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DECOMPOSITION OF CHLORINATED POLYETHYLENE IN AIR WITHOUT IGNITION

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ABSTRACT

Three chlorinated polyethylene samples, CPE (25% Cl), CPE (36% Cl), and CPE (42% Cl), were decomposed in an atmosphere of air using a Du Pont thermogravimetric analyzer. Selected gas products were identified along a thermogram using a Fourier-transform IR spectrometer and a gas chromatograph. These results were compared with those for high-density polyethylene. The effect of the chlorination level on several decomposition parameters was also investigated. These were (1) the temperature at which the rate of weight loss was a maximum, (2) the reactivity at the point of maximum weight loss, and (3) the amount of polymer residue.

INTRODUCTION

High-density polyethylene (HDPE) and various chlorinated polyethylenes: CPE (25% Cl), CPE (36% Cl), and CPE (42% Cl) have been the subject of several investigations in the past [1–3]. The objective of those studies was to determine the effect of heating rate and temperature on the rate of sample weight loss, in order to test the suitability of a thermogravimetric-based method for rating the flammability of the polymers, and to evaluate the effect of a number of factors found to influence time to decomposition. The importance of the latter parameter was taken into consideration in the rate of polymer decomposition and time to ignition. The polymers in the above studies were decomposed in a gas mixture containing an equal volume of oxygen and nitrogen. Under these conditions the polymers ignited before the onset of the combustion stage.

In the present study, we wanted to determine the concentration in air of HDPE and the chlorinated polymers mentioned above. This would serve to identify the decomposition zones along a thermogram. The effect of the amount of chlorine in the polymers on three decomposition parameters was also investigated. The parameters are: the temperature at which the rate of weight loss is a maximum (T_{max}); the reactivity at the point where the rate of weight loss is a maximum (R_{max}); and the polymer residue (%).

EXPERIMENTAL

The HDPE and the CPE samples were obtained from Scientific Polymer Products Inc. The samples were decomposed using a Du Pont 1090B thermogravimetric analyzer (TGA) to determine weight loss and rate of weight loss (dw/dt). The gas flow rate was kept at 50 ml min^{-1} and the sample weight at 10 mg.

A Du Pont 910 differential scanning calorimeter (DSC) was used to generate heat flow vs. temperature profiles and for determining the melting points of the polymer. For the DSC run, the flow rate was kept at 50 ml min^{-1} and the sample weight was less than 5 mg.

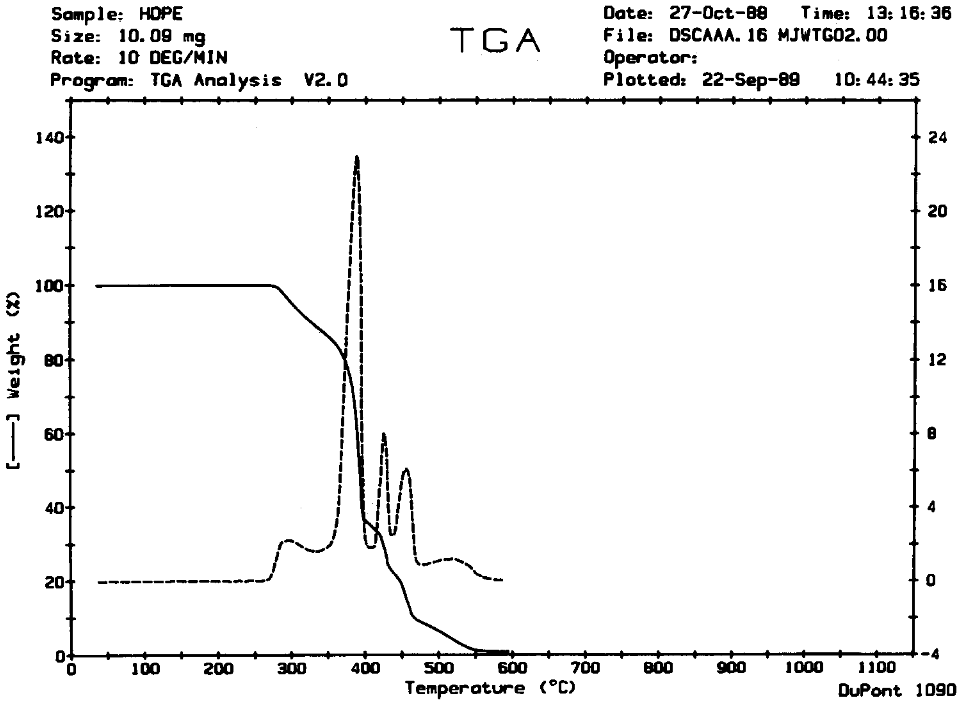
The composition of the stable gas decomposition products flowing out of the TGA were analyzed using both a Nicolet MX1 Fourier transform infrared spectrophotometer (FTIR) and a Shanghai 100 gas chromatograph (GC/TCD). The GC was run with several columns including a Parapole R, a Parapole Q, and a molecular-sieve column. Testing for the presence of evolved HCl gas was accomplished using pH-sensitive paper.

