

## A THERMOGRAVIMETRIC STUDY OF THE DECOMPOSITION RATE OF CHLORINATED POLYETHYLENES UNDER IGNITION CONDITIONS \*

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### ABSTRACT

Decomposition and combustion of three chlorinated polyethylenes (CIPE-25%, CIPE-36% and CIPE-42%) and a high density polyethylene (HDPE) under medium heating rates ( $11.5\text{--}67.5^\circ\text{C s}^{-1}$ ) in an oxidant gas flow was investigated using a Du Pont 951 thermogravimetric analyzer (TGA). The decomposition rate constants prior to ignition and during combustion were obtained using an Avrami–Erofee'v type equation,  $[-\ln(1-C)]^{1/n} = kt + A$  where  $n$  was chosen equal to four. The results showed that the rate constant was sensitive to the isothermal furnace temperature only if a small sample mass (about 2.40 mg) was used. Increasing  $\text{O}_2$  concentration in the gas flow greatly promoted the decomposition rate prior to ignition, but was less significant in the combustion stage. The rate of decomposition for HDPE was much higher than that of the chlorinated polyethylenes, indicating the effectiveness of substituted chlorine in suppressing the decomposition rate of the polymers. On the other hand, increasing the chlorine content from 36 to 42% did not reduce the decomposition rate further under our conditions.

### INTRODUCTION

When a polymer is burned, two processes can be distinguished [1–7]: one occurs in the condensed phase and leads to decomposition of the polymer. The other takes place in the gas phase where products mix and react with the oxidant. The decomposition products and their evolution rate are of primary importance in determining whether ignition will occur, and hence the burning rate after ignition [6,7]

Chlorination of polyethylene results in a class of less flammable materials [8–11]. The presence of chlorine in a polymer raises its oxygen index [10,11],

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and reduces the fuel concentration in the gas phase as well as the heat produced during combustion [12].

Unlike polyethylene, the decomposition of chlorinated polyethylenes (CIPEs) proceeds in two stages similar to poly(vinyl)chloride [13–15]. According to Uehara and Suzuki [13], who pyrolyzed chlorinated polyethylenes at low heating rate ( $0.33^{\circ}\text{C s}^{-1}$ ), the early stage of decomposition was mainly attributable to dehydrochlorination, whereas decomposition in the stage that followed (at higher temperatures) was induced by random scission of the polyethylene components.

In a previous study on the ignition of chlorinated polyethylenes, it was shown that the number of decomposition stages occurring prior to ignition was dependent on the furnace temperature which determined the average sample heating rate [16]. When a chlorinated polyethylene sample was heated rapidly, only one decomposition stage appeared before ignition. The ignition point moved to the second stage when a low heating rate was applied. It was, therefore, necessary to analyze the decomposition rate in both of the stages which occurred prior to ignition. The decomposition rate during the combustion stage following ignition was also of interest as it would provide information regarding the importance of level of chlorine in the polymer on this stage of decomposition.

In this work, the decomposition rates of several chlorinated polyethylenes were measured using a thermogravimetric analyzer. The analysis was performed under various operating conditions. An Avrami–Erofee’v type equation was employed to analyze the decomposition rate prior to ignition and during combustion. This equation has been used to study the thermal or thermo-oxidative degradation of polymers [17], woods [18] and coals [19].

## EXPERIMENTAL

### *Materials*

Three chlorinated polyethylene samples from Scientific Polymer Products, Inc. were studied. They were CIPE-25%, CIPE-36% and CIPE-42%, where the percentages indicate the chlorine contents by mass. For comparison purposes, a high density polyethylene (HDPE) from the same supplier was used. Table 1 presents some of the physical properties of the samples. The melting point  $T_m$ , and the heat of melting  $\Delta H_m$  were measured using a Du Pont differential scanning calorimeter (DSC). The difference in the  $T_m$  values was not significant and fell within the range of experimental error. The samples were also subject to X-ray diffraction analysis. The results indicated that the crystallinity decreased with the amount of chlorine in the polymer [20].

