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A Study of the Flammability of Chlorinated Polyethylene by Thermal Analysis

Michele Whitely
Western Kentucky University

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A STUDY OF THE FLAMMABILITY OF CHLORINATED POLYETHYLENE BY THERMAL ANALYSIS

A Thesis
Presented to
the Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Michele J. Whiteley
July 1989

(Appendix G)

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A STUDY OF THE FLAMMABILITY OF CHLORINATED POLYETHYLENE BY THERMAL ANALYSIS

Recommended July 25, 1989
(Date)

Dempsey Tan
Director of Thesis

Darwin B. Dahl

Lowell W. Shank

Approved July 27, 1989
(Date)

Elmer Gray
Dean of the Graduate College

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A STUDY OF THE FLAMMABILITY OF CHLORINATED POLYETHYLENE BY THERMAL ANALYSIS

Michele J. Whiteley July 1989 102 pages

Directed by: W.P. Pan, L.W. Shank, and D.B. Dahl

Department of Chemistry Western Kentucky University

High Density Polyethylene (HDPE) is a highly flammable compound. Finding a method to reduce HDPE's flammability is of great scientific interest to researchers and industry. Chlorination of the HDPE has been shown to have an effect on the flammability of the polymer. This study looks at the effects of various chlorinated samples on the thermal decomposition of HDPE in atmospheres of nitrogen, air, and oxygen. The thermal analysis instruments used were a Thermogravimetric Analyzer (TGA), and a Differential Scanning Calorimeter (DSC). To study the gaseous products evolved during thermal decomposition of the polymer Fourier Transform Infrared Spectrophotometry (FTIR) and Gas Chromatography (GC) data were obtained. The results obtained showed that increasing chlorination suppresses the decomposition rate of the polymer by decreasing the flammability.

INTRODUCTION

The objective of this research is to study the effects of chlorination on polyethylene's flammability. In order to better understand certain aspects of this type of research it is first necessary to introduce some important concepts concerning such a study. The three concepts that will be discussed are thermal methods, polymer flammability, and the structure of polyethylene. Thermal methods will include such areas as instrumentation, sources of error, and possible applications. Polymer flammability will encompass the possible mechanisms of flame retardants and also the relationship between thermal methods and polymer flammability. Finally, polyethylene and the chlorination of this compound will be discussed.

A. Thermal Methods

Today, a wide variety of thermal methods exist which can be employed by a chemist. They are often used as an important part of materials characterization.(1) Thermal methods are based on the measurement of the dynamic relationship between temperature and some property of a system such as mass, heat of reaction, or volume. The three most widely used thermal methods are thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and differential thermal analysis (DTA). Thermogravimetry measures changes in weight while DTA and DSC measure energy changes. Two other important thermal techniques are evolved gas detection (EGD) which measures the evolution of gas from a sample as a function of temperature and evolved gas analysis (EGA) which analyzes volatile products released from a sample during decompositions. Most recently in thermal analysis multiple techniques have become popular. Multiple techniques can combine more than one thermal technique such as DTA and TGA or a thermal technique with some other chemical analysis method such as DTA and Gas Chromatography (GC).

1. Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) involves a change in sample mass [weight (W)] as a function of temperature (T) or time (t). There are three kinds of thermogravimetry that can be used depending on the way in which the sample is heated.(2) First is isothermal thermogravimetry where the sample mass is recorded as a function of time at constant temperature. Second is quasi-isothermal thermogravimetry where the sample is heated to constant mass at set increments of increasing temperature. Third is dynamic thermogravimetry where the sample is heated according to changes in the environment temperature which have been set. The curve which is produced has a variety of names - thermogram, thermogravimetric curve, thermolysis curve, pyrolysis curve, thermogravigram, and thermogravimetric analysis curve.(2) No matter what the name, this curve provides useful information about the initial sample's thermal stability and composition, any intermediate compounds thermal stability and composition, and the residue's composition.(3) TGA finds its greatest and most accurate use in the area of mass change as a function of temperature associated with thermogravimetric analysis.

A simultaneous technique, is differential thermogravimetry (DTG). DTG is obtained by taking the first derivative of the TG curve as a function of temperature or time. The DTG curve plots rate of mass loss (dm/dt) on the Y axis versus temperature or time on the X axis. There are several advantages to using the DTG curve rather than the TG curve.(4) Some decompositions involve several reactions over a limited temperature range. With the TG curve these overlapping reactions are often not detected. However, the DTG curve may show tnese reactions as separate peaks. Another advantage to DTG is that appearance-wise it looks more like DTA and DSC. This corresponds to easier comparisons of data if more than one thermal method is being used. Finally, DTG is easy to read making it easier to find the temperature at which maximum weight loss occurs.

There are three major factors to be considered when working with the TGA.(3) These are heating rate, sample mass, and gas flow rate. Optimum conditions of these three factors for the material being studied gives the best results and thus allows for maximum reproducibility.

a. Instrumentation

The thermogravimetric analyzer has a fairly simple instrument design centered around a thermobalance. It also has a furnace controlled by a temperature programmer and a means for obtaining data. A schematic diagram is shown in Figure 1.

