

A STUDY OF THE FLAMMABILITY OF CHLORINATED POLYETHYLENE UNDER PYROLYSIS CONDITIONS *

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ABSTRACT

High density polyethylene (HDPE) is highly flammable, and it is therefore of great scientific interest to find a way to reduce its flammability. Chlorination of HDPE has been shown to have an effect on the flammability of the polymer. This is part of an ongoing study to be carried out in atmospheres of nitrogen, air, and oxygen. Four different samples having varying percentages of chlorine were considered for this study: HDPE, 25% chlorinated PE, 36% chlorinated PE, and 42% chlorinated PE. The results obtained indicate suppression of the flammability of the polymer owing to the effect of chlorine on the decomposition rate.

INTRODUCTION

High density polyethylene (HDPE) is a highly flammable compound [1]. Finding a method to reduce the flammability of HDPE is of great scientific interest to researchers and industry because of the wide and varying uses of polyethylene today. Polyethylene is used in construction materials for home furnishings, domestic and industrial buildings, appliances, fabrics, and transportation vehicles. An ideal flame retardant derived from polyethylene would have the following characteristics [2]: high resistance to ignition and flame propagation, low rate of combustion, low rate and amount of smoke generation, low combustibility and toxicity of product gases, retention of reduced flammability during use, acceptability in appearance and properties for specific end uses, no environmental or health safety impact, and little or no economic penalty. Chlorination of polyethylene has been shown to have an effect on its flammability [3]. This work was part of an ongoing study to look at various chlorinated polyethylene samples. The level of polyethylene chlorination was varied and a number of decomposition parameters studied. The samples are: HDPE (unchlorinated), 25% chlorinated (25% Cl-PE), 36%

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chlorinated (36% Cl-PE), and 42% chlorinated (42% Cl-PE). Decomposition of the polymers occurred in a nitrogen atmosphere.

EXPERIMENTAL

Several instruments were used to study the effects of the level of chlorination: a Du Pont 951 thermogravimetric analyzer (TGA) and a Du Pont 1090 B thermal analyzer (TA) were employed to study the thermal decomposition of the samples. To study the change in heat during decomposition a thermogravimetric analyzer-differential thermal analyzer (TG-DTA) and a Du Pont 910 differential scanning calorimeter (DSC) were used. For the TGA, the TG-DTA and the DSC, the experimental conditions were held constant for all runs. The flow rate of nitrogen was maintained at $50 \text{ cm}^3 \text{ min}^{-1}$. The heating rate was held constant at $10^\circ \text{C min}^{-1}$ with an initial temperature of 30°C and a final temperature of 600°C . The composition of the gases evolved at different temperatures was obtained using a Nicolet MX 1 Fourier transform infrared (FTIR) spectrophotometer and a Shanghai 100 gas chromatograph (GC/TCD). For the FTIR data, a Teflon tube was connected to the outlet of the TGA and the inlet of the gas cell on the FTIR. The gas flowed into the gas cell and out through an exit valve. This arrangement allowed the continuous flow of the gases, formed in the TGA, through the FTIR. Gas chromatography data was also obtained by sampling the gaseous products at various temperatures. This was done to establish the nature of the products being formed when polymers of different levels of chlorination were decomposed. The HDPE samples used in this study were obtained from Scientific Polymer Products, Inc.

To establish if the polymer samples were homogeneous the effects of varying sample mass on three kinetic parameters were determined. These were T_{max} , reactivity and the residue. The results are shown in Table 1 for 42% Cl-PE. For the three different samples tested the T_{max} values for peak 1 were similar and in the range $326\text{--}328^\circ \text{C}$, while peak 2 had even closer T_{max}

TABLE 1
Sample homogeneity for 42% Cl-PE in nitrogen

Mass (mg)	Peak 1		Peak 2		Residue at 600°C (%)
	T_{max} ($^\circ \text{C}$)	Reactivity ($\% \text{ min}^{-1}$)	T_{max} ($^\circ \text{C}$)	Reactivity ($\% \text{ min}^{-1}$)	
10	326	0.101	472	0.190	4.9
5	327	0.103	471	0.190	6.2
2.5	328	0.110	471	0.198	5.5

