

A KINETIC ANALYSIS OF THE DEGRADATION OF GRAFTED ANIONIC POLYACRYLAMIDE GEL UNDER NONISOTHERMAL CONDITION

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Abstract

Grafted anionic polyacrylamide gel has been synthesised in the laboratory following radical polymerisation process. Kinetics of thermal degradation of synthesised gel was evaluated under nonisothermal condition by integral approximation method to determine the thermal stability of the material from thermogravimetric study. The activation energy for the thermal degradation was found to be significantly high for the gel material.

Keywords: Grafted anionic, Polyacrylamide gel, Non isothermal kinetics, Integral Approximation kinetics, Thermal Degradation.

1. Introduction

The kinetics of the thermal decomposition and degradation of solid state materials is a highly complex and frequently controversial subject [1]. The practical importance of the subject, however, has lead to a very extensive effort to understand the mechanisms which control such reactions. Extensive studies have been carried out on the non-isothermal decomposition kinetics of solid systems. Multiple techniques were cited in literature for determining the reaction mechanism and deducing the kinetic parameters [2]. Solid state reactions follow complex pathway compared to liquid and gas phase reaction. While the liquid and gas phase reactions can be described by order based kinetics, the solid phase reactions in most of the cases follow complex diffusion or interface controlled mechanism. The influence of heat and mass transfer on the phase boundaries are also to be taken into account for such reactions. Several thermoanalytical techniques are often used to follow the course of solid state reactions and among

Nomenclatures	
A	Pre-exponential factor, s^{-1}
A_0	Pre-exponential factor at 0 K, sec^{-1}
E	Activation energy, kJ/mol
$g(\alpha)$	Integral kinetic function
k	Reaction rate constant, s^{-1}
m	Temperature dependence of pre-exponential factor
n	Reaction order
R	Gas Constant, 8.314 kJ/mol/K
T	Reaction temperature, K
w	Weight at any time, g
w_0	Initial weight, g
w_∞	Final equilibrium weight, g
<i>Greek Symbols</i>	
α	Fraction of reaction
β	Heating rate, $^{\circ}C/min$

these thermo-gravimetry (TG) is the most common technique [3]. In different thermoanalytic techniques, properties like heat absorption, change in temperature, change in weight etc of the material are measured as a function of temperature or time [4]. In thermogravimetry the change in weight is recorded as a function of time or temperature for isothermal and non- isothermal cases, respectively.

Many works have been cited in the literature on the kinetic studies of thermal degradation of polymeric materials. Friedman [5] developed a kinetics equation for rate law and kinetic parameters to describe the thermal degradation of plastic for TGA data. The equation was successfully tested by several techniques, including conformations with constant temperature data that were available in the literature. Nam and Seferis [6] developed a composite methodology for multistage degradation of polymer. This extended methodology established analytical schemes for describing complex decomposition of polymer in rational manner, incorporating both experimental and theoretical considerations. Anderson and Freeman [7] used the non-isothermal method of Freeman and Carroll to investigate of the kinetics of thermal degradation of polyethylene and polystyrene. The authors compared the results of their investigation with the kinetics parameters reported by other investigation for the decomposition of these polymers. Wang et al [8] studied the kinetics of continuous thermal degradation of poly (styrene alkyl alcohol) in supercritical fluid. They interpreted the kinetics results by a mathematical model based on the continuous kinetics for specific and random degradation process, and obtained activation energies in the range of 5.9- 7.4 kcal/ mole for specific degradation process and 35 kcal/mole for random degradation process. Stuggs [9] developed a theoretical framework for characterising single step Arrhenius degradation kinetics in terms of a characteristic temperature range. The author developed an estimate of the average or steady mass loss rate which fully accounted for the interaction between the

degradation kinetics, the external heat flux, the heat losses and the latent heat of vaporization. Madras et al [10] studied the ultrasonic degradation of polystyrene and poly (vinyl acetate) in chlorobenzene and developed a model that successfully simulated the number average molecular weight, the polydispersity of the degraded polymer and the time evolution of the molecular weight distribution. Lee et al [11] studied the thermal degradation of poly(hexamethylene guanidine) phosphate by dynamic thermogravimetric analysis and pyrolysis GC-MS. The authors used Coats-Redfern [16] methods to investigate the degradation mechanisms at different stages.