The oxygen and nitrogen gases, both of which were of high purity, were provided by the Matheson Company.

TABLE 1

Sample properties

Sample	Density (g cm <sup>-3</sup> )	$d^a$ (mm)	$T_m$ (°C)	$\Delta H_m$ (J g <sup>-1</sup> )
HDPE	0.95	0.25	121	703
CIPE-25%	1.10	0.41	122	181
CIPE-36%	1.16	0.41	124	63
CIPE-42%	1.22	0.53	126	10

<sup>a</sup>  $d$  = Effective mean particle diameter, useful as an indication of the order of magnitude only [20].

### *Apparatus and procedure*

The experiments were performed using a Du Pont 951 thermogravimetric analyzer, which was coupled with a Du Pont 990 recorder console for control as well as data acquisition. In order to achieve the conditions that were required for a polymer to ignite, the isothermal mode was used. Thus higher heating rates could be achieved than when the programming mode was used. The experimental procedure was essentially that used by Miller et al. [7] with some modifications [16,20,21].

Before a run, a given amount of sample was weighed in the platinum sample pan. The TGA quartz tube was then mounted in position and a gas flow of O<sub>2</sub> and N<sub>2</sub> mixture at 0.833 ml s<sup>-1</sup>, S.T.P. was allowed to flow through the tube. The system (quartz tube, balance and sample thermocouple) was then quickly introduced into the TGA furnace which had been pre-set to the desired isothermal temperature ( $T_{iso}$ ). The system was driven by a pneumatic driver actuated by air at 20 psi resulting in a travelling time of less than one second.

The sample thermocouple, which recorded the gas temperature during a run, was located next to the sample pan (about 3 mm). The TGA was set to TIME base so that each run provided both the mass-time and temperature-time curves.

The end of the TGA quartz tube was positioned halfway inside a 50 mm i.d. pyrex cone, and connected on the other end to a number of Buchner flasks containing water. The flasks were half filled with glass beads to increase the mass transfer area. A water pump was used to aspirate the combustion gases through the water at a rate of 75 ml s<sup>-1</sup>, S.T.P.

The furnace temperature employed ranged from 550 to 850 °C, and the sample mass varied from 2.40 to 15.50 mg. The oxygen concentration in the gas flow was 50 and 100% by volume. This high oxygen concentration was necessary for ignition to occur due to the high oxygen index of the chlorinated polyethylenes [10,11,13].

## RESULTS AND DISCUSSION

Figure 1 shows a typical TGA thermogram for a HDPE sample heated rapidly from room temperature (about 20°C) to 700°C. The mass-loss curves exhibited a number of features: After the system (sample pan and balance system) was driven into the furnace, it took one to two seconds before the vibrations of the sample pan subsided, after which the curve remained nearly horizontal for the duration of the sample heating stage. Ignition occurred after partial decomposition, and was followed by a sharp decrease in sample mass. This was attributable to flash pyrolysis. At the ignition point, the temperature-time curve showed an abrupt increase indicating a great amount of heat being given off due to ignition. Following ignition, a strong luminosity was produced by the flame which lasted until the end of the burning stage. Interestingly, the flash pyrolysis stage which occurred after ignition was followed by a slow burning region which was named the combustion stage (c).

It has been confirmed that polymer flames are affected by the complex interactions of heat feedback, diffusion and free radical reactions [9]. Therefore, the transition from fast to slow burning was possibly governed by a number of effects, such as the balance between the heat generated in ignition and that required for condensed phase decomposition.

Our previous study [16] indicated that, for chlorinated polyethylenes, the decomposition stage in which ignition occurred was dependent on the isothermal furnace temperature, which determined the sample heating rate. For example, when the sample mass was about 2.40 mg and the oxygen concentration in the gas flow was equal to that of nitrogen, ignition occurred in the first decomposition stage provided that  $T_{\text{iso}}$  was higher than 650°C.