Many thermobalances are available today with a variety of uses. Two possible designs exist for the thermobalance - a horizontal balance design or a vertical balance design. With the vertical balance design the thermocouple, which measures the temperature, is underneath the sample pan. Most instruments incorporate this type of thermobalance. The horizontal balance design places the thermocouple in direct contact with the sample pan. The advantage of having a horizontal balance design is that a more accurate reading of the sample's temperature will be obtained.(5) The two most common types of balances are the Null point balance and the Deflection balance. Another type of balance that can be employed is an Electronic microbalance. A Null point balance is schematically diagrammed in Figure 2. As the mass of the sample changes, the balance beam moves away from its normal position. A sensor registers the movement and then moves the balance beam back to the null or original position. The restoring force is proportional to the change in weight. Two types of deflection balances are currently available - a beam type and a cantilever type. Schematic diagrams of these instruments can be found in Figure 3. With this type of balance the weight loss is measured by the deflection of the beam. The beam type balance measures the deflection about a fulcrum. The cantilever type measures the deflections with

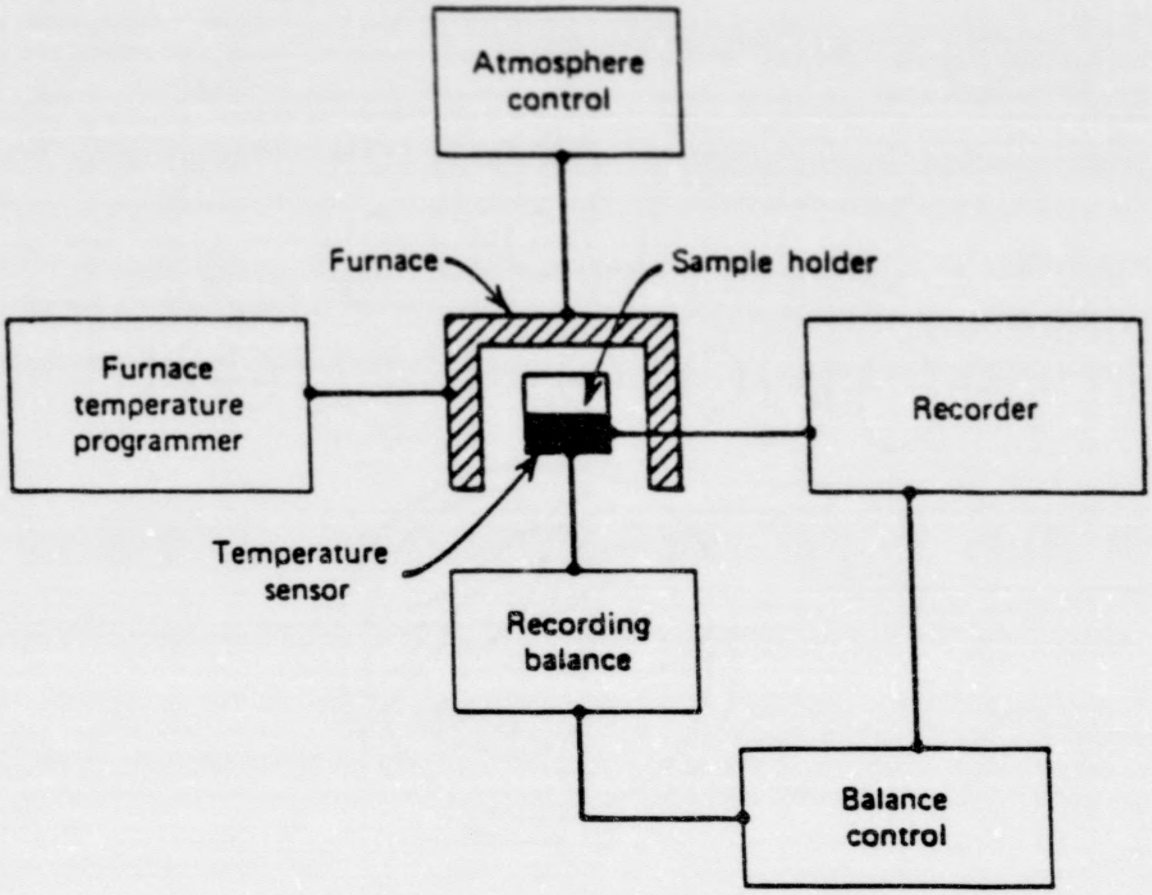


Figure 1 Schematic Diagram of the TGA Instrument

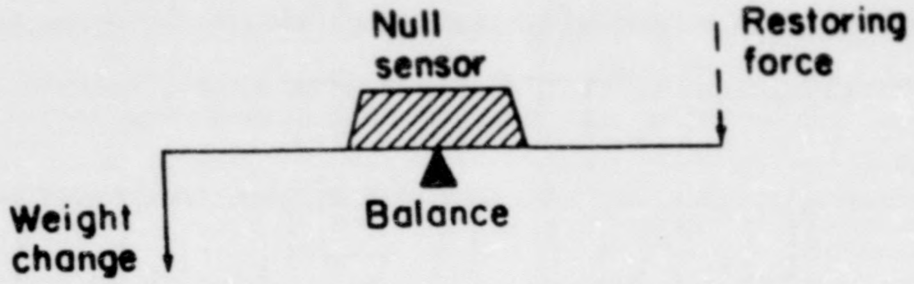
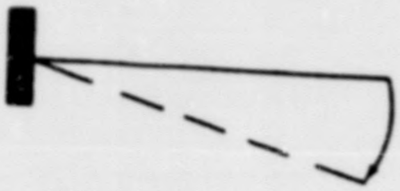


Figure 2 Null Point Balance



Cantilever type

Beam type

Figure 3 Deflection Balances

the beam being fixed at one end. An electronic microbalance uses an electronic bridge circuit to maintain a constant state of electromagnetic balance.