Grafted anionic polyacrylamide gel (GAPAMG) finds lots of important applications, like fire extinguishing composition, fillers and reinforcing agent [12]. In the present investigation, GAPAMG was synthesized at the laboratory. The thermal degradation behaviour of GAPAMG is an important parameter for its characterization in various applications. The proposed degradation pathway of the material is given below [21]

Although many works have been done on the degradation kinetics of different polymers, no literature is presently available on the thermal degradation kinetics of GAPAMG, particularly the mechanism of the degradation. In the present investigation, therefore, the kinetics of decomposition of GAPAMG has been studied under non-isothermal conditions using thermo-gravimetry to determine the kinetic parameters such as order of reaction (n), activation energy (E) pre-exponential factor (A_0) and mechanism of degradation.

Theory

The fractional degradation of polymeric material can be expressed in terms of weight change in the following way

$$\alpha = \frac{w_o - w}{w_o - w_\infty} \quad (1)$$

where w_o , w and w_∞ , are the initial, at any instant during thermal analysis and final weight of the samples, respectively.

Decomposition reaction is expressed in terms of order based reaction kinetics, then it can be written as:

$$-\frac{d\alpha}{dt} = k(1-\alpha)^n \quad (2)$$

i.e, the rate of reaction is proportional to the n th power of un-decomposed part of the sample. The power n is considered as the order of the reaction and k is specific reaction rate. But the specific reaction rate is a function of temperature which can be expressed by Arrhenius equation

$$k = Ae^{-\frac{E}{RT}} \quad (3)$$

where E is the activation energy of the reaction. Substituting k from Eq. (3) into Eq. (2) results in the following equation:

$$-\frac{d\alpha}{dt} = Ae^{-\frac{E}{RT}}(1-\alpha)^n \quad (4)$$

After separating the variables from Eq. (4) the following equation can be obtained

$$-\frac{d\alpha}{(1-\alpha)^n} = Ae^{-\frac{E}{RT}} dt \quad (5)$$

The rate of heating $\beta = \frac{dT}{dt}$ or

$$dt = \frac{dT}{\beta} \quad (6)$$

Putting the expression of dt in Eq. (5) and integrating between limits T_1 and T_2

$$-\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \int_{T_1}^{T_2} e^{-\frac{E}{RT}} dT \quad (7)$$

Integrating between limits

$$-\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \int_{T_1}^{T_2} e^{-\frac{E}{RT}} dT \quad (8)$$

But the integral at the right side $\int_{T_1}^{T_2} e^{-\frac{E}{RT}} dT$ has no analytical solution.

Therefore several approximate solutions of the equations are available in literature [13-16].

In the present investigation the solution given by Coats and Redfren [16] was used to determine the kinetic parameters of the degradation reaction. The approximate solution of the integral as per this method is like the following

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (\text{for } n = 1) \quad (9)$$

and

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

If it is assumed that the expression $\ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right]$ remains constant [17] over the temperature range of degradation then the equation assumes a linear form.

Therefore, a plot of $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$ vs. $1/T$ for $n=1$ and $\ln\left[-\ln\left\{\frac{1-(1-\alpha)^n}{(1-n)T^2}\right\}\right]$ vs. $1/T$ for $n\neq 1$ gives the value of E from the slope $(-E/R)$ and value of A from the intercept $\ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right]$ [18].

2. Materials and Methods

2.1. Synthesis of GAPMAG

Synthesis of GAPMAG was carried out by radical polymerization using acrylamide monomer (E.Merck), potassium persulphate (Aldrich) and urea (Aldrich). 30 % (w/v) acrylamide was dissolved in distilled water and residual oxygen was removed by nitrogen bubbling through the solution for 45 minutes under stirring at 25°C. Then polymerization was initiated by drop wise addition of 5% (w/v) aqueous solution of potassium persulphate to the acrylamide solution over a period of 5 minutes. The reaction temperature was maintained at 60°C and the pH of the solutions was adjusted to 9 with the addition of sodium dihydrogen phosphate. The polymerization was conducted for a period of 3 hours. The final viscous solution was diluted to 3 times with water. The polymer was then isolated by precipitation with ethanol-acetone mixture and the precipitated mass was dried under vacuum at 60°C for a period of 8 hours. The plausible reactions at the different stages of the synthesis have been shown in Fig. 1.