The decomposition profile of CIPE-25% at  $T_{\text{iso}} = 700^\circ\text{C}$  is shown in Fig. 2. In this case, no visible break along the decomposition curve prior to

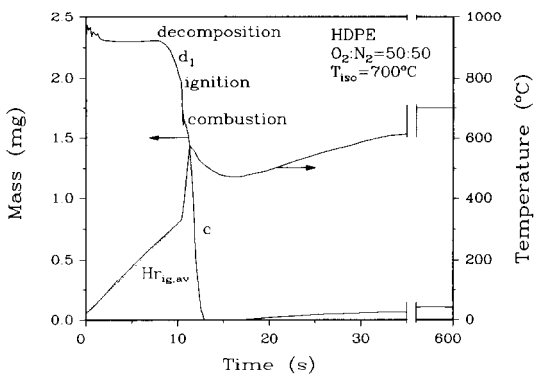


Fig. 1. Ignition of HDPE.

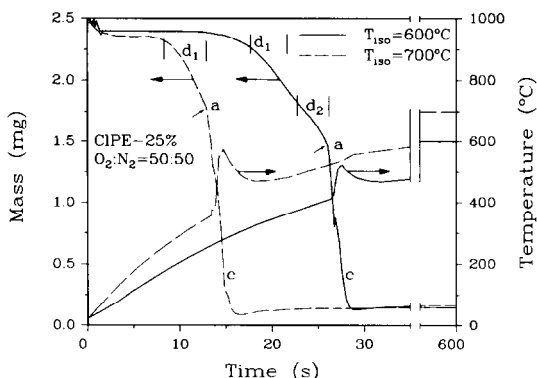


Fig. 2. Ignition of CIPE-25% (a: the ignition point. The two vertical strokes around  $d_1$  and  $d_2$  indicate specific decomposition stages with respect to time).

ignition was observed. This stage was defined as  $d_1$ . However, when the furnace temperature was  $650^\circ\text{C}$  or less, ignition occurred in the second decomposition stage, as shown in Fig. 2. A transition stage with lower mass-loss rate [16] can be observed in Fig. 2 at about 23 s and was not considered in this study. Stage  $d_2$  was, therefore, defined starting from the point where the mass-loss rate began to increase, which marked the end of the transition stage, up to the ignition point.

Similar decomposition stages were also observed prior to ignition when the higher chlorinated polyethylenes (CIPE-36% and CIPE-42%) [16] were combusted at temperatures below  $650^\circ\text{C}$ . HDPE underwent consistently a one-stage decomposition throughout the furnace temperature range tested. For comparison purposes, the decomposition stage prior to ignition for HDPE was also named  $d_1$ , though there was only one stage of decomposition before ignition in this case. When the furnace temperature was too low, e.g.  $525^\circ\text{C}$ , no ignition occurred for all the samples tested [16].

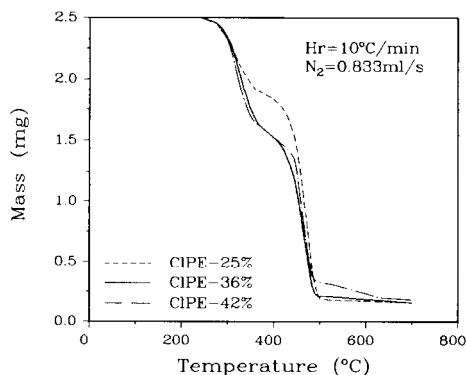


Fig. 3. Pyrolysis of chlorinated polyethylenes in N<sub>2</sub>.

When chlorinated polyethylenes are pyrolyzed at low heating rate (Fig. 3) two main stages are apparent; mostly benzene (along with HCl) is produced in the first stage while aliphatic hydrocarbons are produced in the second stage [13]. Therefore, it is reasonable to expect that ignition can occur in either stage when a polymer is decomposed in an oxidizing environment, as was the case in our study, since the decomposition products would contain combustible hydrocarbons and/or oxygenated species in both stages.

