

Thermal Degradation Study of Poly(vinyl Chloride): Kinetic Analysis of Thermogravimetric Data

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SYNOPSIS

The thermal degradation of a poly(vinyl chloride) (PVC) resin was studied using a non-isothermal thermogravimetric technique. Kinetic parameters such as activation energies, reaction orders, and preexponential factors are calculated using integral and differential methods reported in the literature. Advantages and disadvantages of these methods are discussed in order to characterize PVC. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In polymer science thermal methods of analysis have found important applications, among them the determination of kinetic parameters. For this purpose thermogravimetric analysis (TGA) is a technique widely used because of its simplicity and the information afforded from a simple thermogram. There are, however, many proposed methods to calculate kinetic parameters,¹⁻⁸ and these reported values depend not only on experimental conditions but also on mathematical treatment of data. In this paper we study the suitability of some of these methods in poly(vinyl chloride) (PVC) analysis.

THERMAL DEGRADATION OF PVC

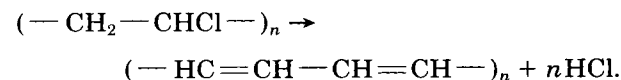
PVC degradation studies are very important because they make it possible to develop processing methods for PVC. The thermal degradation of PVC in a broad range of temperatures (up to and above 1000 K) is substantially a two-step process. The first step (up to 600 K) mainly involves dehydrochlorination of the polymer and formation of macromolecules with conjugated double C=C bonds that suffer cracking during the second step (up to 800 K). At tempera-

tures above 600 K the product also undergoes a partial carbonization with the release of free carbon among other products. At higher temperatures the decomposition mechanism becomes much more complicated. Therefore, it would be necessary to consider decomposition below and above 600–800 K separately. The first process is of the most interest because temperatures used in industrial processing never exceed 500 K and it is the most important for environmental reasons.

PVC Degradation at Moderate Temperatures (Below 600 K)

The main reaction at this temperature range is dehydrochlorination resulting in the formation of C=C bonds in macromolecules. Up to this temperature, HCl is the main volatile product (96–99.5%), the amount of other products being very low (1–3%) including quantities of benzene and some other hydrocarbons.

Usually, after a certain induction period, the dehydrochlorination of PVC can be expressed as:



Many mechanisms for dehydrochlorination have been proposed, mostly involving free radical reactions.⁵

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Higher Temperature Decomposition (Above 600 K)

When exposed to a continuously increasing temperature, PVC dehydrochlorination is completed at 600 K. Above this temperature the polymer has already become the dechlorinated product and the degradation under nitrogen (or inert atmosphere) continues with cracking and pyrolysis to low hydrocarbons of linear or cyclic structure (more than 170 products C₁–C₇ have been identified). Normally, at temperatures within the range 620–800 K there are more aromatic than aliphatic products. This situation is reversed above 800 K.

The residue of PVC pyrolysis at 670–730 K contains compounds whose molecular weight is 700–800 (principally aromatic hydrocarbons from three to five rings and unsaturated chains). Pyrolysis at higher temperatures (830–1100 K) yields a carbonaceous residue with a high carbon content (C : H > 2) and a mixture of simple composition gases.

The aim of this study is the determination of kinetic parameters for PVC degradation using some methods that have been used for other polymers and discussing and comparing the application of these methods to PVC. We have only considered the first step of PVC thermal degradation, namely dehydrochlorination of the polymer.

KINETIC METHODS

In these methods the following symbols are usual:

| | |
|----------|--|
| E_a | Apparent activation energies (kJ mol ⁻¹) |
| A | Preexponential factor (min ⁻¹) |
| n | Apparent order of reaction |
| R | Gas constant (8.3136 J mol ⁻¹ K ⁻¹) |
| T | Temperature (K) |
| α | Degree of conversion or fractional mass loss |
| t | Time (min) |
| β | Heating rate (K min ⁻¹) |
| k | Rate constant |

All kinetic studies utilize the basic rate equation:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

that expresses the rate of conversion, $d\alpha/dt$, at a constant temperature as a function of the reactant concentration loss and rate constant.