RESULTS AND DISCUSSION

TG combustion curves

When HDPE was pyrolyzed in a nitrogen atmosphere only one DTG peak appeared at about 470 °C [4]. However, when the polymer was decomposed in an air atmosphere the DTG curve (shown in Fig. 1) exhibited a first decomposition peak at around 300 °C. This was followed by another large decomposition peak at around 370 °C. Several smaller minor peaks were present at temperatures above 400 °C. These smaller peaks are due to the effect of air on the polymer which caused rearrangement of its structure and secondary reactions.

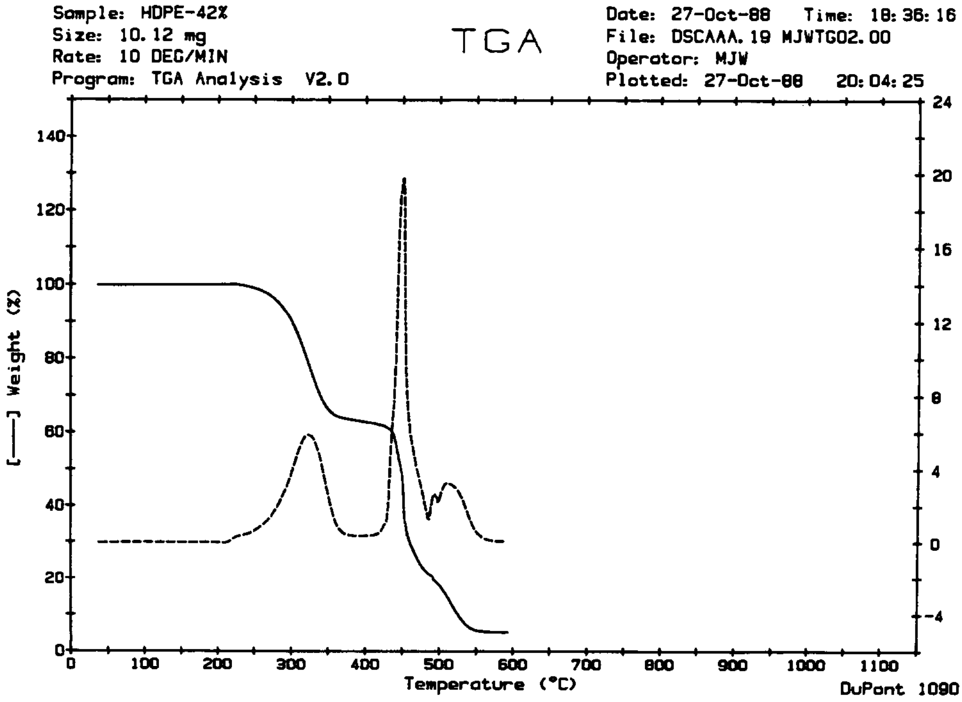
Figure 2 shows similar curves for the CPE (42% Cl) sample decomposed in air. Two distinct decomposition zones are observed. The first zone, as will be established later, is primarily due to the release of HCl and the second zone is due to the decomposition of the main polymer structure. The latter



Sample: HDPE
Size: 10.09 mg
Rate: 10 DEG/MIN
Program: TGA Analysis V2.0

Date: 27-Oct-88 Time: 13:16:36
File: DSCAAA.16 MJWTG02.00
Operator:
Plotted: 22-Sep-89 10:44:35

Fig. 1. TG heating curve for HDPE in an air atmosphere.