#### *Average heating rate to ignition, $Hr_{ig,av}$*

Since the rate of decomposition was mainly dependent on the sample heating rate [7,22], it was necessary to define an equivalent heating rate for each sample run. In most cases, the temperature–time curve in the part prior to ignition was not linear. The difficulty in this case was that there was no specific point on the temperature–time curve from which a representative heating rate could be defined by taking the tangent at this point. It was believed at first that by averaging the heating stage prior to decomposition a more representative value of the heating rate would be obtained. However, considering the possible influence of time to decomposition on time to ignition [21], and hence on the corresponding heating rate, was the main reason for not choosing this alternative. To simplify the problem, an average heating rate to ignition,  $Hr_{ig,av}$  was defined as shown in Fig. 1. The value of  $Hr_{ig,av}$  can be therefore understood to be the average rate of heat gained by the sample prior to ignition. It has been shown that this heating rate worked adequately for interpreting most of the ignition data [16,20]. In this study,  $Hr_{ig,av}$  was varied from 11.5 to 67.5 °C s<sup>-1</sup>. This was achieved by varying the isothermal furnace temperature from 550 to 850 °C.

As indicated above, an isothermal furnace temperature of 650 °C was a critical value above which only one stage of decomposition appeared prior to ignition. The mean  $Hr_{ig,av}$  at  $T_{iso} = 650$  °C for the three CIPes was  $21.4 \pm 1.7$  °C s<sup>-1</sup>, where the uncertainty represented one sample standard deviation.

#### *Effect of chlorine content on the rate constant, k*

The rates of decomposition in the d<sub>1</sub>, d<sub>2</sub> and c stage marked in Figs. 1 and 2 were studied using an Avrami–Erofee'v type equation. The transition stage between d<sub>1</sub> and d<sub>2</sub> which occurred in the case of the CIPes when  $T_{iso}$  was equal to or less than 650 °C was not of interest, since ignition did not occur in this stage except in a few cases.

The Avrami–Erofee'v equation takes the form of

$$[-\ln(1 - C)]^{1/n} = kt + A \quad (1)$$

where  $A$  is a constant;  $C$  is the fraction converted;  $k$  is the rate constant (s<sup>-1</sup>);  $n$  is an empirical constant; and  $t$  is the time in seconds.

TABLE 2

Effect of  $n$  on the value of the adjusted correlation coefficient and  $k_c$  for HDPE and CIPE-25% combusted at  $T_{\text{iso}} = 700^\circ\text{C}$ ,  $m_i = 2.40$  mg and  $\text{O}_2 : \text{N}_2 = 50 : 50$  by volume

$n$	HDPE		CIPE-25%	
	$k_c$ ( $\text{s}^{-1}$ )	$r_{\text{adj}}$	$k_c$ ( $\text{s}^{-1}$ )	$r_{\text{adj}}$
1	$2.42 \pm 0.25^a$	0.970	$1.57 \pm 0.12$	0.988
2	$0.93 \pm 0.04$	0.993	$0.64 \pm 0.03$	0.995
3	$0.58 \pm 0.04$	0.996	$0.42 \pm 0.03$	0.995
4	$0.42 \pm 0.01$	0.998	$0.29 \pm 0.02$	0.994
5	$0.33 \pm 0.01$	0.999	$0.23 \pm 0.01$	0.993
6	$0.27 \pm 0.01$	0.999	$0.23 \pm 0.01$	0.993

<sup>a</sup>  $\pm$  One standard deviation.