In the case of polymer degradation, it is assumed

that the rate of conversion is proportional to the concentration of material that has to react.

$$f(\alpha) = (1 - \alpha)^n. \quad (2)$$

The combination of these equations and the empiric Arrhenius expression gives the following relationship:

$$\frac{d\alpha}{dt} = A(1 - \alpha)^n \exp(-E_a/RT). \quad (3)$$

And introducing the heating rate, β :

$$\frac{d\alpha}{(1 - \alpha)^n} = \frac{A}{\beta} \exp\left(\frac{-E_a}{RT}\right) dT. \quad (4)$$

This is the fundamental expression of analytical methods to calculate kinetic parameters on the basis of TG data. These methods can be distinguished as based on degree of conversion measurement, α , and based on heating rate, β .

Methods Based on Degree of Conversion Measurement

Differential Methods

The most general method, the direct application of kinetic eq. (4), is by Friedman,⁹ which is based on comparison of mass loss rates ($d\alpha/dt$) for a fractional mass loss, α , determined using different heating rates. This method utilizes the following logarithmic differential equation.

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A + n \ln(1 - \alpha) - \frac{E_a}{RT}. \quad (5)$$

Thus, by plotting $\ln(d\alpha/dt)$ against $1/T$ for a constant α , it is possible to obtain values for activation energies, reaction orders, and preexponential factors.

Chatterjee and Conrad¹⁰ have proposed a method similar to Friedman by plotting $\ln(d\alpha/dt) - \ln \alpha$ against $1/T$.

Horowitz and Metzger¹¹ use the next expression:

$$\ln\left[\ln\left(\frac{1}{1 - \alpha}\right)\right] = \frac{E_a\theta}{RT_s^2} \quad (6)$$

where T_s is the temperature such that $1/(1 - \alpha) = 1/e$ and $\theta = T - T_s$.

Coats and Redfern¹² utilize the equation obtained by independent integration of both terms of eq. (4).

Assuming the approximation:

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{1 - (1-\alpha)^{1-n}}{1-n} \quad (7)$$

followed by integration of the second term:

$$\log \left[\frac{1 - (1-\alpha)^{1-n}}{T^2(1-n)} \right] = \log \frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a} \right) - \frac{E_a}{2.303RT} \quad (8)$$

Thus, a plot of:

$$-\log \left[\frac{1 - (1-\alpha)^{1-n}}{T^2(1-n)} \right] = f \left(\frac{1}{T} \right) \quad (9)$$

will give straight lines with slope $-E_a/2.303R$ from which the activation energy can be calculated.

For comparison, the Van Krevelen et al. method¹³ has also been applied to the same sample although it is usually used in carbons. According to this method, at a fixed temperature T_m , a maximum rate can be measured. Supposing that in the range $0.9T_m < T < 1.1T_m$ the next equation can be obtained.

$$\ln \left[\frac{1}{1-\alpha} - 1 \right] = \ln \left[\frac{A}{\beta} \left(\frac{0.368}{T_m} \right)^{E_a/RT} \frac{1}{\frac{E_a}{RT_m} + 1} \right] + \left(\frac{E_a}{RT_m} + 1 \right) \ln T \quad (10)$$

Thus, by plotting $\ln[1/(1-\alpha)]$ against $\ln T$, a straight line is obtained whose slope and intercept permit easy determination of activation energies and preexponential factor A .

Methods Based on Heating Rate Measurements

The main method is the one established by Flynn and Wall.¹⁴ This method needs several curves at different heating rates. The next expression can be obtained:

$$\frac{-d \log \beta}{d \left(\frac{1}{T} \right)} = 0.457 \frac{E_a}{R} \quad (11)$$

By plotting $d(\log \beta)$ against $d(1/T)$, activation energy can be calculated.

EXPERIMENTAL

Apparatus

Thermogravimetric analysis was performed using a Mettler TG 50 microbalance coupled with a Mettler TC 11 TA microprocessor, controlled by a Graphware TA 72 program. This microbalance was calibrated making use of the discontinuous change in the magnetic properties of certain metals on heating. The Curie point of every metal can be calculated and therefore the microbalance was calibrated at different heating rates.

Particulate size measurements were performed using a MALVERN 2600C size tester and a 5.4 version software equipped with a programmed algorithm independent from any known mathematical model.

Molecular weight measurements were performed with a Shimadzu LC-10AD using a Viskotek 404 version software.