In TGA, the furnace surrounds the thermobalance. Furnace windings, a wire coil coated with ceramics and surrounded by an insulator, are found inside the furnace. The type of wire used for furnace windings depends upon the temperature to be used. Nichrome wire can be used for temperatures up to 1000^0C and platinum wire for temperatures up to 1500^0C. To achieve reproducible thermograms the furnace must have a uniform hot zone and be able to ensure linear heating rates over a wide temperature range.(2) Various materials may be used for the thermocouple. Chromel-alumel thermocouples measure up to 1000^0C and platinum-metal alloys measure up to 1500^0C. The programmer controls the furnace and a temperature sensor which is in direct contact with the furnace sends information to the programmer. This allows for control of the electrical power sent to the furnace. Finally, a recorder is used to provide a continuous record of sample weight as a function of temperature.

b. Sources of Error for the TGA

There are several sources of error which can occur in thermogravimetry. These can lead to inconsistencies in temperature and inaccuracies in the change in mass. These errors may pertain to either instrumental or sample factors. Some instrumental factors include shape of the sample container, sensitivity setting of the instrument, heating rate, and chart speed used to record the TG curve.(6,7)

Sample factors include the atmosphere surrounding the sample, degree of sub-division of the sample, amount of sample used, and packing characteristics of the sample.(6,7) Following is a list of other possible sources of error:(4)

(A) buoyancy effect of sample container

(B) random fluctuations of balance mechanism

(C) electrostatic effects on balance mechanism

(D) condensation on balance suspension

(E) measurement of weight by balance

(F) convection effects from furnace

(G) turbulence effects from gas flow

(H) induction effects from furnace

(I) measurement of temperature by thermocouple

(J) reaction between sample and container

c. Optimum Conditions for the TGA

In conjunction with these sources of error are certain conditions that give optimum results for thermogravimetry data. Increasing the mass of the sample used in a TG experiment, decreases the resolution of the TG data.(8) This is a result of the significant temperature gradient within a large sample and also increased difficulty for volatile products to escape from a large sample. Therefore a small sample must be used consistent with the limits of the balance. A few milligrams of sample is typically used which should be spread into a thin layer of powder. Other factors which can effect TG results are particle size and the degree to which a sample is packed.(8,9) Optimum results are also obtained when the heating rate is as slow as is acceptable for each individual experiment.(10) The reason for this is to keep the actual temperature of the sample and the recorded temperature closer which will in turn increase the resolution of the TG curve. A slower heating rate also results in recording the intermediate steps of the TG processes. Using an open sample container with an inert gas flowing through it also allows for optimum conditions.

d. Applications of TGA

There is a wide range of uses for the thermogravimetric analyzer. It is widely used in chemistry and also in allied fields of study. In the 1950's it was applied to the area of inorganic gravimetric analysis with good results.(2) In the 1960's it took on polymer chemistry with equally good results.(4) Furthermore, the TG can be used to solve applied science problems such as characterization of road construction materials and the study of moisture content of various materials.(11) It can also be used in the application of analytical problems such as metallurgy, paint, ceramics, food technology, inorganic and organic chemistry, polymer chemistry, biochemistry, coal chemistry, and others.(2)

2. Differential Scanning Calorimetry and Differential Thermal Analysis

Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA) are similar in nature and will be discussed concurrently. DTA and DSC measure enthalpy changes in a particular sample when under fixed conditions it is heated or cooled. These methods detect heat lost (exothermic) or heat gained (endothermic) by chemical reactions occurring during the thermal process. Phase changes can also be detected by DSC and DTA. DTA is a method which measures the change in temperature (ΔT) between a sample (S) and an inert reference (R) material (See Figure 4). The change in temperature is usually plotted on the ordinate and temperature is plotted on the abscissa. An endotherm (heat gain) is plotted downwards and an exotherm (heat loss) is plotted upwards. They are plotted differently according to the temperature of the sample and the reference. When the temperature of the sample is greater than that of the reference an exothermic reaction is indicated and the curve is plotted upwards. An endothermic reaction is the opposite where the sample temperature lags behind that of the reference and the curve is plotted downwards. DSC as mentioned above is quite similar to DTA. In DSC, the sample and reference are maintained at the same temperature. The amount of heat needed for the sample and reference to maintain this equivalence in temperature is constantly measured over a programmed temperature range. This recorded heat flow measures the amount of energy absorbed or evolved in a particular transition, which as a result gives calorimetric measurements directly. DSC thus gives a quantitative measurement of energy changes that occur.(12) It also operates under the principal of measuring the energy that has to be applied to keep the

