Thermochimica Acta, 117 (1987) 157–166
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

EFFECT OF OPERATING PARAMETERS ON TIME TO DECOMPOSITION OF HIGH DENSITY POLYETHYLENE AND CHLORINATED POLYETHYLENES *

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(Received 1 January 1987)

ABSTRACT

An investigation was made to determine the influence of furnace temperature (500–800 ° C), concentration of oxygen in the gas flow (0–100%, v/v) and sample mass (2–15 mg) on the decomposition time of several polymers. These were high density polyethylene and chlorinated polyethylenes (25, 36 and 42% by mass chlorine). Thermal oxidative degradation was undertaken in a Du Pont 951 thermogravimetric analyzer in the isothermal mode using a gas flow of 0.833 ml s^{-1}, STP.

The results indicated that the average sample heating rate influenced the decomposition time most. Operating at higher furnace temperature ($\geqslant 700\,^\circ$C) and using a small sample mass ($\leqslant 2.5$ mg) reduced the variance in t_d. The activation energy for decomposition of the polymers was 39.3 ± 0.5 kJ mol^{-1}.

NOMENCLATURE

B	pre-exponential factor in the Arrhenius equation (s^{-1})
E	activation energy for decomposition (kJ mol^{-1})
$Hr_{d,av}$	average heating rate to decomposition (° C, s^{-1})
P_{O_2}	oxygen partial pressure in the gas flow (N m^{-2})
R	gas constant (J mol^{-1} K^{-1})
T_{iso}	isothermal furnace temperature (° C)
$T_{iso,corr}$	corrected isothermal furnace temperature (° C)
t_d	time to decomposition (s)
t_{ig}	time to ignition (s)
Δt	the difference between time to decomposition and time to ignition (s)
δ_d	standard deviation of time to decomposition (s)
δ_{ig}	standard deviation of time to ignition (s)

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* Presented at the 42nd ACS Fall Scientific Meeting, 8 November 1986, Midland, MI, U.S.A.

0040-6031/87/$03.50

INTRODUCTION

Thermogravimetry is an effective tool for studying the degradation of a polymer to ignition [1–5]. The ignition profile for a given sample is dependent on the amount and shape of the material used. It is also dependent on the furnace temperature, concentration of oxygen in the gas flow, the gas flow rate and the operating mode. TGA ignition tests are usually conducted in the isothermal mode [1–4] rather than in the programming mode because the former allows for higher sample heating rates. The time a polymer takes to decompose at a given furnace temperature is an important parameter since it determines the resultant processes, such as the rate of decomposition and time to ignition [2]. The temperature level will greatly influence the time to ignition.

This work will evaluate the effect of some factors found to influence time to decomposition, t_d, for a number of chlorinated polyethylenes. The error involved in the measurement of t_d and the effect of the error on the value of time to ignition will also be examined.

EXPERIMENTAL

Material

Four polymers were investigated, high density polyethylene (HDPE) and three chlorinated polyethylenes (ClPE-25%, ClPE-36% and ClPE-42%). The polymers were provided by Scientific Polymer Products, Inc. They were all in powder form except for HDPE which was in pellet form.

The samples were subjected to X-ray diffraction analysis. The results indicated that crystallinity decreased with the degree of chlorination, with HDPE showing the highest level of crystallinity. The particle size was also measured using a WILD stereomicroscope (MDS 51-5). The average particle diameter for the chlorinated polyethylenes was around 0.5 mm. The HDPE pellets were size-reduced to around 0.25 mm. Since the polymer particles were not spherical, there values are only useful to indicate their order of magnitude.

Equipment

The polymers were decomposed inside the electric furnace of a Du Pont 951 thermogravimetric analyzer (TGA). A given amount of sample was added to the platinum pan connected to the TGA balance. An equimolar mixture of $N_2 + O_2$ (0.833 ml s^{-1}, STP) was allowed to flow over the sample, after the quartz tube which enclosed the sample was put in place. The sample and the balance system were then introduced rapidly into the

TGA furnace which was set at a predetermined temperature. The temperatures spanned the range 500–800 °C. (This provided an equivalent average heating rate ranging from about 10 to 50 °C s^{-1}.) A pneumatic mechanism was used to drive the system (sample pan, balance and enclosing tube) into the furnace. This served to reduce operator error.