Material

As a first material Vestolit B 7021 (HULS) PVC resin has been used. This is a homopolymer non-prestabilized and capable of forming low viscosity pastes easily. This dispersion PVC resin, normally used for rotational moulding, has been characterized by calculating the K value using DIN 53726 standard giving a final result of 72.0. By measuring molecular weight we have obtained $M_w = 130,000$.

Another parameter for characterizing the resin is the particulate size distribution. Obtained values are: volume mean diameter: $[D(4, 3)] = 23.4 \mu\text{m}$; surface mean diameter: $[D(3, 2)] = 5.7 \mu\text{m}$.

The last parameter is the one that better reflects the true mean size for the purpose of the present work because pyrolysis is rather characterized by surface characteristics.

Operating Procedure

The PVC degradation process is followed by monitoring weight loss according to temperature in a controlled atmosphere (air or N_2). For these measurements, cylindrical alumina crucibles ($4.7 \times 5.9 \times 5.9$ mm) have been used in which every sample of PVC resin has been placed without a previous treatment. Working conditions (gas flow, heating rate, and polymer weight) have been separately established in every particular case. The temperature range of the experiments was between 30 and 900°C

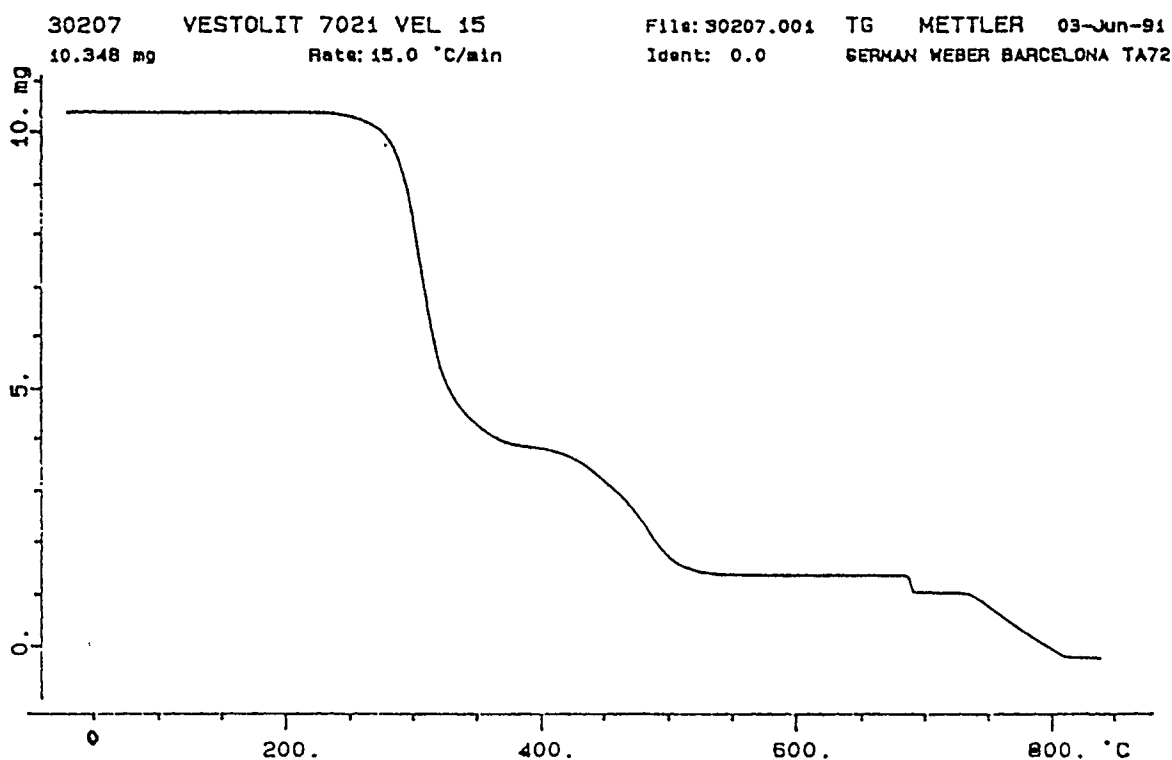


Figure 1 TG curve for PVC sample heated in N_2 atmosphere.

in order to completely decompose the polymer and was conducted at a constant heating rate.