Sample: HDPE-42%
Size: 10.12 mg
Rate: 10 DEG/MIN
Program: TGA Analysis V2.0

Date: 27-Oct-88 Time: 18:36:16
File: DSCAAA.19 MJWTG02.00
Operator: MJW
Plotted: 27-Oct-88 20:04:25

Fig. 2. TG heating curve for CPE (42% Cl) in an air atmosphere.

TABLE 1

FTIR data for HDPE in air

Temperature (° C)	Peak height [a]			Peak area [a]	
	CH_3OH	HCOOH	H_2O	CO_2	CO
275	0.10	0.12	0.3	0.68	0.19
315	0.08	0.07	0.3	1.20	0.28
345	0.12	0.10	0.6	1.87	0.49
385	0.17	0.08	1.1	3.40	2.16
425	0.34	0.16	2.2	4.70	1.89
465	0.24	0.08	0.5	2.90	0.33
525	0.30	0.00	0.0	5.20	0.48

[a] Arbitrary units

stage occurred in several steps, as indicated by the multiple DTG peaks. Decomposition of the chlorinated polymers in an air atmosphere brought both decomposition zones closer as compared with the case when nitrogen was the gas atmosphere. This is due to shifting of the peak maximum for the second zone to a lower temperature.

Gas analysis by FTIR and GC

Tables 1 and 2 give the gaseous decomposition products detected by FTIR for HDPE and CPE (42% Cl). The FTIR results are tabulated at selected intervals for five gaseous products (CH_3OH, HCOOH, CO_2, CO, and H_2O). By cross-reference between Fig. 1 and Table 1, one can deduce several points: HCOOH was formed very early during the decomposition process (below 300 ° C); the point at which the concentration of CO was maximum occurs at the second DTG peak (ca. 370 ° C); the points of

TABLE 2

FTIR data for CPE (42% Cl) in air

Temperature (° C)	Peak height [a]		Peak area [a]	
	CH_3OH and HCl	H_2O	CO_2	CO
245	2.2	0.0	0.22	0.0
285	6.6	0.1	0.47	0.0
325	7.9	0.1	0.59	0.0
375	8.1	0.1	0.72	0.0
405	7.2	0.1	1.08	0.1
435	11.0	0.2	1.94	0.1
465	11.4	1.8	5.11	0.4
495	6.0	0.8	7.76	0.4
525	3.1	0.5	12.00	0.7
555	2.3	0.3	9.54	0.5

[a] Arbitrary units

TABLE 3

GD data for HDPE and chlorinated samples in air [a]

Temperature (°C)	HDPE	CPE		
		25% Cl	36% Cl	42% Cl
120–200	H_2O	H_2O	H_2O	H_2O
200–212	H_2O			
212–420	CO_2 C_2^{2-}, H_2O	CO_2 H_2O HCl	CO_2 H_2O HCl	CO_2 H_2O HCl
420–465	CO_2 C_2^{2-}, C_3^{2-} C_4^{2-} H_2O	CO_2 C_2^{2-}, C_3^{2-} H_2O	CO_2 C_2^{2-}, C_3^{2-} H_2O	CO_2 C_2^{2-}, C_3^{2-} H_2O
465–600	CO_2 H_2O	CO_2 H_2O, C_2^{2-} C_3^{2-}	CO_2 H_2O, C_2^{2-} C_3^{2-}	CO_2 H_2O
Weight loss (%)	100	97	97	97

[a] HCl was detected using pH-sensitive paper.

maximum concentration of HCOOH, H_2O and CO_2 are located around the third DTG peak (ca. 420 ° C); and second maximum point for CH_3OH occurs at the fifth DTG peak (ca. 520 ° C).