RESULTS AND DISCUSSION

A typical output of a sample run is shown in Fig. 1. The time to decomposition was determined by extending the horizontal portion of the mass–time curve in the heat up stage (dotted line in Fig. 1). The point where the mass–time curve began to deflect from the horizontal line was defined as the time to decomposition. The initial or zero time was determined at the first point where the temperature underwent a sudden increase from room temperature. The ignition time, on the other hand, was located at the second inflection point; it was immediately followed by a steep rate of mass loss.

Effect of initial sample mass

Figure 2 shows the effect of initial sample mass on time to decomposition, t_d for ClPE-25%. It is clear that t_d increased linearly with initial sample mass because of a longer sample heating time. When the sample mass was greater than 10 mg, it became difficult to spread the sample evenly on the sample pan. Since the rate at which a sample was heated up was dependent on the surface exposed to the heating source, an error was induced in this stage which increased with sample mass. It is clear from Fig. 2 that using a small mass, e.g., 2.5 mg, minimizes this effect.

Also from Fig. 2, one can find that the dependence of t_d on initial sample mass was greater at the lower isothermal furnace temperature. For example,

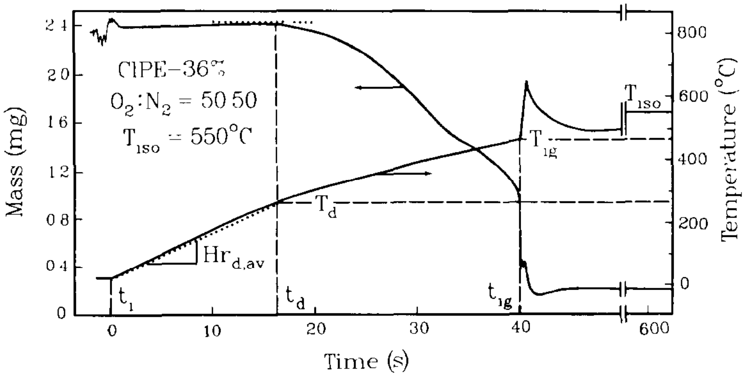

Fig. 1. Thermogram of ClPE-36%, T_{iso} = 550 °C.

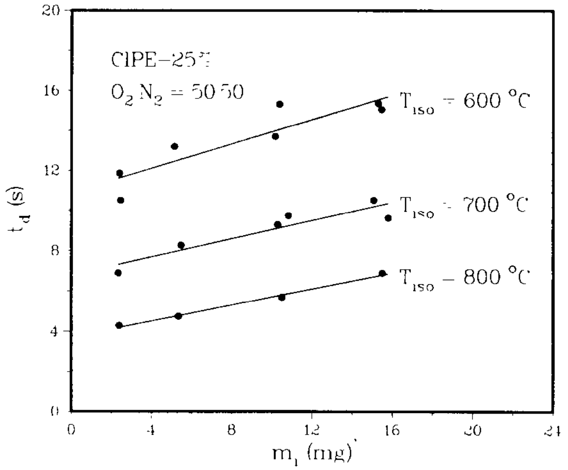

Fig. 2. Effect of initial sample mass on time to decomposition.

the gradient of the line at $T_{iso} = 600\,°C$ was about 0.3 s mg^{-1}, whereas at $T_{iso} = 800\,°C$ it was about 0.2 s mg^{-1}. Therefore, it is expected that at higher furnace temperatures, $\geqslant 1000\,°C$, the effect of sample mass will be negligible under these conditions.

Effect of oxygen concentration in the gas flow

Figure 3 shows that, for ClPE-25%, t_d decreased as the oxygen partial pressure in the gas flow was varied from 0 to 30.4 kN m^{-2} (0–30% O_2 by

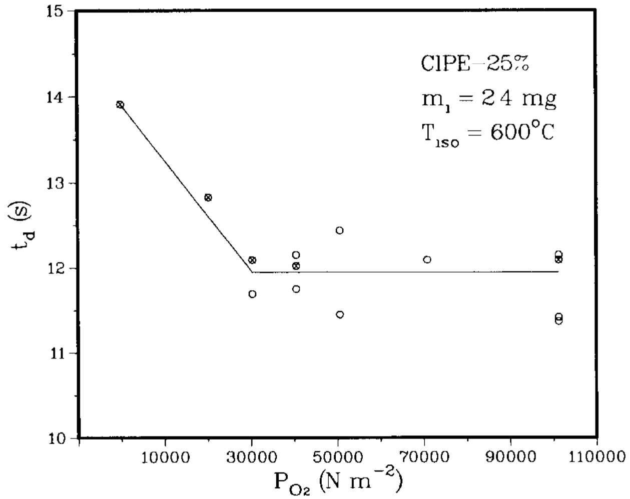

Fig. 3. Effect of oxygen partial pressure on time to decomposition ($T_{iso} = 600\,°C$). ⊗ Corrected values.

