initiated free radical polymerization of freshly distilled monomer at $100 \pm 1^\circ\text{C}$. The molecular mass of synthesized PMMA

was deduced over Varian Pro Star 230 HPLC/GPC system coupled with RI detector. THF was used as mobile phase at the flow rate of 1.0 mL/min .

Thermal characterization of PMMA was made through simultaneous TG-DTA-DTG over NETZSCH-Geratebau GmbH Thermal Analyzer model Perkin Elmer (Pyris Dimond) 1000°C. The sample size was 10.95 mg. The samples were allowed to decomposed in nitrogen at heating rate of 26°C/5.0 (Cel/min)/1000°C using alumina as a reference TABLE 1. Thermal data were used for calculations of thermodynamic parameters through Horowitz-Metzger (HM)^[7] and coats-Redfern (CR) methods TABLE 2^[8]. Non-isothermal kinetics of solid-state decomposition of samples has been calculated from TG data to ascertain the rate controlling process according to the procedure reported by Sestak Berggren and Satava^[9]. In this procedure evaluations were made from, different integral forms of kinetic expressions and the declaring rate equation based on diffusion was studied in terms of parabolic law satisfied to one dimensional transport (D_1), two dimensional diffusion (D_2), three dimensional diffusion according to Jander equation (D_3) and three dimensional diffusion according to Ginstling-Brounshtein equation (D_4) and the rate laws at one dimensional, zero order (R_1), two dimensional; cylindrical symmetry (R_2) and three dimensional spherical symmetry (R_3) TABLE 3.

RESULTS AND DISCUSSION

Thermal decomposition of PMMA was investigated through simultaneous TG-DTA-DTG in nitrogen. PMMA showed two step decomposition figure 1, with increasing order of weight loss at temperature ranging 100-500°C. Within this temperature range, PMMA has shown maximum of 16% weight residue at 300°C. This was further supported with a DTA endotherm at 275°C

TABLE 1: Thermal properties of PMMA

Thermal properties	Temperature (°C)	Assignment
TG [Weight residue (%) / °C]	100	0.64
-	200	4.48
-	300	16.00
-	400-500	35.2
DTA [ΔH (°C/ mJ/ mg)]	275	31.5
DTG [°C/ mg/ min]	143	0.2
-	280	0.1
-	330	0.4

TABLE 2: Kinetic and thermodynamic data of solid state decomposition of PMMA

Reaction order (n)	Method	E (kg/mol. $\times 10^3$)	Z (min^{-1})	ΔS ($\text{JK}^{-1}/\text{min}$)
0	CR	48.804	5.731	-13.456
	HM	82.764	6.130	-12.886
1	CR	56.328	2.894	-20.497
	HM	100.987	6.876	-7.342
2	CR	80.6732	5.895	-16.8876
	HM	145.870	10.976	-0.98534

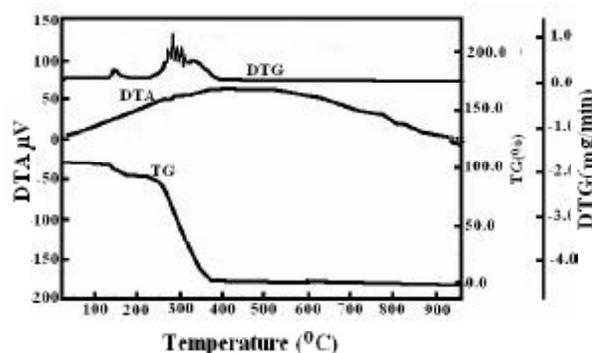


Figure 1: TG-DTA-DTG spectrum of PMMA

associated with ΔH (°C/mJ/mg) as 31.5. A three successive DTG profiles were shown by PMMA at 143, 280 and 330°C respectively, corresponding to their respective rate of decompositions ranging 0.1-0.4 with maximum at 330°C TABLE 1.

The kinetic and thermodynamic data of solid state decomposition of PMMA deduced through CR figures 2(a-c) and HM figures 3(a-c) methods and are sum-

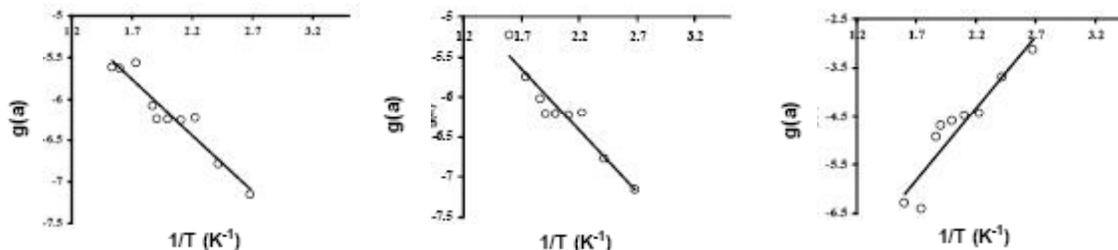


Figure 2(a): CR plot of PMMA for n=0, (b): CR plot of PMMA for n=1, (c): CR plot of PMMA for n=2