For the CPE (42% Cl) sample, the first peak at around 320 ° C is mainly attributed to a dehydrochlorination stage. However, small amounts of CO_2 and CH_3OH were also detected at 245 ° C, which indicates that oxidation occurs at low temperatures. Because the HCl spectrum was masked by that of CH_3OH, it was difficult to quantify the amount of HCl evolved. HCOOH was not detected in the chlorinated samples. Carbon monoxide was detected in significant amounts at about 405 ° C, which is the beginning of the second DTG peak as opposed to 275 ° C for the HDPE sample. The maximum points for CH_3OH and CO_2 occur at 465 ° C and 520 ° C, respectively.

The results obtained using the gas chromatograph (GC) are shown in Table 3. Water was the only species detected below 230 ° C. Aliphatic hydrocarbons including methane, ethylene, and propylene were given off between 212 ° C and 600 ° C.

T_{max}, *reactivity and residue*

The T_{max} values for the four polymers studied are summarized in Table 4 along with the maximum reactivities (R_{max}) for each decomposition zone. R_{max}, in Table 4, was calculated from

$$R_{max} = (dw/dt)/W_i \tag{1}$$

where dw/dt is the rate of weight change and W_i is the initial sample

TABLE 4

Comparison of HDPE and chlorinated samples in air

Chlorination (%)	Weight (mg)	Peak 1		Peak 2		Residue at 600 ° C (%)
		T_{max} (° C)	R_{max} (% min^{-1})	T_{max} (° C)	R_{max} (% min^{-1})	
0	10	–	–	387	0.91	0.5
25	10	327	0.064	454	0.59	4.1
36	10	334	0.102	454	0.36	4.0
42	10	321	0.098	456	0.33	4.5

weight. There are large differences between the T_{max} for HDPE and those for the chlorinated polymer samples. HDPE has a T_{max} around 387 ° C while the chlorinated samples have a T_{max} of between 453 and 456 ° C. The reactivities of the first decomposition zone are also dependent on the level of chlorination showing a maximum at the 36% chlorination level. However, the reactivity for the second zone decreased, suggesting that the reactions responsible for the breakdown of the polymer backbone are inhibited. The residues for the chlorinated polymers are several percent larger than that of HDPE. This is due to the reaction of chloride in the polymer with the remaining polyethylene material forming a cross-linked material that is more resistant to oxidation [1,5]. Therefore, reaction inhibition via a condensed-phase mechanism is an important factor under these conditions.

Level of chlorination

Figures 3 and 4 show several TG curves combined and result in a number of interesting correlations. At 360 ° C, the HDPE has already lost 15% of its total weight, and the chlorinated samples have completed the first decomposition stage, which is mainly dehydrochlorination. The weight loss that occurred throughout this stage for CPE (25% Cl) and CPE (36% Cl) was nearly equal to the amounts of chloride present in the polymers; this was the case, even though traces of CO_2 were detected at temperatures as low as 212 ° C.

At temperatures above 360 ° C, the thermograms for CPE (36% Cl) and CPE (42% Cl) follow each other closely (Fig. 4). This suggests that increasing chlorination above 36% has little effect on the level of polymer decomposition (see Table 5). This effect is also indicated during pyrolysis [4] and in an oxidizing atmosphere, under conditions in which the polymer ignited [3].

Most of the HDPE (ca. 80%) had decomposed at about 440 ° C. At this point, the chlorinated samples begin their second decomposition stage in which the polyethylene backbone breaks down. If we look at the percentage