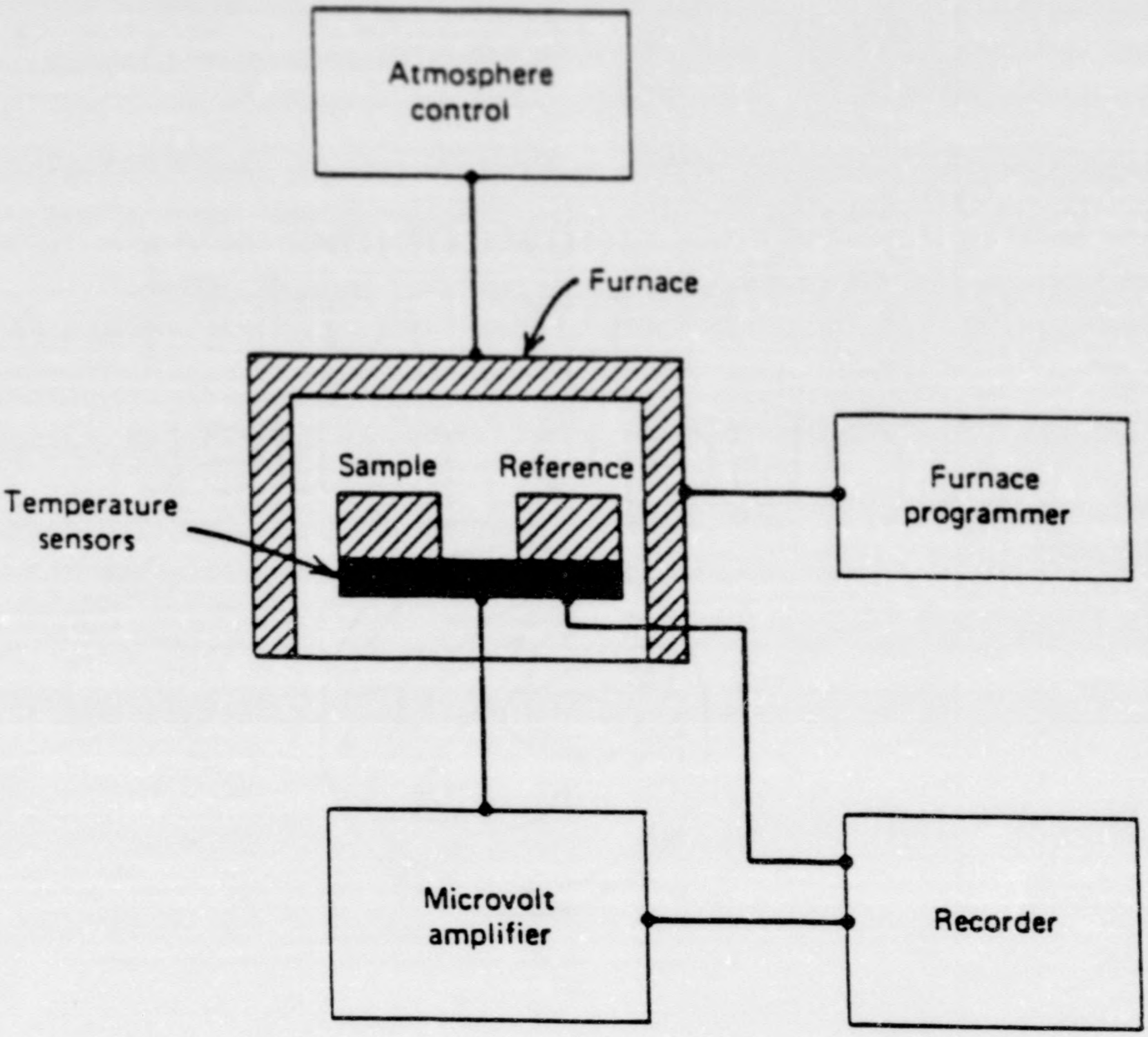


Figure 4 Schematic Diagram of DTA Instrument

sample and reference temperatures the same. Endothermic and exothermic processes relate to some type of chemical reaction or physical change in a material. Endothermic changes include fusion reactions, vaporization, sublimation, decomposition, dehydration, desolvation, and others.(3) Exothermic changes, on the other hand, involve adsorption reactions, crystallization, oxidation processes, chemisorption, and others.(18) Phase or crystalline transitions can be either endothermic or exothermic in nature.