RESULTS AND DISCUSSION

A typical thermogravimetric curve is given in Figure 1 for the nominal heating rate of 15 K min^{-1} and using an inert atmosphere. It will be noted that at $\sim 600\text{ K}$ the dehydrochlorination step is finished and the second step occurs at 800 K . Air is introduced at $\sim 1000\text{ K}$ and this change of atmosphere is the responsible for the third jump in Figure 1.

Parameters Optimization

A study of different gas flows and sample sizes was conducted in order to select those experimental conditions that gave the best reproducibility of relative weight losses.

Gas Flow

A number of blanks with different N_2 flows (0, 100, 200, 300, and 400 mL/min) were run. Only slight drifts ($\sim 0.001\text{ mg}/^\circ\text{C}$) were observed especially at temperatures above 1000 K and higher flows. Similar

drifts were observed using PVC samples. To ensure measurement reproducibility 300 mL/min was chosen as a convenient gas flow. Gas flow is not a critical variable.

PVC Weight

At gas flow (300 mL/min) and heating rate (20 K/min) fixed, the percent weight losses were measured for PVC from 2.5 to 20 mg at intervals of 2.5 mg. Values for percent weight loss and temperatures for maximum losses in every particular case are given in Table I.

Table I Percent Weight Loss and Temperature for Maximum Loss. Variations With PVC Weight

| Weight (mg) | %W ₁ | T ₁ (°C) | %W ₂ | T ₂ (°C) |
|-------------|-----------------|---------------------|-----------------|---------------------|
| 2.210 | 64.0 | 307 | 24.4 | 478 |
| 4.833 | 63.7 | 307 | 25.3 | 478 |
| 7.830 | 63.7 | 307 | 24.2 | 479 |
| 10.623 | 63.2 | 307 | 23.7 | 479 |
| 12.448 | 63.5 | 304 | 23.2 | 479 |

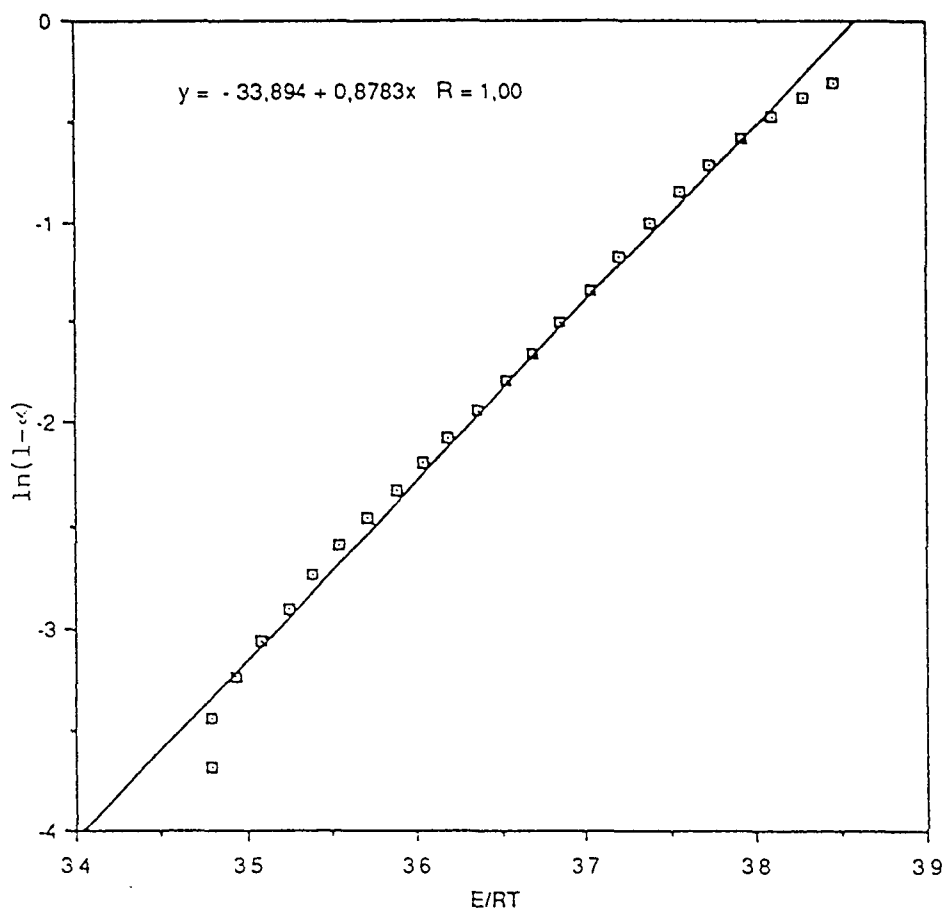


Figure 2 Friedman method applied to experimental data. Heating rate 20°C/min. Activation energies calculation.