Since there is no theoretical foundation behind eqn. (1) for organic solids, as in the case of inorganic solids [23], the appropriate value of  $n$  had to be determined first using the linear least-square method. A number of values ranging from 1 to 6 were assumed. It was found that for  $n$  between 2 and 4, the adjusted correlation coefficient  $r_{\text{adj}}$  as well as the rate constant did not significantly change for the data in the  $d_1$  stage [20]. The adjusted correlation coefficient was usually higher than 0.98. However, in the combustion stage (c) the goodness of fit was significantly affected by the value of  $n$  chosen. The results obtained using a series of  $n$  values ranging from 1 to 6 are shown in Table 2 for HDPE and CIPE-25% at  $T_{\text{iso}} = 700^\circ\text{C}$ ,  $m_i = 2.40$  mg and  $\text{O}_2 : \text{N}_2 = 50 : 50$  by volume in the gas flow. For HDPE, the correlation coefficient  $r$  increased with an increase in the value of  $n$ . For example in the case of CIPE-25%,  $r_{\text{adj}}$  reached a maximum when  $n$  was equal to two.

In order to be able to compare the decomposition behavior of the polymers, the empirical constant  $n$  was chosen equal to four in all cases, including the decomposition stages prior to ignition. The lowest  $r_{\text{adj}}$  value obtained was 0.95 which was considered high enough to ensure that eqn. (1) fitted the data well.

The rate constants  $k_{d_1}$  and  $k_{d_2}$  refer to the first ( $d_1$ ) and the second ( $d_2$ ) decomposition stage prior to ignition (Fig. 2). Irrespective of whether one or two decomposition stages occurred prior to ignition,  $k_c$  is the rate constant for the combustion (c) stage. The  $d_1$  stage for the CIPEs was defined from the 3% decomposition point up to the beginning of the transition stage when  $T_{\text{iso}}$  was equal to or less than  $650^\circ\text{C}$ , and up to the ignition point when  $T_{\text{iso}}$  was greater than  $650^\circ\text{C}$ . That portion of the data was left out as it was poorly fitted by eqn. (1) for all the values of  $n$  tested.

The effect of  $n$  and  $T_{\text{iso}}$  on the  $k$  values for HDPE and CIPE-25% is summarized in Tables 2 and 3. Each rate constant  $k$  is the slope of the straight line resulting from plotting  $[-\ln(1 - C)]^{-1/4}$  against time. Such plots are shown in Figs. 4 and 5. The  $k_{d_1}$  and  $k_c$  values for HDPE were

TABLE 3

Effect of O<sub>2</sub> (% by vol.) in the gas flow on the decomposition rate of CIPE-25% prior to ignition and during combustion

$T_{\text{iso}}$ (°C)	$k_{d_1}$ (s <sup>-1</sup> )		$k_c$ (s <sup>-1</sup> )	
	50% O <sub>2</sub>	100% O <sub>2</sub>	50% O <sub>2</sub>	100% O <sub>2</sub>
600 (17) <sup>a</sup>	0.050 ± 0.002 <sup>b</sup>	0.123 ± 0.003	0.21 ± 0.01	0.33 ± 0.04
700 (27)	0.079 ± 0.003	0.154 ± 0.004	0.25 ± 0.02	0.38 ± 0.03
800 (39)	0.095 ± 0.006	0.194 ± 0.007	0.35 ± 0.03	0.35 ± 0.02

<sup>a</sup> Equivalent average heating rate in °C s<sup>-1</sup>.

<sup>b</sup> ± one standard deviation.

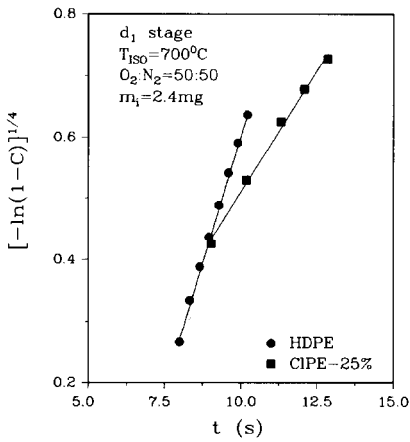


Fig. 4. Plots of  $[-\ln(1-C)]^{1/4}$  vs.  $t$  for the decomposition of HDPE and CIPE-25% in the  $d_1$  stage.