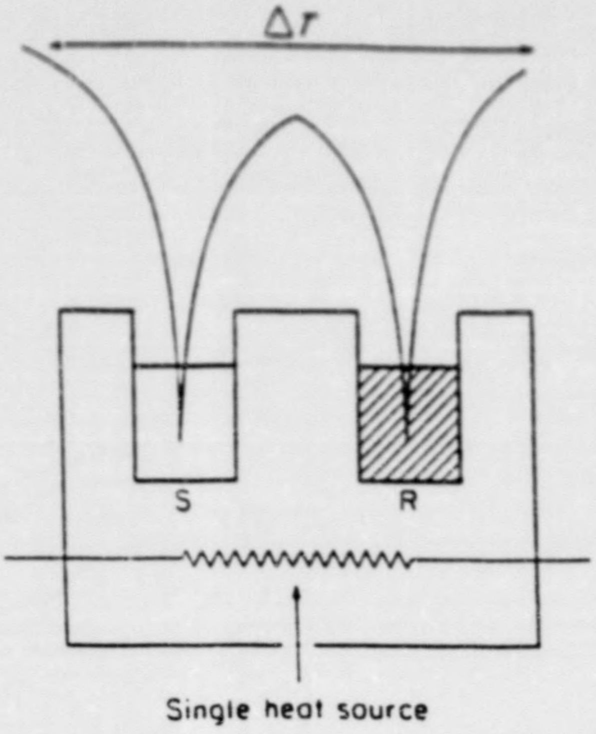
There are several differences between the DSC and the DTA, though.(12) One is that for quantitative measurements such as ΔH, the DSC technique is easier to use since the calibration coefficient does not change with temperature. Therefore, DSC gives both quantitative and qualitative information. DSC also has advantages in that it allows for easier sample handling and an equivalent temperature range coverage. In studies below 800^0C, DSC is usually the method of choice over DTA. DTA gives equally good results though and can allow for easy comparison of the two methods if both are used.

a. Instrumentation - DTA/DSC

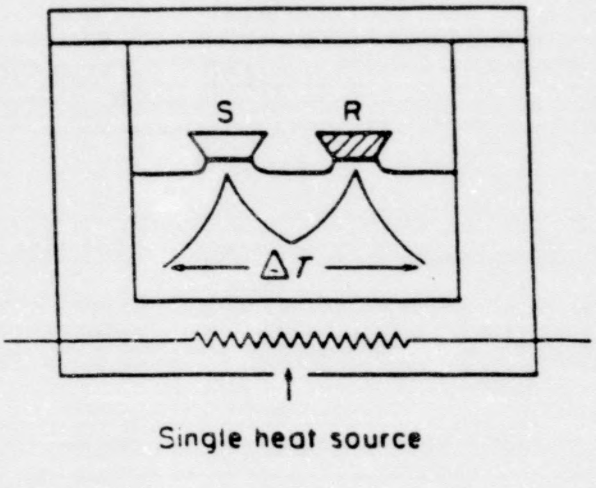
There are two types of systems for differential thermal analysis - Classical and Boersma. In both systems, the sample and reference containers are heated by the same device. The difference between the two systems is in the placement of the temperature sensors. In the classical system the temperature sensors are inserted directly into the sample and reference materials. In the Boersma system, the temperature sensors do not touch the sample and reference materials but instead are in contact with their containers. The difference in temperature (ΔT) between the sample and the reference can then be determined by the temperature sensors. Schematic diagrams of both systems can be seen in Figure 5.

With the DSC instruments, the sample and reference materials have their own heaters and temperature sensors. The sample and reference materials are then maintained at the same temperature. A schematic diagram of the DSC is shown in Figure 6.

Both the DTA and the DSC instruments contain the same type of components. First, they contain the sample holder assembly which was described in detail above. Besides the sample and reference holders, the sample holder assembly contains the thermocouples. When temperatures below 500^0C are being used, thermocouples are found under the sample and reference pans. When the temperatures used are above 500^0C, the sample and reference materials are surrounded by a ceramic or metal block with the thermocouple directly in the sample. The block helps to insure an even distribution of heat. The second component to be considered is the furnace. Like the TGA, this must contain a uniform hot zone and have a linear heating rate.(2) The furnace windings for processes involving temperatures up to 1000^0C are usually made from Nichrome wire. For temperatures up to 1500^0C the furnace windings are usually composed of platinum. Some type of cooling system is often