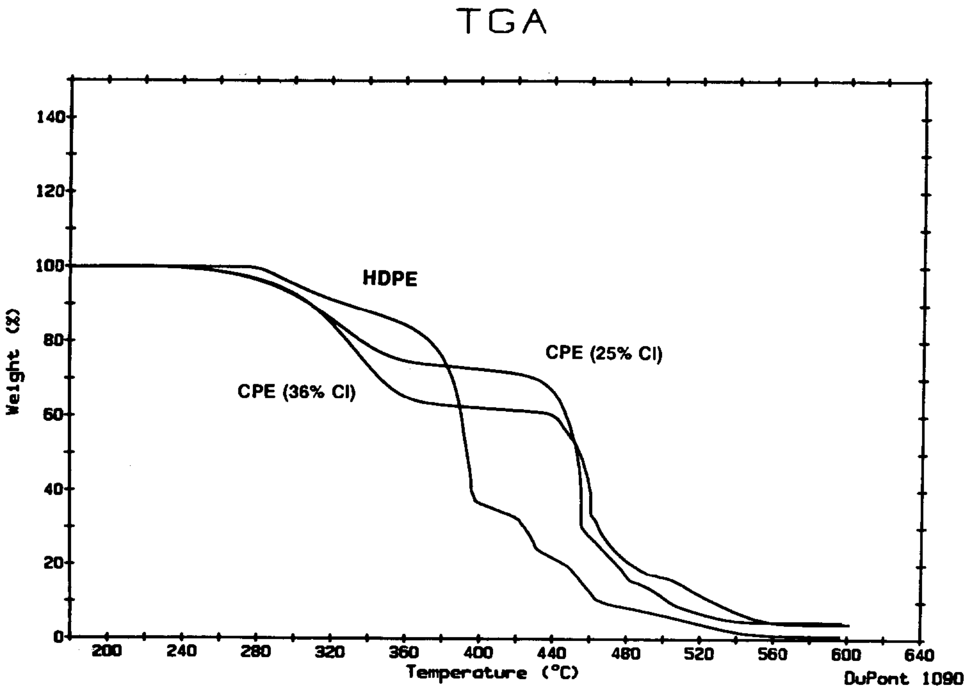


Fig. 3. TG heating curves: HDPE, CPE (25% Cl), and CPE (36% Cl) in air.

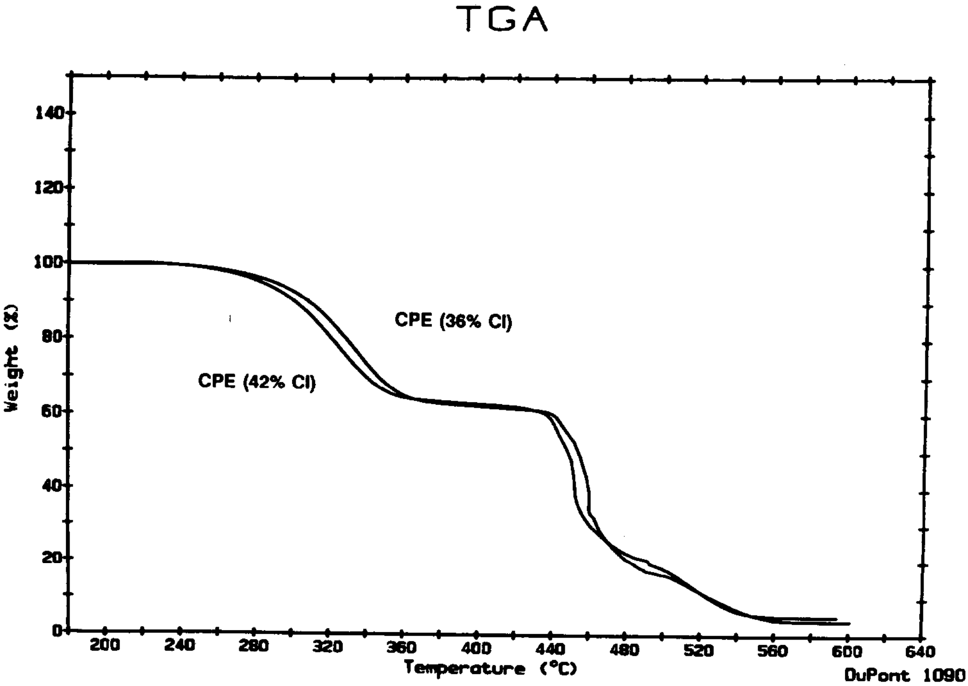


Fig. 4. TG heating curves: CPE (36% Cl) and CPE (42% Cl) in air.