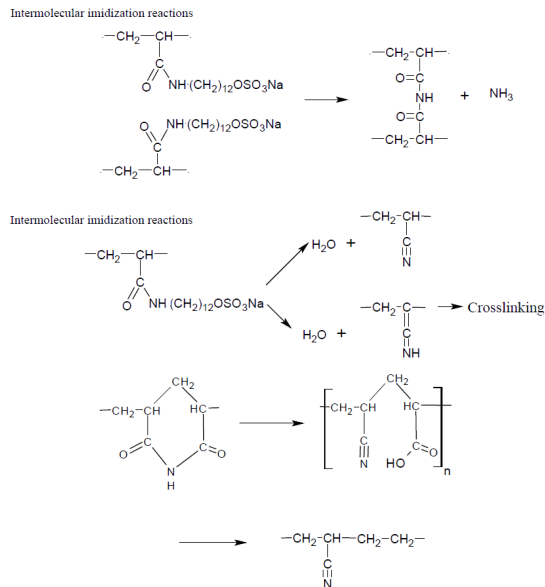


Fig. 1. The Proposed Schematic Reaction for Synthesis.

2.2. Degradation kinetics of the material

A weight of 0.5 g of the sample was taken in the form of powder for the thermo-gravimetric (TG) study with a TG apparatus (Model PerkinElmer Pyris 1 TGA). The weight change of the samples were recorded as a function of heating temperature and TG curves were obtained at four different heating rates (5, 7.5, 10 and 12.5°C/minutes) between 30 to 600°C; the precision of reported temperatures was estimated to be $\pm 2^\circ\text{C}$.

3. Results and Discussion

From the thermo-gravimetric curves (Fig. 2) it is apparent that there are three major inflections in the decomposition at three different temperature ranges, 250°C, 350°C and 450°C. The first stage decomposition indicates the breakage of primary bonds, second stage indicates the breakage of secondary bonds and the third stage decomposition indicates the breakage of tertiary bonds in the polymer structure [8]. The fraction decomposition values (α) were calculated from the thermo-gravimetric data and the values continuously increased with the increase in temperature (Fig. 3).

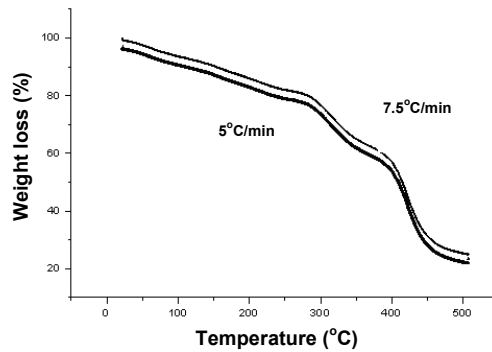


Fig. 2. TGA Result for Anionic Polyacrylamide Gel with Different Heating Rates.

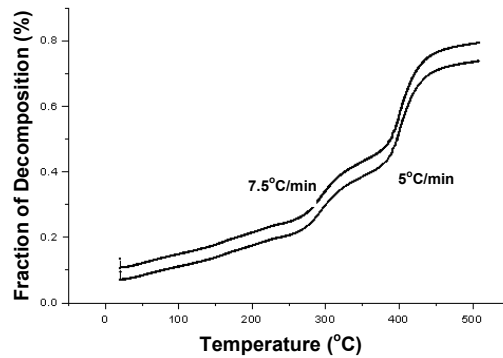


Fig. 3. Fraction Decomposition (α) versus Temperature $^\circ\text{C}$.

Using different 'n' values Eqs. (5) and (6) were plotted as discussed above. From these plots the 'n' value, which resulted in the best correlation coefficient was selected as the order of the reaction. The activation energy and the pre-exponential factors of the degradation reaction were determined from the slope and the intercept respectively of the linear plot for this particular 'n' value.

By integral approximation method we have determined the activation energy and reaction order for the degradation assuming that the reaction follows an order based kinetics. But in reality solid state reactions follow different complex reaction mechanisms, like diffusion controlled, interface controlled, nucleation and growth controlled etc. The actual mechanism of the degradation reaction in this case was determined using the method developed by Maitra et al [19]. In this method the integral form of kinetic function is expressed in the following form,

$$g(\alpha) = k [T_2^{n+1} - T_1^{n+1}] \quad (11)$$

where, T_2 and T_1 are the maximum and minimum values of the temperature for the degradation reaction.

$$k = \exp\left[\frac{\ln\{(A_0/T^m)/\beta\} - (E/RT_{\max})}{m+1}\right] \quad (12)$$

where A_0 is the pre-exponential factor, m shows the temperature dependence of the exponential factor. Considering the validity of transition state theory the value of m was taken as 1 [20].