(a) Classical DTA



(b) 'Boersma' DTA

Figure 5 Classical and Boersma DTA Instruments

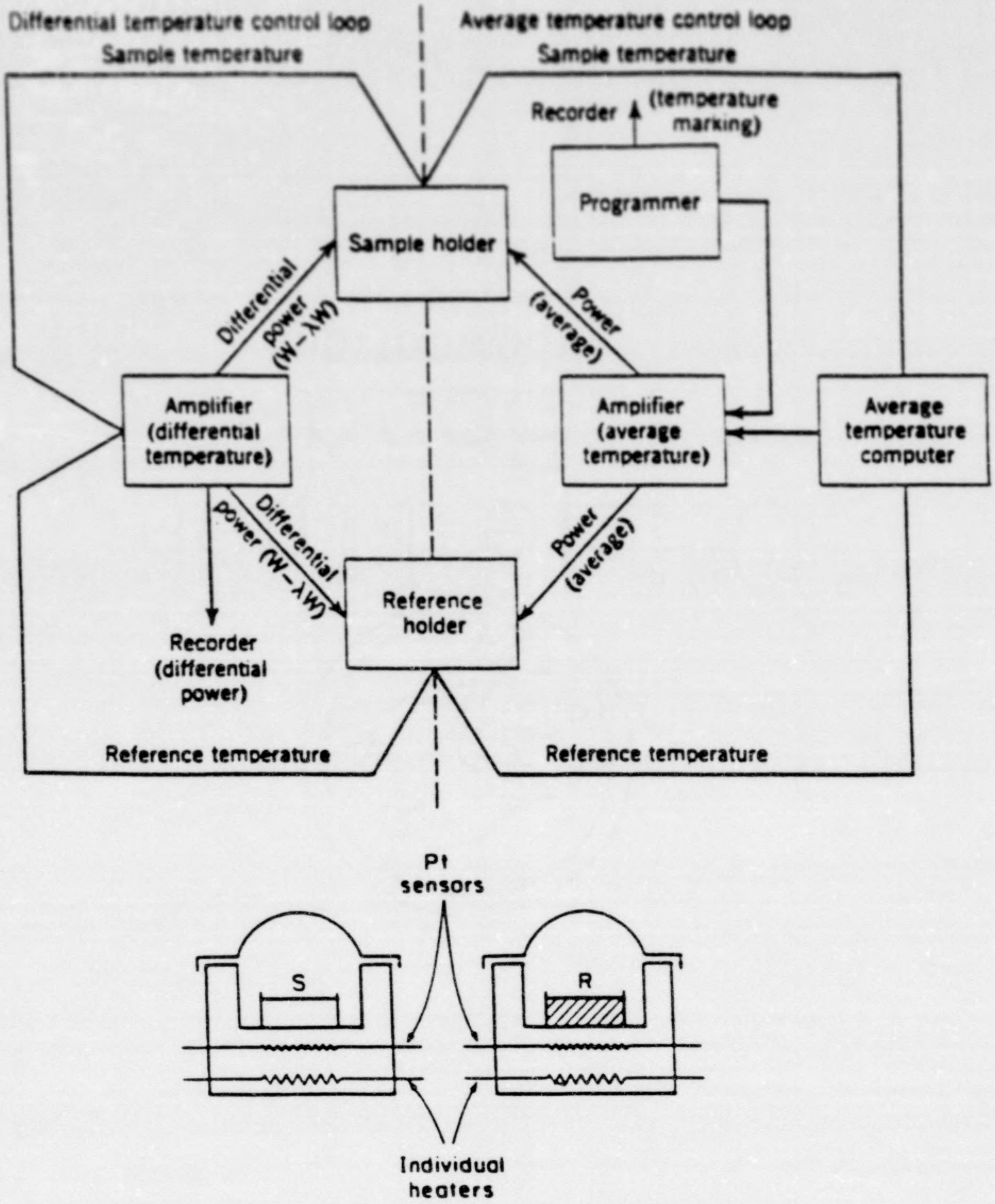


Figure 6 Schematic Diagram of DSC

incorporated to return the temperature to the starting temperature. The next component is a programmer. It should be capable of a range of heating rates anywhere from 1^0C to 50^0C per minute and it is often an advantage to have an isothermal mode of operation. The final essential component is a recording system. This usually incorporates an amplifier to detect signals from the temperature sensors and the temperature thermocouples.

b. DTA and DSC curves

The DTA curve has found its greatest use qualitatively but some studies have indicated that a DTA curve can be useful quantitatively.(13) Despite this, quantitative data is most often obtained from DSC curves. The DTA peak area depends upon several factors. Peak area depends on the mass of sample (m) used, the heat of reaction or enthalpy change (ΔH), plus additional factors like sample geometry and thermal conductivity. Sample geometry and thermal conductivity give rise to an empirical constant (K). This results in the following equation for peak area:(3)

$$\text{Peak Area (A)} = \pm K \times \Delta H \times m$$

As mentioned above DSC curves give information of both a quantitative and a qualitative nature.(12) DSC curves record the differential heat input to the sample expressed as a heating rate (dH/dt) in units of eg mJ s^{-1} or mcal s^{-1} on the ordinate. The abscissa is usually temperature or time. Like DTA, the exotherms plot upwards and the endotherms plot downwards. When the change in heat (ΔH) for a chemical reaction is greater than zero, the sample heater is activated and a signal for this is obtained. For the exothermic change ($\Delta H<0$), the reference heater is activated in order to maintain an equilibrium between sample and reference temperatures. This gives the opposite signal. Peak areas in DSC are proportional to the thermal effects experienced by the sample as it is subjected to the temperature program. DSC also has a proportionality constant (K), like DTA, but instead of being dependent on a sample characteristic it is basically an electrical conversion factor. When the components for the DSC are designed well, the constant K for the peak area equation is assumed to be independent of temperature. This is an important feature of the DSC method, and helps to explain its popularity as a technique for calorimetric determinations of a quantitative nature. Once again the equation

$$\text{Peak Area } (A) = \pm \Delta H \times m \times K$$

can be used where ΔH represents the samples enthalpy change and m is the sample mass.(3)

c. Factors Affecting DTA/DSC Curves

Like thermogravimetric studies there are numerous factors which effect the DTA/DSC curves. These are often complex because several factors can be acting on the sample at one time and sometimes the factors are interrelated by their very nature. As with the TGA, there are two main groups with which these DTA/DSC factors can be associated - sample factors and instrumental factors. Sample factors include such things as amount of sample, particle size, and sample packing.(14,15) Instrumental factors include such things as heating rate, sample holder materials, thermocouples, and the atmosphere around the sample.(15,16,17)

d. Applications of DTA/DSC

DTA and DSC have numerous applications in chemistry as well as other fields. These methods have found successful operation with a wide range of materials. Some of the materials studied include catalysts, polymers, pharmaceuticals, metals, wood, and organic substances.(2) It has been found to be extremely useful in analytical procedures. One analytical use is as a control for comparing similar materials.(2) If the instrument is properly calibrated, DTA and DSC may be used for the quantitative estimation of materials or to determine purity of a sample.(18)