Results in all cases are very similar, so that we can characterize the two known jumps by corresponding mean values for mass losses and temperatures: %W₁ = 63.6% (S_{n-1} = 0.3%); %W₂ = 24.2% (S_{n-1} = 0.8%); T_1 = 306°C (S_{n-1} = 1°C); T_2 = 479°C (S_{n-1} = 1°C).

Precision of results up to 12 mg is very satisfactory. Above 15 mg, however, temperatures for maximum weight losses are less reproducible, probably because of difficulties for combustion of carbonaceous products that appear in a higher quantity. Thus, as a suitable sample amount we have taken 10 mg because of the reproducibility and a certain insensitivity to relative errors in weighing.

Application of Kinetic Methods

Obtained data were analyzed by applying the above methods. Thus, experimental data fulfill the preci-

sion of the Friedman method⁹ as shown in Figures 2 and 3. From them, we can obtain activation energies data, reaction orders and preexponential factors which appear in Table II. As it can be seen, PVC

Table II Kinetic Constants Determination Using Friedman Method⁹

| Heating Rate (°C/min) | E_a (kJ/mol) | n | $\ln A$ |
|--------------------------|-------------------|------|---------|
| 5 | 209.9 | 0.84 | 33.4 |
| 10 | 199.7 | 0.79 | 33.7 |
| 15 | 170.0 | 0.86 | 31.1 |
| 20 | 182.2 | 0.88 | 33.9 |
| 25 | 173.0 | 0.77 | 27.9 |
| 30 | 156.0 | 0.96 | 31.2 |
| 35 | 162.9 | 1.00 | 33.8 |
| 40 | 166.5 | 0.78 | 27.0 |
| 45 | 163.3 | 0.80 | 27.2 |
| 50 | 148.8 | 0.84 | 25.9 |