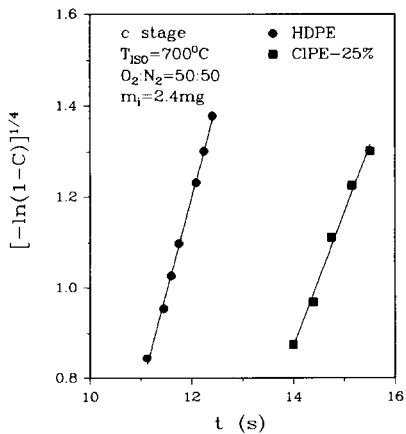


Fig. 5. Plots of  $[-\ln(1-C)]^{1/4}$  vs.  $t$  for the decomposition of HDPE and CIPE-25% in the combustion stage at  $T_{\text{iso}} = 700^\circ\text{C}$ .



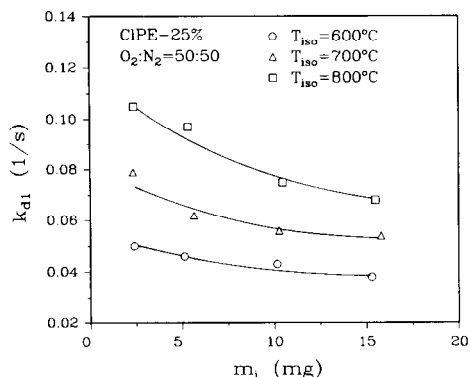


Fig. 6. Effect of initial sample mass on the decomposition rate in the  $d_1$  stage.

greater than those of the CIPEs pointing to the inhibiting effect of the chlorine in the polymer. Also, the  $k_c$  values were always greater than the  $k_{d1}$  values as may be induced from a comparison of the values at  $700^\circ\text{C}$  in Tables 2 and 3.

#### *Effect of initial sample mass*

Figure 6 shows the effect of initial sample mass,  $m_i$  on the rate constant in the  $d_1$  stage for CIPE-25% at three isothermal furnace temperatures.  $k_{d1}$  tended to decrease with the sample mass. When a low sample mass was used, i.e. 2.40 mg, the effect of the isothermal furnace temperature was more significant than when a high sample mass was used. This can also be seen in Fig. 7 where the rate constant in the combustion stage ( $k_c$ ) was plotted against  $m_i$ . The furnace temperature  $T_{iso}$  had no effect on  $k_c$  when the sample mass was greater than 5 mg. When  $m_i = 2.40$  mg, the effect of the

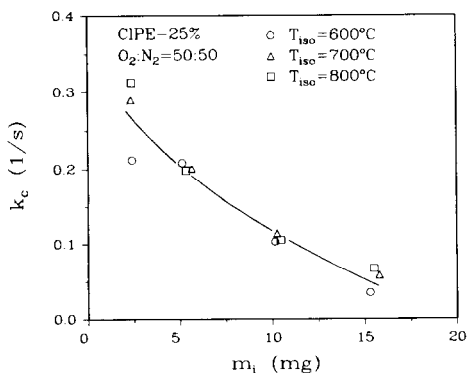


Fig. 7. Effect of initial sample mass on the decomposition rate during combustion.

furnace temperature was quite clear. That is, the rate of decomposition during combustion increased with  $T_{\text{iso}}$ . This indicated that when a small sample mass was used the  $k$  values were more sensitive to furnace temperature. Also, using a small sample mass reduced the error in the measurement of the time to decomposition [21]. This was the reason that the initial sample mass was fixed, in that study, at 2.40 mg to investigate the effect of furnace temperature, sample type and the oxygen concentration in the gas flow.