3. Multiple Techniques

Multiple techniques of thermal analysis have recently taken on a significant role in thermal analysis studies. They are most useful in studying the mechanisms of thermal decompositions such as a solid to a gas.(19) Multiple techniques are of three specific types - simultaneous, combined, and coupled.(3) Simultaneous techniques are the most useful because the results are directly comparable. The reason for this is that this involves the application of two or more techniques to the same sample at the same time. Examples of this include TG-DTA, TG-DTG, TG-DTG-DTA, and TG-EGD or EGA. TG-DTG as a simultaneous technique was discussed earlier including advantages of obtaining the DTG curves. Combined techniques refer to the use of separate samples for each technique. This is less effective because different portions of the same sample may give dissimilar results. Finally, there are coupled techniques. This involves the use of two or more techniques on the same sample with the two instruments being connected by an interface. One example of this is a mass spectrophotometer (MS) linked to a TGA. As decomposition occurs in the TGA, the gaseous products resulting from the sample are passed to the mass spectrophotometer to be analyzed. Other possible forms of coupling include gas chromatography (GC), fourier transform infrared spectrometry (FTIR), and mass spectrometry (MS) which can be linked to either the TGA, the DTA, or the DSC. The gaseous products formed from the decomposition of the sample can be more closely analyzed to understand the chemical decompositions which are occurring. This is often useful for research purposes in order to more closely understand a sample and to aid in a material's characterization.

B. Polymer Flammability

Polymer flammability has become an important topic in recent years because of the increased usage of polymers in construction materials.(12) Polymers are currently being used in the construction areas of home furnishings, domestic and industrial buildings, appliances, fabrics, and transportation vehicles.(20) Polymer usage is often restricted because of its flammability. Because of its versatility and popularity a means of reducing its flammability must be found. This is easier said then done because of the poor understanding of polymer flammability and the lack of regulations governing this area.(21) Despite the lack of knowledge in this area it is believed an ideal flame retardant system should have the following characteristics:(20) 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. One quick, reproducible way of studying polymer flammability is through thermoanalytical techniques. Although they are sometimes considered a small scale test, thermoanalytical techniques are still capable of providing valuable results.

1. Polymer Flammability Under Combustion Conditions

When polymer flammability is studied under conditions of combustion (air), Pearce and Liepins believe there are four basic processes involved.(22) These are preheating, decomposition, ignition, and combustion and propagation. Preheating involves raising the temperature of the polymer by means of some external source such as a furnace for the TGA. Several factors should be taken into consideration concerning the increase in the sample's temperature. Factors such as the heating rate should be dependent on the thermal intensity of the ignition source, the thermal conductivity and specific heat of the material, and the latent heat of fusion of a crystalline substance. The sample finally reaches a temperature where it begins to decompose and form gaseous combustible products. The rate at which the gaseous products are formed is dependent on things such as the intensity of the external heat, the temperature at which decomposition occurs, and the rate of the decomposition itself. The combustible gases increase in concentration until the gases can attain oxidation in the presence of the ignition source. Two factors which are of importance to the ignition process are availability of oxygen and ignition characteristics of the gas. After ignition occurs and the ignition source is removed it is possible under certain conditions for combustion to become self-propagating. This is possible when enough heat is generated and radiated back to the sample to continue the decomposition process. These include the rate at which heat is generated, the rate of heat transfer to the surface, the surface area, and the rate of decomposition.(20)

2. Mechanisms of Polymer Flammability

Polymer flammability, although a complex process, is believed to occur in two different phases - a vapor phase and a condensed phase.(23) By altering these phases it is believed that polymer flammability can be reduced. A vapor phase approach to reducing polymer flammability points to inhibiting free radical reactions involved in the steps of flame formation and propagation. This can be accomplished by incorporating fire-retardant additives, impregnating the material with a flame-retardant substance, or by using flame-retardant comonomers in the polymerization or grafting processes.(20) A condensed phase approach to reducing polymer flammability involves a change in the decomposition chemistry that leads to an increase in residue (char). This can be achieved by incorporating additives that catalyze char formation rather than flammable product formation or by creating polymers that structurally favor char formation.(24) There is one other approach to reducing polymer flammability which is considered a miscellaneous category that includes adding nonflammable materials as fillers to the polymer, adding materials that decompose to give nonflammable gases, and the formation of products that decompose endothermically.(25)

a. Vapor Phase Mechanism

As mentioned above, one mechanism by which a flame retardant can operate is through a vapor phase mechanism. It is able to reduce flammability because it can remove free-radical intermediates from the flame reaction or it can replace the major propagating species with those that do not propagate the flame readily. Halogenated flame retardants are commonly used and have been found to have certain properties that are characteristic of a vapor phase mechanism.(26) These properties, compiled by Hastie, are as follows:(27)

(A) Flame-retardant element is lost from the substrate.