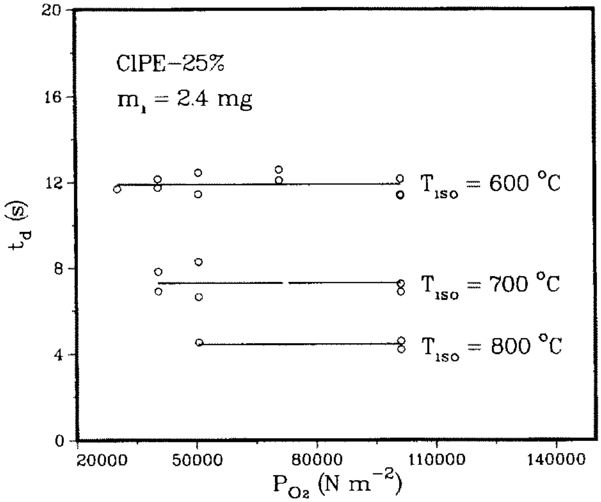

Fig. 4. Effect of oxygen partial pressure on time to decomposition (T_{iso} = 600–800 °C).

vol.). However, when the partial pressure was increased above 30.4 kN m^{-2}, the effect became insignificant. As shown in Fig. 4, the t_d values were practically unchanged when the oxygen partial pressure was varied from 40.5 to 101.3 kN m^{-2}. This trend was observed throughout the major furnace temperature range tested (600–800 °C).

Effect of chlorination level

This effect was analyzed in two steps. First, the activation energy for decomposition, E, was obtained by linear regression using the following equation

$$1/t_d = B\exp(-E/RT_{iso}) \qquad (1)$$

where t_d is the time to decomposition, B is a constant, (for a given mass of polymer and oxygen partial pressure [6]), R is the gas constant, and T_{iso} is the furnace temperature (K).

The results for the four polymers are listed in Table 1 and indicate that

TABLE 1

Effect of the level of chlorination on activation energy for decomposition (T_{iso} = 500–800 °C)

Sample	E (kJ mol^{-1})	B	r^2 [a]
HDPE	35.4 ± 0.8	10.7	0.997
ClPE-25%	38.8 ± 2.1	16.8	0.949
ClPE-36%	38.6 ± 1.4	17.3	0.976
ClPE-42%	36.5 ± 1.8	12.7	0.962

[a] r^2 = square of the correlation coefficient.

TABLE 2

Effect of the level of chlorination and T_{iso} on t_d

T_{iso} (°C)	Time to decomposition			
	HDPE	ClPE-25%	ClPE-36%	ClPE-42%
550	16.05	17.18	15.38	15.15
575	13.70	15.50	14.63	12.33
600	12.23	11.45	12.45	13.37
650	9.75	9.75	9.42	9.66
700	7.64	6.66	7.01	6.45
750	5.91	6.95	5.40	5.54
800	4.86	5.27	4.32	4.52

there is a statistical difference in the values of E, with higher values occurring in the case of 25 and 36% chlorinated polyethylenes. These results could be interpreted to indicate that there was a slight effect at the lower chlorination levels.

An ANOVA table was next set up to evaluate the effect of the chlorination level on time to decomposition. The results for the data in Table 2, summarized in Table 3, indicated that there was no significant effect at the 95% level of confidence. The cause of the variance in t_d was, therefore, to be found elsewhere.

The main source of the error in t_d

Since the effect of the level of chlorination was eliminated, a plot of $\ln(1/t_d)$ vs. $1/T_{iso}$ (using all samples) was drawn, as shown in Fig. 5, to obtain the activation energy for decomposition. The results indicated that there was considerable variance at each isothermal furnace temperature.