#### *Effect of oxygen concentration in the gas flow*

Table 3 summarizes the effect of both oxygen in the gas flow and furnace temperature on the rate constant in the  $d_1$  and c stages. In the  $d_1$  stage, higher  $O_2$  concentration greatly promoted the decomposition rate. However, in the combustion stage (c), the effect of  $O_2$  concentration was not as significant as that in the  $d_1$  stage. For example, when  $T_{\text{iso}}$  was set at  $600^\circ\text{C}$ , the  $k_c$  value when pure oxygen was used was about 1.5 times that when the gas flow contained 50%  $O_2$ . However, when the furnace temperature was increased to  $800^\circ\text{C}$ , the  $k_c$  values were identical indicating that the rate was not altered as a result of varying the oxygen level in the gas flow. This was probably induced by the fact that the polymer decomposition rate at  $T_{\text{iso}} = 800^\circ\text{C}$  was very high, and thus prevented the  $O_2$  in the gas flow from reaching the sample surface to any appreciable extent.

#### *Effect of chlorine content and heating rate*

These effects were investigated using an initial sample mass of 2.40 mg and 50%  $O_2$  by volume in the gas flow. The results were plotted as  $k$  values against the average heating rate to ignition,  $Hr_{\text{ig,av}}$  and are presented in Figs. 8, 9 and 10.

Figure 8 shows that a linear relationship exists between  $k_{d_1}$  and  $Hr_{\text{ig,av}}$ . As one would have expected, the rate of decomposition increased with the heating rate. HDPE had the highest decomposition rate, and its dependency on heating rate was also more significant than those of chlorinated polyethylenes. The slope resulting from a plot of  $k_{d_1}$  against  $Hr_{\text{ig,av}}$  was  $7.8 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$  for HDPE,  $2.3 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$  for CIPE-25%, and  $2.1 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$  for both CIPE-36% and CIPE-42%. There was indication that HDPE started to decompose at slightly higher temperatures (less than  $10^\circ\text{C}$  difference) when  $T_{\text{iso}}$  was equal to or less than  $700^\circ\text{C}$ , and at about the same temperature as CIPEs when  $T_{\text{iso}}$  was greater than  $700^\circ\text{C}$ . The gas flow in this case contained 50%  $O_2$  [20]. Also the fact that HDPE decomposed more rapidly than the CIPEs was evidence that the presence of chlorine inhibited the thermo-oxidative degradation of the chlorinated polyethylenes.

CIPE-25% had a slightly higher  $k_{d_1}$  value than CIPE-36% and CIPE-42% within the heating rate range studied. The points for CIPE-36% and CIPE-42%

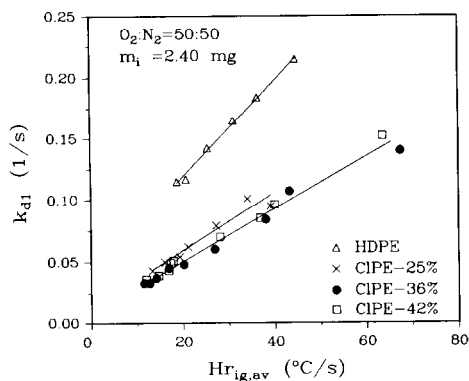


Fig. 8. Effect of heating rates on the rate constant in the first decomposition stage ( $d_1$ ).

fell on one straight line, which suggested that the efficiency of chlorine in suppressing the thermo-oxidative degradation was not improved further by substituting more than 36% of chlorine under these conditions.

In the  $d_2$  stage, which appeared when  $T_{iso}$  was less or equal to  $650^{\circ}C$ , CIPE-36% and CIPE-42% had lower  $k_{d_2}$  values than CIPE-25% at a given heating rate (Fig. 9). These results can be explained as follows: the first stage of decomposition was mainly attributable to the elimination of HCl, resulting in an equivalent amount of unsaturated bonds. Subsequently, the sample underwent partial cross-linking and cyclization via these unsaturated C-C bonds [13,24]. Therefore, the lower decomposition rates ( $k_{d_2}$ ) of CIPE-36% and CIPE-42% were probably a result of higher degrees of cross-linking or more cyclized components than CIPE-25% after dehydrochlorination because they had higher chlorine contents.