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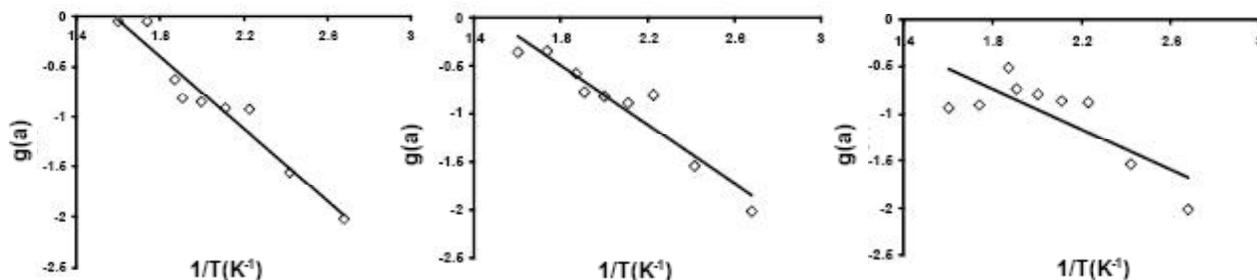


Figure 3: (a): HM plot of PMMA for $n=0$, (b): HM plot of PMMA for $n=1$, (c): HM plot of PMMA for $n=2$

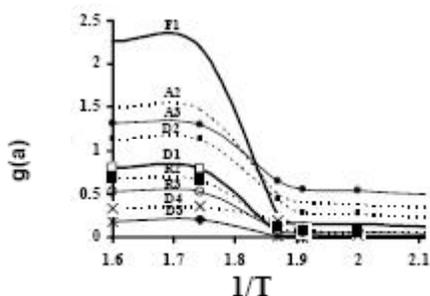


Figure 4: Kinetic models of solid state decomposition of PMMA

TABLE 3 : Mechanism of solid state decomposition verified for PMMA

D_1	$\alpha^2=kt$	1-dimensional diffusion (Parabolic law)
D_2	$(1-\alpha)[- \ln(1-\alpha)] + \alpha = kt$	2-Dimensional diffusion, cylindrical symmetry
D_3	$[1-(1-\alpha)^{1/3}]^2 = kt$	3-Dimensional diffusion, spherical symmetry (Jander equation)
D_4	$(1-2\alpha/3-(1-\alpha)^{2/3}) = kt$	3-Dimensional diffusion, spherical symmetry (Giastiling Brownshtein equation)
F_1	$-\ln(1-\alpha) = kt$	Random nucleation; One nucleus on each particle (Mampel equation)
A_2	$[-\ln(1-\alpha)]^{1/2} = kt$	Random nucleation (Avrami equation I)
A_3	$[-\ln(1-\alpha)]^{1/3} = kt$	Random nucleation (Avrami equation II)
R_2	$1-(1-\alpha)^{1/2} = kt$	Phase boundary reaction; cylindrical symmetry
R_3	$1-(1-\alpha)^{1/3} = kt$	Phase boundary reaction; spherical symmetry

marized in TABLE 2. It is evident that both of the methods have rendered a large discrepancy towards energy of activation, frequency factor and entropy change associated with solid state decomposition of PMMA at all the orders ranging 0.0-2.0. In general, HM method, has rendered higher values of the energy of activation and frequency factors over CR method. Both of the methods indicated negative entropy change indicating

heat resistant characteristics of PMMA .

The mechanism of solid state decomposition of PMMA has been verified through investigation of various kinetic models TABLE 3. This was studied in terms of variation $g(a)$ functions with $1/T$. The TG data indicated that the decomposition of PMMA was executed to higher $g(a)$ functions corresponding to various type of random nucleation models, followed by 2-dimensional diffusion (cylindrical symmetry), 1-dimensional diffusion, (parabolic law), phase boundary reaction (cylindrical symmetry) phase boundary reaction (spherical symmetry) and 3-dimensional diffusion, spherical symmetry (Giastiling Brownshtein equation), 3-dimensional diffusion, spherical symmetry (Jander equation) respectively figure 4.

CONCLUSION

PMMA with molecular mass $M_w: 1.5 \times 10^4$ was synthesized through free radical polymerization. The sample was characterized through HPLC/GPC and simultaneous TG-DTA-DTG in nitrogen. TG data were investigated for the evaluation of non isothermal kinetics and thermodynamics of the solid state decomposition of PMMA. The data indicated that the energy of activation, frequency factor and entropy change corresponding to decomposition of PMMA were higher for Horwitz Metzger over Coats and Redfern methods. In general, the decomposition of PMMA has satisfied possible kinetic models.

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