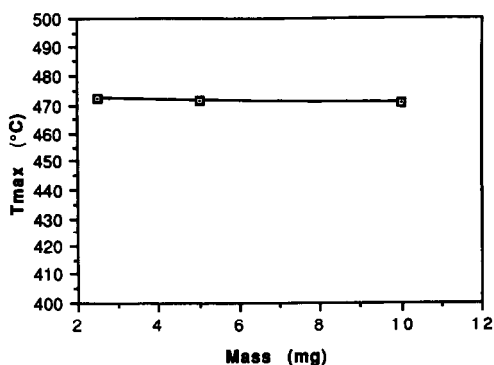


Fig. 1. Sample homogeneity: 42% Cl-PE in nitrogen.

values in the range 471–472°C. The reactivities were even closer, with all runs for peak 1 having a reactivity ($\% \text{ min}^{-1}$) of 0.10 ± 0.009 and peak 2 having a reactivity ($\% \text{ min}^{-1}$) of 0.19 ± 0.008 for all runs. The residue (%) ranged from 4.91 for the 10 mg sample to 6.28 for the 5 mg sample. When T_{max} values were plotted against mass a relatively straight line resulted (Fig. 1). Because different sample sizes resulted in similar T_{max} values, it was concluded that our samples were homogeneous.

Once it was established that the polymer sample was homogeneous, it was necessary to test to see whether or not high reproducibility could be obtained. Table 2 shows three different runs using 42% Cl-PE in nitrogen. All three runs involved the same experimental conditions with a sample mass of 10 mg. All of the T_{max} values were in the ranges 325–328°C for the first peak and 472–473°C for the second peak. The reactivities ($\% \text{ min}^{-1}$) were even closer, with all peak 1 values being 0.10 ± 0.0062 and all peak 2 values being 0.19 ± 0.002 . The residue (%) had an average value of 4.91 ± 0.99 . Since the three kinetic factors studied resulted in similar values for all trials, 10 mg was chosen as the most reproducible mass for pyrolysis. Therefore, all subsequent runs for pyrolysis used a sample size of 10 mg.

TABLE 2

Reproducibility for 42% Cl-PE in nitrogen (mass, 10 mg)

Run	Peak 1		Peak 2		Residue at 600°C (%)
	T_{max} (°C)	Reactivity ($\% \text{ min}^{-1}$)	T_{max} (°C)	Reactivity ($\% \text{ min}^{-1}$)	
1	325	0.103	472	0.190	4.5
2	325	0.102	472	0.189	4.7
3	329	0.097	473	0.191	5.5
Average	326	0.101	472	0.190	4.9

RESULTS AND DISCUSSION

A thermogravimetric heating curve of the 42% chlorinated HDPE in nitrogen is shown in Fig. 2. Two different thermo-decomposition stages are seen for the 42% chlorinated sample, which are represented by two peaks on the DTG curve. For simplicity, these two decompositions will be labeled peak 1 and peak 2 for all chlorinated samples. Peak 1, the first thermo-decomposition stage, occurs between 280°C and 350°C and is due to the loss of HCl. Peak 2, the second thermo-decomposition stage, occurs between 350°C and 500°C and is due to the loss of various aliphatic hydrocarbons. Three kinetic factors were considered for all data obtained. The first is the temperature at which maximum weight loss occurs. This is abbreviated to T_{\max} . The second kinetic factor is the reactivity (R_{\max} , % min^{-1}) at T_{\max} and the third kinetic factor is the residue (%) or char left after heating to 600°C.