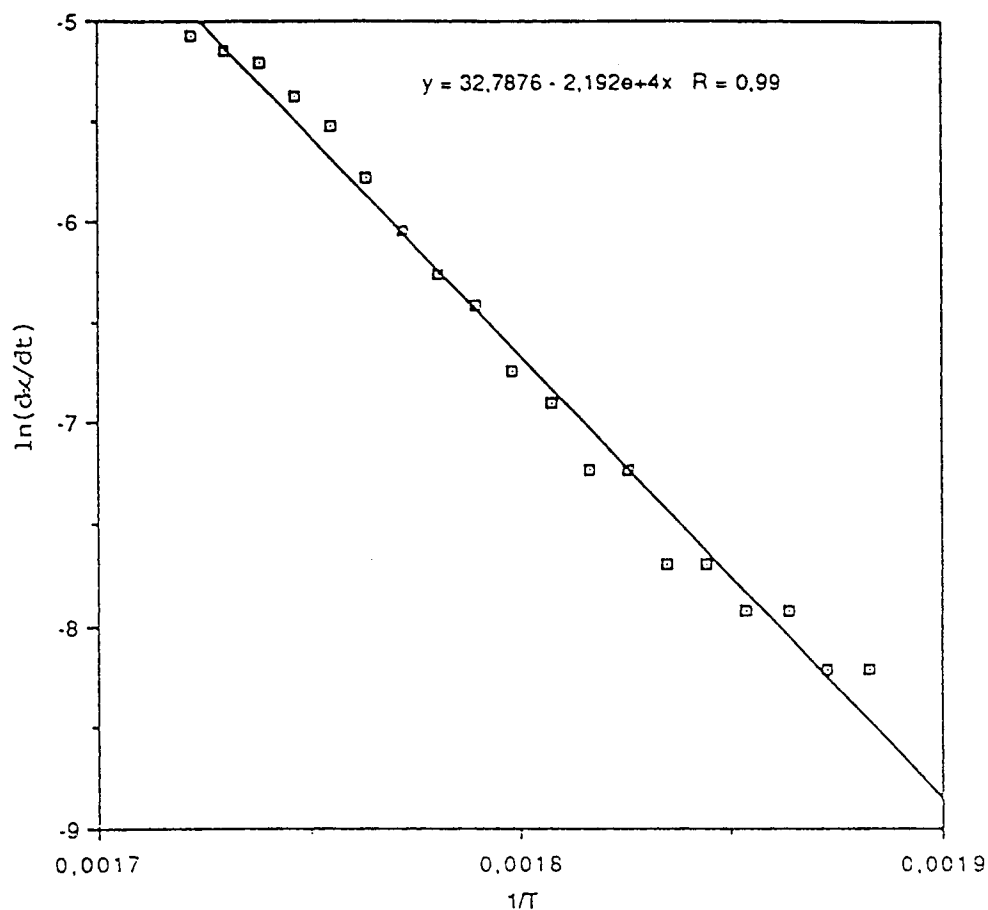


Figure 3 Friedman method applied to experimental data. Heating rate 20°C/min. Reaction order calculation.

dehydrochlorination can be adequately considered as a first order reaction in the range of heating rates we have used. A similar conclusion has already been reported in the literature.¹⁹ But we must caution about the validity of the concluded order of this re-

action in other conditions. A summary of activation energy results for differential methods is presented in Table III.

Similarly, according to Flynn and Wall method,¹⁴ applying eq. (11), activation energies can be ob-

Table III Activation Energies (kJ/mol) Variation With Heating Rates (°C/min) Calculated Using Several Kinetic Methods

| Rate | Friedman ⁹ | Chatterjee and Conrad ¹⁰ | Horowitz and Metzger ¹¹ | Coats and Redfern ¹² | Van Krevelen et al. ¹³ |
|------|-----------------------|-------------------------------------|------------------------------------|---------------------------------|-----------------------------------|
| 5 | 209.9 | 180.9 | 217.7 | 201.8 | 276.4 |
| 10 | 199.7 | 177.9 | 212.4 | 190.6 | 237.7 |
| 15 | 170.0 | 158.7 | 199.8 | 174.3 | 213.7 |
| 20 | 182.2 | 153.1 | 189.1 | 184.0 | 252.0 |
| 25 | 173.0 | 150.2 | 184.0 | 170.9 | 246.2 |
| 30 | 156.0 | 131.8 | 193.8 | 160.8 | 195.7 |
| 35 | 162.9 | 133.9 | 194.5 | 167.5 | 201.4 |
| 40 | 166.5 | 131.9 | 185.8 | 159.9 | 193.8 |
| 45 | 163.3 | 130.7 | 185.6 | 160.5 | 196.0 |
| 50 | 148.8 | 124.0 | 191.6 | 162.8 | 217.0 |