The right hand side of Eq. (11) therefore can be evaluated at different T values and it is then compared with all possible $g(\alpha)$ functions with α values at these T 's. A list of all possible $g(\alpha)$ values is listed in Table 1. Each of this function describes the relevant mechanism for solid state reactions [22]. The function that results minimum difference between the L.H.S and the R.H.S is chosen as the kinetic function of the concerned heterogeneous reaction. In the present case it was found to follow mostly two dimensional diffusion controlled reaction (D_2).

Table 1. Classification of Kinetic Models for Reaction Mechanism [22].

Kinetic classification	$g(\alpha) = \int d\alpha / f(\alpha)$
(1) Sigmoidal α - t curves	
Avrami-Erofeev (A_2)	$[-\ln(1-\alpha)]^{3/2}$
Avrami-Erofeev (A_3)	$[-\ln(1-\alpha)]^{1/3}$
Avrami-Erofeev (A_4)	$[-\ln(1-\alpha)]^{1/4}$
Prout-Tompkins (B_1)	$[-\ln\alpha(1-\alpha)]+C$
(2) Acceleratory α - t curves	
Power law (P_1)	$\alpha^{1/n}$
Exponential Law (E_1)	$\ln(\alpha)$
(3) Deceleratory α - t curves	
(3.1) Based on Geometrical Models	
Contracting area (R_2)	$1-(1-\alpha)^{1/2}$
Contracting volume (R_3)	$1-(1-\alpha)^{1/3}$

Table 1. (cont'd).

Kinetic classification	$g(\alpha) = \int d\alpha / f(\alpha)$
(3.2) Based on diffusion mechanism	
One-dimensional (D_1)	$1/2 \alpha^2$
Two dimensional (D_2)	$(1-\alpha)\ln(1-\alpha) + \alpha$
Three Dimensional (D_3)	$[1-(1-\alpha)^{1/3}]^2$
Ginstling-Brounshtein (D_4)	$(1-2\alpha/3)-(1-\alpha)^{2/3}$
(3.3) Based on "order" of reaction	
First-order (F_1)	$-\ln(1-\alpha)$
Second-order (F_2)	$(1-\alpha)^{-1}$
Third-order (F_3)	$(1-\alpha)^{-2}$

The results are shown in Table 2. The decomposition reactions of the grafted polymer followed mostly 1.3 order reaction kinetics. The reason for fractional order may be ascribed to the incomplete availability of the gel surface for degradation, which can be related to the coverage of the un-degraded gel particles with the decomposed products. So, the degradation reaction of GAPAMG was likely to follow multi-stage process. The nucleation and growth of the decomposed product at the surface of the gel and the diffusion of volatiles like, CO₂ and other volatiles through the un-degraded material controls the rate of reaction. The activation energy for decomposition was found to be quite high (94.43 kJ/mol) compared to the data available for other polymers in literature [7-11]. The relatively higher value of activation energy for the degradation reaction is indicative of the significant thermal stability of the gel. The value of the pre-exponential factor was observed to be quite low ($3.7 \times 10^3 \text{ s}^{-1}$), which indicate the gel is relatively inert towards the formation of thermally induced activated complex.

Table 2. Variation in Standard Error (SE) for Grafted Anionic Polyacrylamide Gel (GAPAMG) with Different n Values.

n	Correlation Coefficient (SE)
0.25	0.8818
0.5	0.8792
0.7	0.9008
1	0.9052
1.1	0.9153
1.3	0.9802
1.5	0.9276
1.7	0.9331
1.9	0.9379
2	0.9217

4. Conclusions

The degradation kinetics reactions of the grafted polymer was studied under non-isothermal condition using Coats and Redfern integral approximation method was used to determined the kinetics parameters. The degradation kinetics reaction of the gel followed mostly 1.3 order reaction kinetics. The kinetic function for the degradation reaction was also determined, which was found to follow mostly two dimensional diffusion controlled reaction. The activation energy for decomposition was found to be quite high (94.43 kJ/mol) compared to the data available for other polymers in literature which is an indication of relative thermal stability of the gel.

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