Figure 2 also shows an HDPE sample under pyrolysis conditions. If this is compared with the TG curve for the chlorinated sample, obvious differences are apparent. One difference is that only one decomposition stage is present (440–510°C). This peak corresponds to the loss of aliphatic hydrocarbons similar to those found for the 42% Cl-PE in the second thermo-decomposition stage. Since no chlorine is present there should be no stage

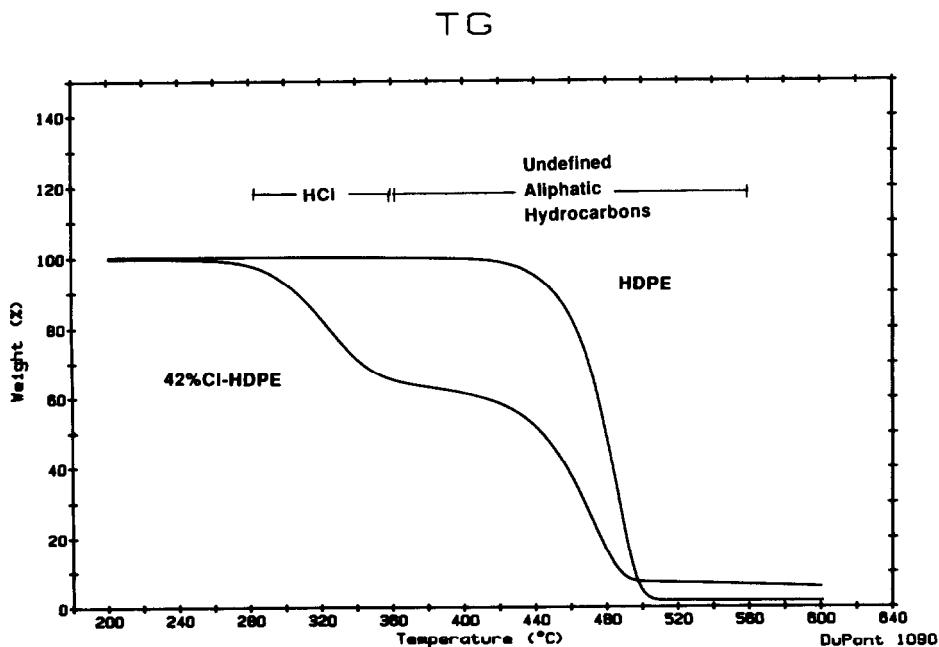


Fig. 2. TG heating curves: 42% Cl-PE and HDPE in nitrogen.

corresponding to the loss of HCl. Therefore, the single peak of HDPE may be labeled as peak 2.

Pyrolysis

Thermogravimetry

After we had established that our samples were homogeneous and had chosen a sample weight (10 mg) which allowed for high reproducibility, we wanted to study the effects of chlorination on the thermal decomposition of HDPE under pyrolysis conditions. Pyrolysis involves a chemical change when a material undergoes thermal degradation in the absence of oxidation. The gaseous atmosphere used for this study was pure nitrogen. Pyrolysis may also occur during combustion of the polymer, but this occurrence is not easily distinguished (4). We therefore ran the HDPE in pure nitrogen to obtain a clearer understanding of the effect of temperature. Table 3 shows the T_{\max} , reactivity, and residue values for all four samples in nitrogen. Several general differences are apparent at a first glance. The T_{\max} value for the unchlorinated sample is slightly higher than that for the 42% chlorinated sample. On the other hand, the reactivity was found to be lower than the reactivity of the unchlorinated sample. The final difference occurs in the residue. For the unchlorinated sample the residue is slightly greater than 1%, meaning that only a very small percentage of the polymer did not decompose. The chlorinated sample had a higher residue, between 4% and 5%.

Polymer flammability is a complex process which is believed to contain two different phases [5]. The first is the vapor phase where a flame retardant, such as chlorine, reduces free radical reactions which are involved in flame formation and propagation [6]. The second is the condensed phase. If the material studied has a flame retardant which modifies its thermodecomposition and enhances char formation, then the flame retardant is working in the condensed phase [6].