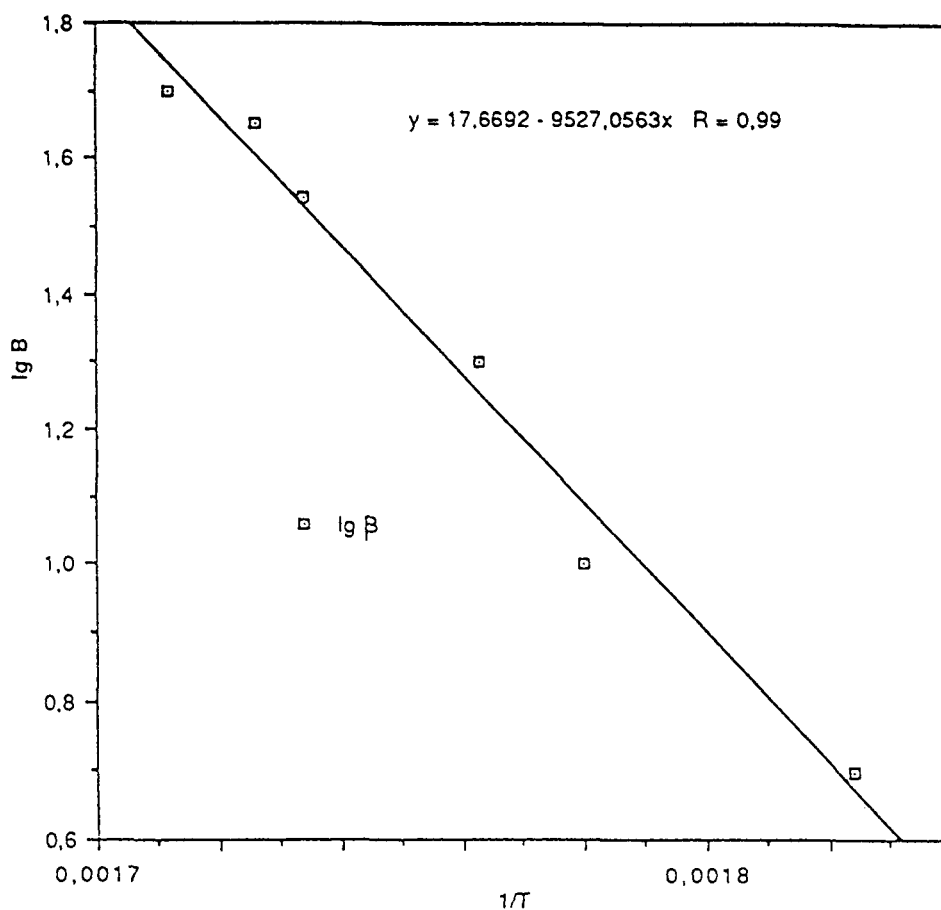


Figure 4 Flynn method applied to experimental data. Conversion grade 0.50. Activation energy calculation.

tained from the slope of the plot $\log \beta$ against $1/T$ as is shown in Figure 4. This procedure has been repeated for several conversion grades obtaining results indicated in Table IV.

As shown in Figure 5, activation energies obtained for nearly all the methods are dependent on heating rate. Using Friedman,⁹ Coats and Redfern,¹² or Horowitz and Metzger¹¹ approaches it seems clear

that more reproducible results are obtained inside the interval from 15 to 40 K min⁻¹. Outside this range of heating rates, calculated activation energies decrease dramatically from 5 to 15 K min⁻¹. There is another drop in estimated activation energy value for the highest heating rates, probably because thermal lag in the instrument as well as in the sample thermal conductivity.

Table IV Activation Energies Determination Using Flynn-Wall Method¹⁴

| α | E_a (kJ/mol) | r |
|----------|-------------------|------|
| 0.10 | 176.9 | 0.96 |
| 0.25 | 193.2 | 0.98 |
| 0.50 | 173.3 | 0.99 |
| 0.75 | 154.6 | 0.99 |
| 0.90 | 153.6 | 0.99 |

Table V Summary of Activation Energy Results for Thermal Dehydrochlorination of PVC

| Method | E_a (kJ/mol) |
|---------------------------------|----------------|
| Friedman ⁹ | 165.3 ± 10.2 |
| Chatterjee-Conrad ¹⁰ | 139.3 ± 12.7 |
| Horowitz-Metzger ¹¹ | 190.5 ± 5.4 |
| Coats-Redfern ¹² | 167.6 ± 8.9 |
| Flynn-Wall ¹⁴ | 170.3 ± 14.8 |

Values are mean ± SD.