TABLE 5

Percentage weight loss in air at various temperatures

Chlorination (%)	Temperature (° C)		
	360	440	466 [a]
0	15.0	77.7	90.0
25	25.3	33.6	50.0
36	35.0	40.0	34.0
42	35.7	42.4	31.0

[a] Based on PE loss only.

weight loss at 466 ° C we find that all the samples, for the most part, have completed their decomposition. The percentage chlorination was subtracted out so that we could compare the percentage weight loss of the polyethylene part of the polymer. The CPE (36% Cl) and the CPE (42% Cl) showed similar percentage weight loss, ranging from 31 to 34%.

DSC curves

Figure 5 shows a typical DSC curve for HDPE in air. One endothermic peak appears at 120 ° C and a broad range of peaks appear from 250 ° C up

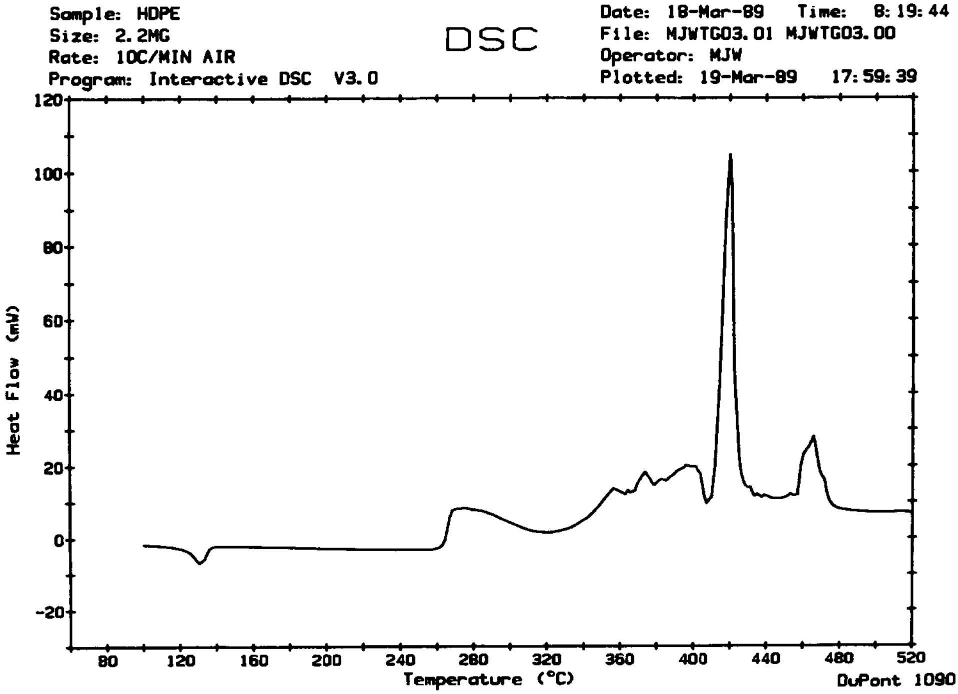


Fig. 5. DSC curve for HDPE in air.

to 480 °C. The sharp peak around 120 °C represents the heat of melting. The other peaks are due to decomposition and structural rearrangements which the polymer undergoes.

The melting point for the chlorinated samples is also around 120 °C; however, the intensity of the peak at this point decreases with degree of chlorination. This is possibly due to the decrease in crystallinity with increasing chlorination. The dehydrochlorination stage (endothermic) occurred between 160 °C and 360 °C. The HCl generated during decomposition of the polymers reacted at some point with the aluminum pans used. This reaction is believed to be responsible for the poor reproducibility of the broad exothermic zone observed above 380 °C.

CONCLUSIONS

The maximum reactivity (R_{max}, % min^{-1}) is a useful parameter for comparing the lability of the polymer materials. The level of chlorination has a greater effect on T_{max} in the dehydrochlorination stage and only a small effect in the zone in which most of the oxidation of the polymer occurs. The residue from the chlorinated samples is considerably larger than that for HDPE; it does not, however, follow the level of chlorination.

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