A trend can be seen in the data obtained in nitrogen. For the first peak, correlating to the loss of HCl, the T_{\max} value decreases and the reactivity

TABLE 3
Comparison of HDPE and chlorinated samples in nitrogen

Chlorination (%)	Mass (mg)	Peak 1		Peak 2		Residue at 600 °C (%)
		T_{\max} (°C)	Reactivity (% min ⁻¹)	T_{\max} (°C)	Reactivity (% min ⁻¹)	
0	10	—	—	487	0.451	1.1
25	10	340	0.058	490	0.261	5.4
36	10	336	0.087	473	0.190	5.1
42	10	326	0.101	472	0.190	4.9

increases as the chlorination increases. For the second peak, correlating to the loss of aliphatic hydrocarbons, a similar trend occurs. As the chlorination increases, the T_{\max} value again decreases, but in this case the reactivity decreases. There is also a significant difference between the residues of HDPE and the chlorinated samples. HDPE had a residual (char) of about 1% (ranging from 0.747% to 1.49%), while the chlorinated samples had a residue ranging between 4% and 5%. Flame retardants have the characteristics proposed by our data. A highly effective flame retardant, such as chlorine, results in a lower T_{\max} value and a higher residue. A significant similarity was found between the 36% chlorinated HDPE and the 42% chlorinated HDPE. If we compare T_{\max} values with the amount of chlorination (Table 3), we find that increasing chlorination decreases T_{\max} values. The 42% chlorinated sample is similar to the 36% chlorinated sample. We next compared reactivity to percent chlorination (Table 3). As the chlorination increases, the reactivity decreases. Once again the reactivity levels off above 36% chlorination. We believe that increasing the chlorination above 36% under these conditions has little effect on the extent of decomposition of the polymer. This result agrees with a previous study [1] in which an equal mixture of nitrogen and oxygen was used as the gas atmosphere.

FTIR and GC data

If an FTIR spectrophotometer or gas chromatograph is linked with the TGA as mentioned in the Experimental section, the gaseous products evolved during the thermal decomposition of the polymer can be studied. Three different aliphatic hydrocarbon peaks were studied in order to determine the difference between the gaseous products for the chlorinated samples versus the unchlorinated samples. The first is the out-of-plane bending (OOP) of an unsaturated C–H unit which occurs at 1463 cm^{-1} . The second is a set of peaks at 3188 and 2788 cm^{-1} which correlates to the C–H stretching of a saturated hydrocarbon unit (SHU) [7]. The third is another set of peaks at 2400 and 2240 cm^{-1} representing the C–H stretching of ethylene or an acetylenic C–H unit (CHE) [7]. Finally, the loss of HCl was studied for the chlorinated samples. Table 4 gives the FTIR data obtained for the HDPE sample in nitrogen. Figure 3 shows the FTIR data of peak height (area) versus temperature for both the chlorinated and unchlorinated samples. The temperature is given along with the area of the peaks for OOP, SHU, and CHE. Below 375°C it is noted that no decomposition of the polymer has occurred. Figure 2, the 42% Cl–PE sample, supports the FTIR data that the polymer has not decomposed before 375°C . Above 375°C , we get both stretching and bending of the C–H units. For comparison, Table 5 gives the FTIR data obtained for the 42% chlorinated HDPE sample in nitrogen. This data includes the decomposition of HCl. Before 375°C , only HCl is given off as product, but after 375°C the C–H units begin to break off. After 375°C no HCl gas was detected, giving strength to the belief that

TABLE 4
FTIR data for HDPE sample in nitrogen

Temperature (°C)	Peak height ^a OOP	Peak area ^a	
		SHU	CHE
285	0.0	0.00	0.000
315	0.0	0.00	0.000
345	0.0	0.00	0.000
375	0.4	0.05	0.030
405	0.9	0.09	0.038
435	2.7	0.16	0.050
465	9.9	0.17	0.038
495	3.6	0.36	0.076
525	3.5	1.07	0.072

^a Arbitrary units for peak height and peak area.

peak 1 is strictly due to the loss of HCl. If the FTIR spectra for the 42% Cl-PE (Figs. 4 and 5) are considered, there are two areas of the spectra to consider. First are the two sharp well-defined peaks at 3200 cm^{-1} . These correspond to the loss of HCl at peak 1 on the thermogravimetric curve (see Fig. 2). Next, the numerous peaks occurring at temperatures above 350 °C