It is worth noting that the t_d values followed a weak trend with the average heating rate, $Hr_{d,av}$, at a given T_{iso}, i.e., an increase in heating rate

TABLE 3

ANOVA table for t_d

Source of variation	Sum of squares	Degree of freedom	Mean squares	F_0	$F_{0.05,\alpha_1,\alpha_2}$ [a]
T_{iso}	443.04	6	73.84	127.31 $\gg$	2.70
Cl level	2.56	3	0.85	1.47 <	3.20
Interaction	0.30	1	0.30	0.52 $\ll$	4.45
Error	9.90	17	0.58		
Total	445.80	27			

[a] α_1 = degree of freedom of the source of variation, α_2 = degree of freedom of the error.

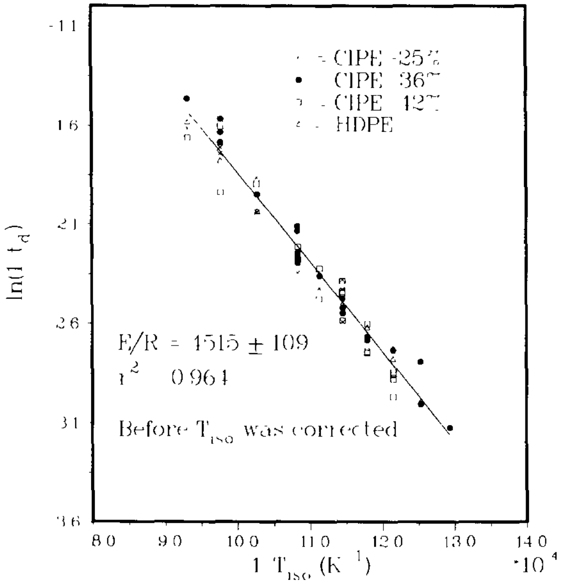

Fig. 5. Activation energy for decomposition (T_{iso} uncorrected).

reduced the time to decomposition (Table 4). Also, the variation in one sample was about equal to that between samples. This implied that the error in t_d (at a given T_{iso}) was mainly induced by a difference in the rate at which a sample was heated up inside the furnace. This could have been caused by three factors: (a) different distributions of the sample on the sample pan, (b) variation in the speed at which the system was being pushed into the furnace and (c) introducing the sample at different stages of the furnace temperature controlling cycle. The last point was believed to be the most important factor in the present case.

A procedure for adjusting the value of T_{iso} was devised as follows. First, the relationships between T_{iso} and $Hr_{d,av}$ (average heating rate at which the sample was heated up to the decomposition point) were determined for each temperature range

$$T_{iso} = 421 + 8.88\ Hr_{d,av} \quad \text{at } T_{iso} < 650\,^{\circ}\mathrm{C} \tag{2}$$

$$T_{iso} = 517 + 5.48\ Hr_{d,av} \quad \text{at } T_{iso} > 650\,^{\circ}\mathrm{C} \tag{3}$$

TABLE 4

Experimental values of t_d (s) and $Hr_{d,av}$ ($^{\circ}C\ s^{-1}$) at $T_{iso} = 600\,^{\circ}C$

HDPE		ClPE-25%		ClPE-36%		ClPE-42%	
$Hr_{d,av}$	t_d	$Hr_{d,av}$	t_d	$Hr_{d,av}$	t_d	$Hr_{d,av}$	t_d
20.94	12.23	18.61	13.28	18.37	12.80	17.85	13.37
–	–	19.75	11.45	19.24	12.45	20.41	11.34
–	–	20.97	10.88	20.03	11.88	22.31	10.80

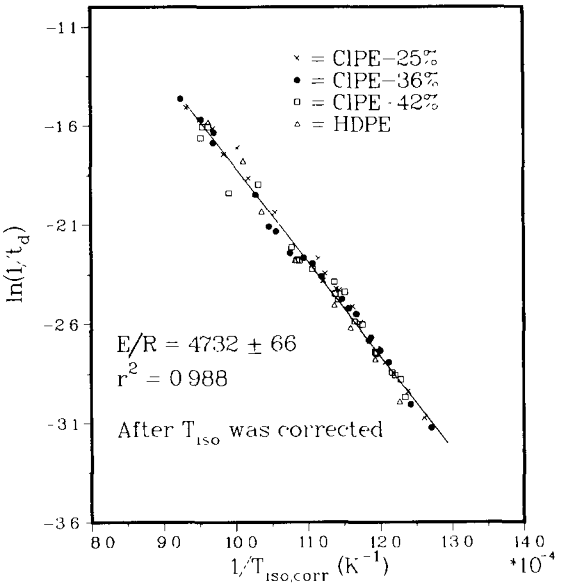

Fig. 6. Activation energy for decomposition (T_{iso} corrected).