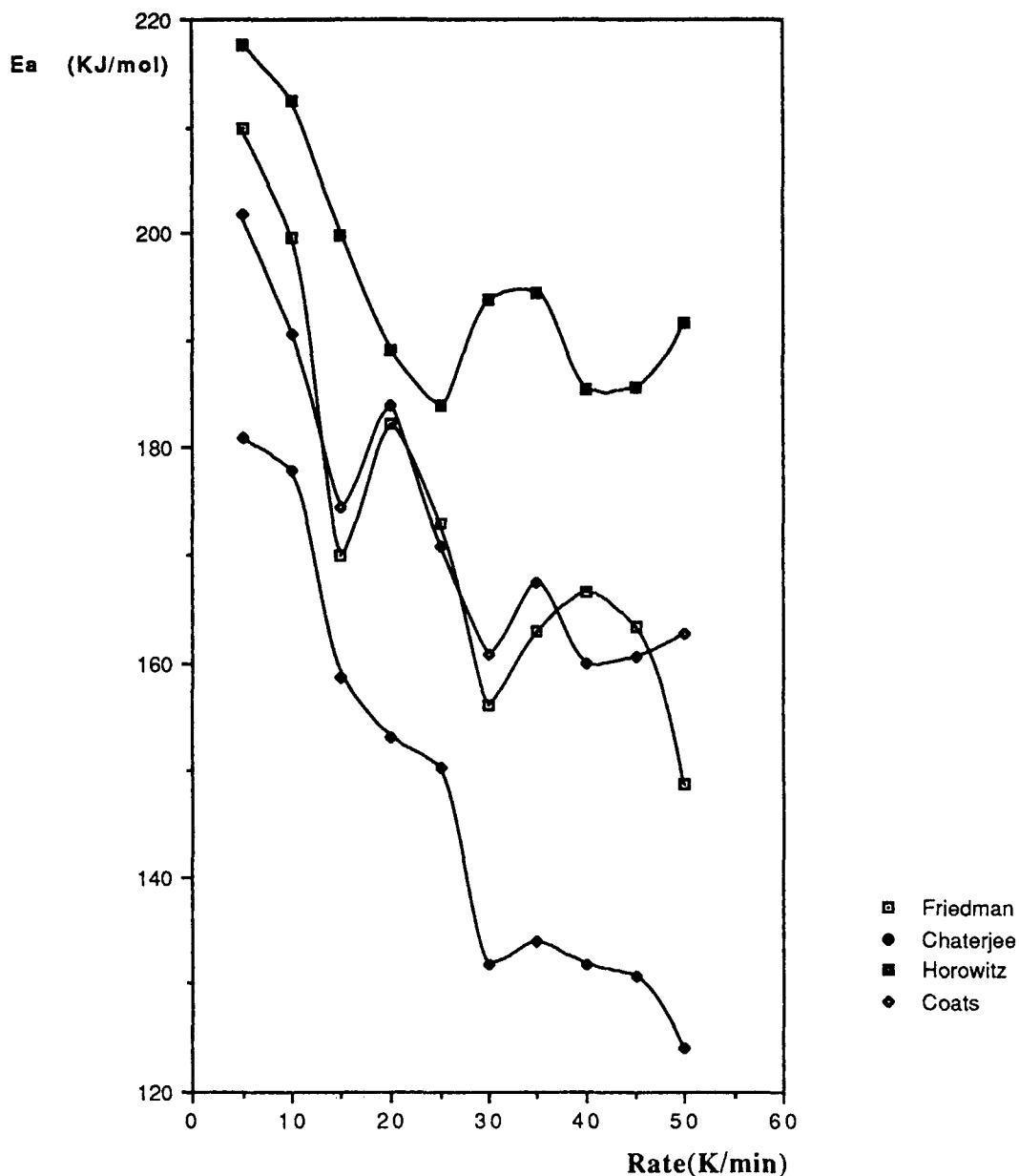


Figure 5 Activation energies variation with heating rates calculated using several kinetic methods.

A comparison summary of activation energy values obtained are shown in Table V. These results are only valid for indicated conditions in reference to sample weight and gas flow. Mathematical treatment of experimental data has influence on obtained values (Table V). Other important factors over kinetic parameters are heating rate and conversion grade used on calculation. These facts indicate limitations of analytical methods to characterize PVC thermal degradations.

CONCLUSIONS

It can be stated that the Coats and Redfern,¹² Friedman,⁹ and Flynn and Wall¹⁴ methods applied to PVC, in spite of their differences, afford similar consistent results of activation energies of dehydrochlorination. The use of a multiple heating rate technique was also felt to more realistically represent the variety of heating rates during pyrolysis and combustion reactions occurring when a polymeric

material burns. Moreover, using these methods, obtained data fit reasonably with literature data of activation energies that fluctuate between 130 and 170 kJ/mol.¹⁵⁻²⁰

Comparing these methods, Coats and Redfern¹² and Friedman⁹ allow us to calculate every point in a TG curve and variations produced by heating rates. The Flynn and Wall¹⁴ method works well with any conversion grade. An additional advantage of Friedman and Flynn-Wall approaches is that they are characterized by not assuming any value for $(1 - \alpha)$ and therefore both are capable of providing reasonably reliable data from dynamic TG. It would appear that either the differential Friedman method or the integral Flynn-Wall method provide satisfactory mathematical approaches to obtain kinetic parameters for the thermal degradation of PVC. Using one of them it is possible to identify every stage and derive values for the kinetic parameters.

Finally, it must be emphasized that in applying and reporting thermal analysis data of PVC, heating rates should be indicated because of the critical influence of this variable on results. We recommend heating rates from 15 to 40 K min⁻¹ to ensure a good thermogram, making it easier to obtain kinetic parameters as activation energies or reaction orders.

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