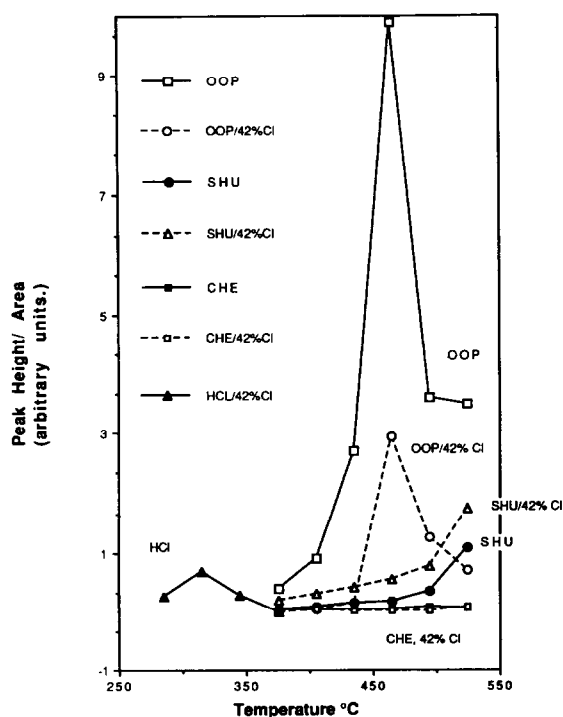


Fig. 3. FTIR data for chlorinated and unchlorinated samples.

TABLE 5

FTIR for 42% Cl-PE in nitrogen

Temperature (°C)	Peak height ^a OOP	Peak area ^a		
		SHU	CHE	HCL
285	0.00	0.00	0.000	0.263
315	0.00	0.00	0.000	0.675
345	0.00	0.05	0.000	0.290
375	0.00	0.19	0.018	0.000
405	0.05	0.31	0.043	0.000
435	0.14	0.42	0.024	0.000
465	2.95	0.55	0.008	0.000
495	1.26	0.77	0.025	0.000
525	0.70	1.74	0.094	0.000

^a Arbitrary units for peak height and peak area

on the FTIR spectra (Fig. 5) should be considered. The other large peak shown at approximately 2800 cm^{-1} is due to the presence of alkenes such as ethylene and propylene stretching. Smaller peaks occur at 1463 cm^{-1} and 908 cm^{-1} : these are also due to alkane units such as $-\text{CH}$ breaking off. Another sharp peak found below 800 cm^{-1} is possibly due to the $\text{C}-\text{Cl}$ bond. This indicates that not all the chlorine is released as HCl , but instead some of the chlorine attaches to carbon and is retained by the polymer.

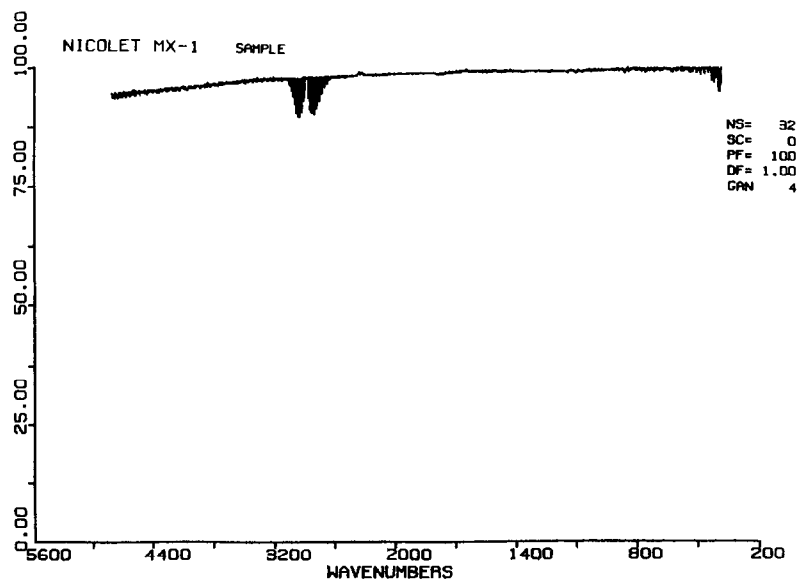


Fig. 4. FTIR spectrum for 42% Cl-PE at temperatures between 280°C and 380°C .