Secondly, a corrected isothermal furnace temperature, $T_{iso,corr}$, as determined in each case by substituting the value of $Hr_{d,av}$ obtained from the corresponding TGA temperature–time curve into eqn. (2) or (3).

A significant reduction in the width of the band around the solid line occurred in Fig. 6 where $T_{iso,corr}$ was used, as compared to Fig. 5 where T_{iso} was not corrected. The activation energy for decomposition, E for all the polymers (including HDPE), was found to be 39.3 ± 0.5 kJ mol^{-1}. This also indicated that chlorination of HDPE did not affect the activation energy for decomposition.

Contribution of the variance in t_d *on* t_{ig}

Time to ignition, t_{ig}, may be defined as the sum of two periods as follows:

$$t_{ig} = t_d + \Delta t$$

where Δt is the time lapsed from the moment the material decomposed up to that at which it ignited, Fig. 1. Therefore, the error induced in the heat-up stage may affect t_{ig}. To investigate this point, the variance associated with each value of t_d, Δt, and t_{ig} was determined at several isothermal temperatures. As shown in Figs. 7 and 8, the coefficient of variation for t_d, δ_d/t_d, for the whole temperature range was around 0.08 (δ_d is the standard deviation of t_d). On the other hand, δ_{ig}/t_{ig} was around 0.1 at low furnace temperatures ($\leqslant 650\,°C$) and decreased to around 0.05 at $T_{iso} = 750\,°C$. The

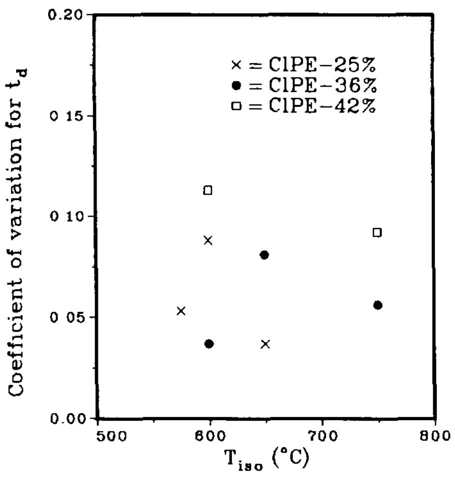

Fig. 7. Effect of furnace temperature on the coefficients of variation for t_d (coefficient of variation = δ_d/t_d).

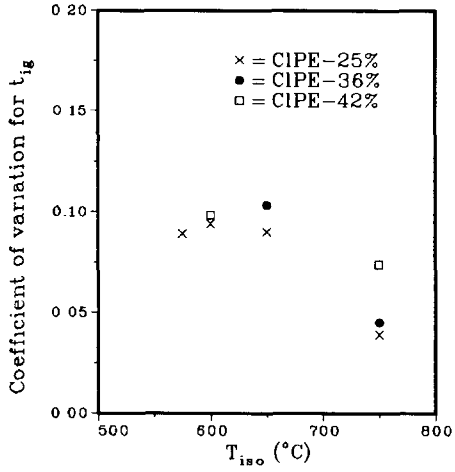

Fig. 8. Effect of furnace temperature on the coefficients of variation for t_{ig} (coefficient of variation = δ_{ig}/t_{ig}).

lower variance observed at high furnace temperatures might be partly due to the fact that t_{ig} was better defined on the TG curves.

CONCLUSIONS

(1) The level of chlorination did not play an important role in determining time to decomposition.

(2) The average rate at which a sample was heated influenced time to decomposition most.

(3) Operating at high furnace temperatures ($\geqslant 700\,^{\circ}\mathrm{C}$) and using small sample mass ($\leqslant 2.5$ mg) reduced the error in t_d.

(4) It was not possible to quantify accurately the contribution of the error in t_d on t_{ig}.

ACKNOWLEDGMENTS

The authors would like to thank Mr. J.A. Brusso, a graduate student in the Metallurgy Department, for taking the X-ray analysis of the polymer samples and also Dr. W.-M. Lee at the Dow Chemical Co., Midland, MI for arranging for the size reduction of the HDPE sample.

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