Figure 10 shows the relationship between the decomposition rate constant in the combustion stage,  $k_c$  and the average heating rate to ignition,  $Hr_{ig,av}$ .

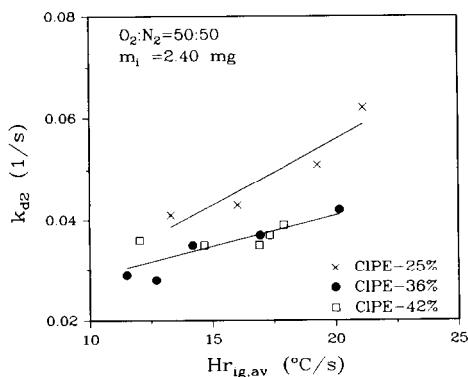


Fig. 9. Effect of heating rates on the rate constant in the second decomposition stage ( $d_2$ ).

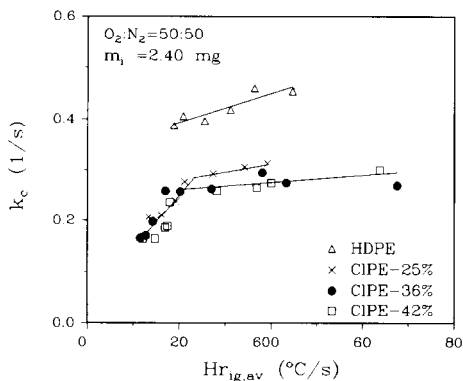


Fig. 10. Effect of heating rates on the rate constant during combustion.

The decomposition rate in this stage was higher for HDPE than for those of CIPEs. Again, this points to the effectiveness of chlorinated materials in reducing the decomposition rate during combustion.

For the chlorinated polyethylenes, several important features shown in Fig. 10 are summarized as follows: first, when  $Hr_{ig,av}$  was less than  $21^{\circ}\text{C s}^{-1}$  (in this case ignition took place in the second decomposition stage), the  $k_c$  values for all three CIPEs practically fell on one line, indicating no effect of degree of chlorination on the decomposition rate during combustion which resulted from ignition in the second decomposition stage. Second, when  $Hr_{ig,av}$  was greater than  $21^{\circ}\text{C s}^{-1}$ ,  $k_c$  values for CIPE-25% were slightly higher than those for CIPE-36% and CIPE-42%, where all values of  $k_c$  fell on one line as was the case before for  $k_{d_1}$  and  $k_{d_2}$  (Figs. 8 and 9). This suggests that there was no advantage under the present conditions in increasing the degree of chlorination above 36%; Third, the dependency of  $k_c$  upon the heating rate was less significant when  $Hr_{ig,av}$  was less than  $21^{\circ}\text{C s}^{-1}$  than when it was above  $21^{\circ}\text{C s}^{-1}$ .

One may therefore conclude that the decomposition mechanism during the last (i.e. combustion) stage depended on the heating rate, which determined the number of decomposition stages that occurred prior to ignition. Although a detailed explanation cannot be given at this stage, it is very likely that halogen acids and chlorinated hydrocarbons play an important role at the higher heating rates. For example, hydrogen chloride can reduce decomposition by interfering with chain branching reactions. It can also act as a diluent and thus result in more unburned material.

## CONCLUSIONS

1 Substitution of chlorine in polyethylene up to 36% by mass greatly reduced the rates of the thermo-oxidative degradation prior to ignition and the decomposition during combustion.

- 2 No difference between the decomposition rates for CIPE-36% and CIPE-42% was observed in our experiments. This indicated that there was an upper limit in the chlorine content to which the flammability of chlorinated polyethylenes was reduced under these conditions.

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