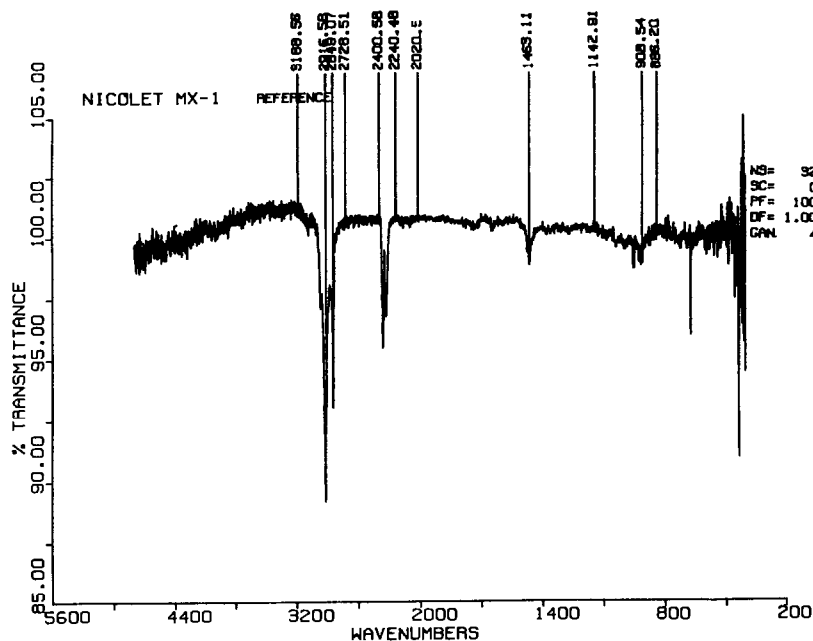


Fig. 5. FTIR spectrum for 42% Cl-HDPE at temperatures between 380 °C and 520 °C.

Based on the GC data various aliphatic hydrocarbons, including hydrogen, methane, ethylene, and propylene, were evolved due to the thermal decomposition of the polymer over a temperature range of between 360 °C and 490 °C in all four samples (Table 6). After about 490 °C only hydrogen and ethylene were noted as gaseous products. The GC results are similar to those obtained by Miller and Martin [8].

TABLE 6

GC data for all four samples in nitrogen

Temperature range (°C)	HDPE	25% Cl-PE	36% Cl-PE	42% Cl-PE
120				
240-360		HCl	HCl	HCl
360-460		H ₂ , CH ₄ C ₂ ²⁻ , C ₃ ²⁻	H ₂ , CH ₄ C ₂ ²⁻ , C ₃ ²⁻	H ₂ , CH ₄ C ₂ ²⁻ , C ₃ ²⁻
460-504	H ₂ , CH ₄ C ₂ ²⁻ , C ₃ ²⁻	HCl H ₂ , CH ₄ C ₂ ²⁻ , C ₃ ²⁻	HCl H ₂ , CH ₄ C ₂ ²⁻ , C ₃ ²⁻	HCl H ₂ , CH ₄ C ₂ ²⁻ , C ₃ ²⁻
504-600	H ₂ , C ₂ ²⁻	H ₂ , CH ₄ C ₂ ²⁻ , C ₃ ²⁻	H ₂	H ₂ , C ₂ ²⁻
Weight loss (%)	100	95	95	95

Differential scanning calorimetry data

The effects of chlorination on the polymer using differential scanning calorimetry (DSC) were then considered. A TG-DTA was also run which gave identical results to the DSC; hence only the DSC data will be discussed. The DSC data could establish endothermic or exothermic reactions and compare these observations with the TG results. DSC endothermic peaks are associated with sublimation and decomposition, and exothermic peaks with decomposition. Figure 6 shows a typical DSC curve for high density polyethylene in nitrogen. This curve has two endothermic peaks, one at 130°C (peak maximum) and the other a broad peak starting at about 180°C and ending at about 500°C. From the TG data we observed only one peak, the one occurring at 465°C (see Fig. 2). The sharp, well-defined peak at 138°C can be correlated with the melting of polyethylene. The GC data at this temperature indicate that no gaseous products are evolved. A phase transition of a solid to a liquid (melting or fusion) has occurred. The second broad endothermic peak was due to the heat loss from the decomposition of HDPE. The three chlorinated samples in nitrogen give similar curves with three endothermic peaks. Figure 7 shows the DSC curve for 42% Cl-PE. The first peak is due to melting. The intensity of the first peak is decreased with increased chlorination (Fig. 8). According to Vanzo, high density polyethylene has a crystallinity limit of 80–90% [9]. The product

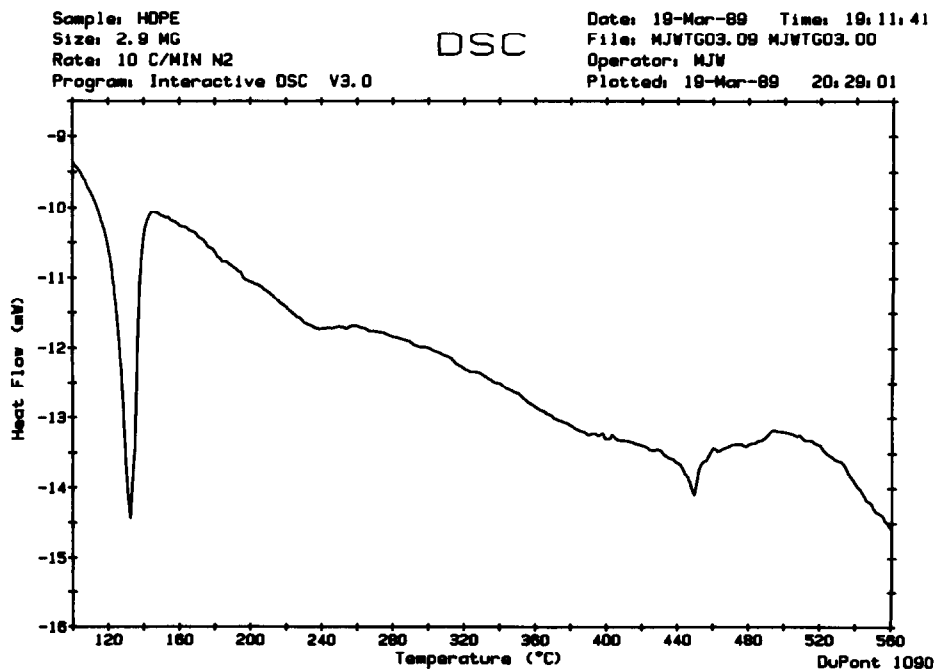


Fig. 6. DSC curve for HDPE in N₂.

DSC

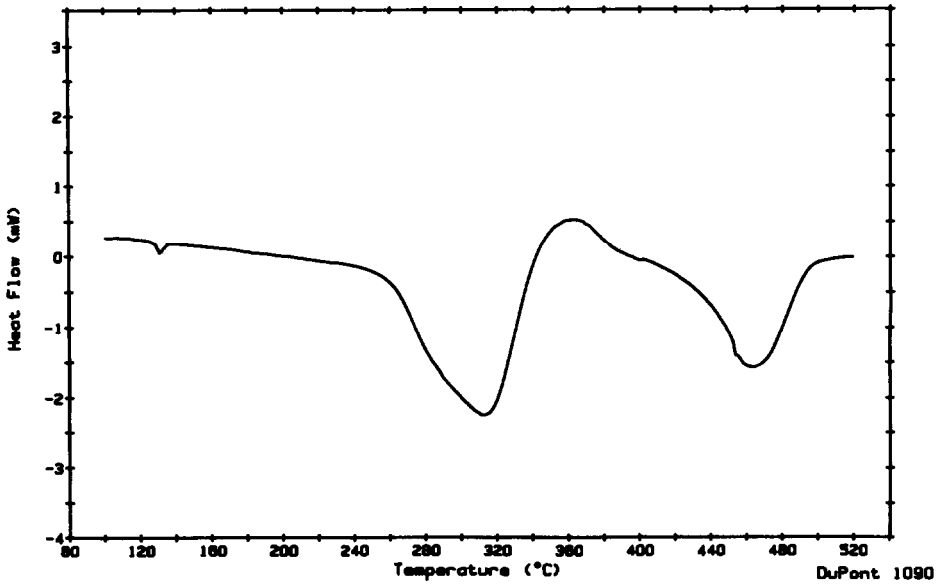


Fig. 7. DSC curve for 42% Cl-PE in N₂.

DSC

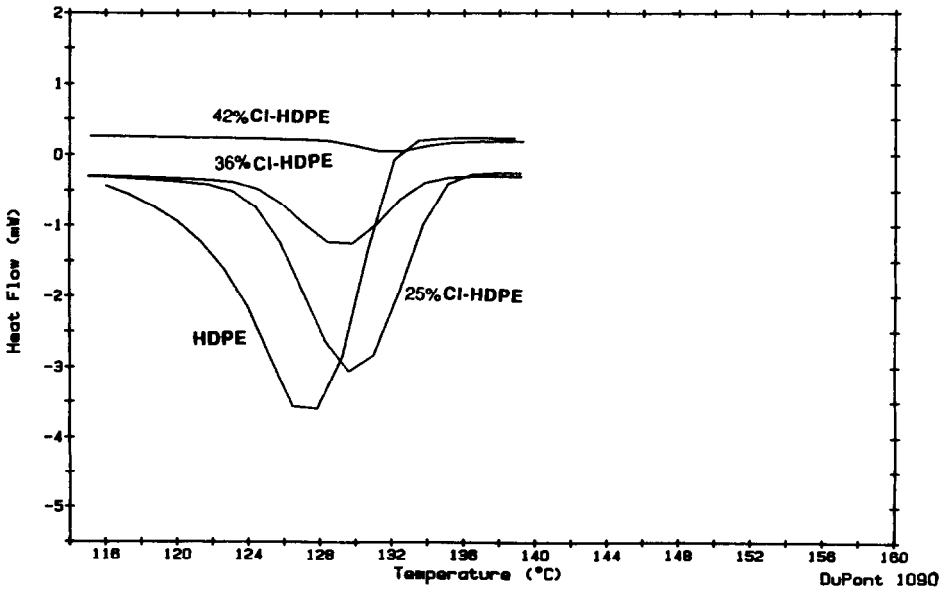


Fig. 8. DSC curves for HDPE, 25% Cl-HDPE, 36% Cl-HDPE and 42% Cl-HDPE in N₂.

with 25% chlorination has 25% crystallinity, while the 36% and 42% chlorinated products have less than 2% crystallinity [9]. The second endothermic peak is due to the heat associated with the loss of HCl noted by TG (see Fig. 2). This peak starts at 260°C and ends at about 360°C. The third peak, which has a temperature range of 360–520°C is due to the decomposition of HDPE. The decomposition of HDPE in the unchlorinated sample shows a more gradual loss of the polymer over a wider range of temperatures. The chlorinated samples lose HCl and possibly some of the polyethylene at the second endothermic peak. The majority of the HDPE is decomposing and volatilizing in the temperature encompassed by the third endothermic peak.

For the above results, we propose that the chlorinated HDPE did not alter the composition of volatiles (H_2 , CH_4 , C_2H_4 , C_3H_6), but instead produced the actual flame-inhibiting species (HCl). These observations strongly suggest that the fire-retardant effect of chlorination on the flammability of HDPE, must be in the vapor phase [1,5,6]. However, the chlorination also results in enhanced char formation. It may also indicate a condensed-phase mechanism for a flame-retardant [5,6]. Therefore, the chlorination of the HDPE may occur by more than one mechanism [5,6].

CONCLUSIONS

(1) Increasing the degree of chlorination will retard the decomposition of HDPE.

(2) Increasing the degree of chlorination will decrease the crystallinity of HDPE.

(3) Increasing the percentage of chlorination above 36% does not have significant effects on the thermal decomposition of HDPE.

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