(B) Flame inhibition is insensitive to substrate structure.

(C) Flame retardance is sensitive to oxidant, e.g., O_2 or N_2O.

(D) Flame retardance does not change the composition or amount of volatiles.

Thermal analysis methods, such as TGA and DTA, and also the use of multiple techniques have proven to be useful in studying the vapor phase mechanism. To more closely understand the reactions taking place when a polymer decomposes, it is often necessary to first consider the hydrogen-oxygen combustion scheme. Burning most polymers is regarded as a hydrogen containing combustion scheme therefore it is appropriate and necessary to look at the H_2-O_2 reaction scheme. The following equations dominate the H_2-O_2 combustion process because of their chain branching nature:(28)

$$H\cdot + O_2 \text{ -----> } OH\cdot + O\cdot$$

$$O\cdot + H_2 \text{ -----> } OH\cdot + H\cdot$$

Now if we consider the mechanisms by which the halogenated flame retardant (MX) decomposes we find that the flame inhibiting species (HX) is actually produced:(20)

$$M - X \text{ -----> } M\cdot + X\cdot$$

$$RH + X\cdot \dashrightarrow R\cdot + HX$$

or

$$H_2 + X\cdot \dashrightarrow H\cdot + HX$$

M is whatever hydrocarbon species that the flame retardant (X) is attached to. Once the flame inhibiting species, HX, is produced it can inhibit the chain-branching step of the hydrogen-oxygen combustion scheme, such as:(20)

$$H\cdot + HX \dashrightarrow H_2 + X\cdot$$

and

$$OH\cdot + HX \dashrightarrow H_2O + X\cdot$$

Other theories have been proposed for the reaction scheme but at this time this appears to have the most widespread support.(29)

b. Condensed Phase Mechanism

Another mechanism, which appears to reduce flammability, is the condensed phase mechanism. Flame retardants that follow this mechanism tend to result in increased char formation during pyrolysis and thus decrease the formation of flammable, carbon containing gases. The char aids in shielding the substrate so as to limit oxygen's access. It has also been proposed that formation of char on the polymer surface acts as a heat shield for the base material.(30) Phosphorus-based additives have been characterized as working by a condensed phase mechanism.(24)

There are certain characteristics that indicate a condensed phase mechanism. These are as follows:(27)

(A) Flame-retardant results in enhanced char formation.
(B) Flame-retardant element is retained in the substrate.
(C) Flame retardant element is often ineffective in the vapor phase.
(D) Flame retardance is sensitive to the substrate structure.
(E) Flame retardance is insensitive to oxidant, e.g., N_2O or O_2.
(F) Flame-retardant changes the composition of volatiles.

Thermogravimetric analysis has proven to be very useful in detecting a condensed phase mechanism. The TGA can be used to measure the residual (char) after the sample has undergone all major decompositions.

c. Vapor-Condensed Phase Mechanisms

Although, studies have been done that point to an either/or situation when dealing with vapor and condensed phase mechanisms, this is rarely the case. Determining whether a retardant is operating in the condensed phase or the vapor phase is very complicated for many systems. Although, halogens are said to usually operate in the vapor phase and phosphorus-based additives are said to usually operate in the condensed phase, there are cases where the opposite is true.(20) There are also studies that have shown that the flame retardant is working by both the vapor phase and the condensed phase mechanism.(31)

d. Miscellaneous Mechanisms

Besides the vapor and condensed phase mechanisms proposed above, there are other mechanisms by which a flame retardant can operate.(25) One such mechanism involves the production of a large volume of noncombustible gases. The formation of these gases dilutes the oxygen supply to the flame. These gases may also dilute the fuel concentration which is needed to sustain the flame. Another mechanism is a result of the endothermic decomposition of the fire retardant. This mechanism would result in lowering the temperature on the polymer's surface and in turn retard pyrolysis of the polymer. Finally, a flame retardant could act as a thermal sink. With this mechanism, the heat capacity of the combustion system could be decreased below the limits of flammability.

3. The Use of Thermal Methods to Study Polymer Flammability

As mentioned earlier thermal analysis can be used to study polymer flammability. It is an important tool in the characterization of the degradation patterns of flammable polymers.(32) The most frequently used means of thermal analysis is thermogravimetric. It is used primarily as a means of tracing the thermal decomposition of a sample. It can also be used to determine whether or not the mechanism is occurring in the vapor or condensed phase. DTA and DSC can also be used to study the changes prior to and during thermal decomposition of a polymer. There are several other techniques that are used less frequently which include thermal evolution analysis (TEA), thermomechanical analysis (TMA), and dynamic mechanical analysis (DMA). TEA is used as a means of identifying gaseous decomposition products. TMA and DMA measure the mechanical properties before and after the flame retardation modification.

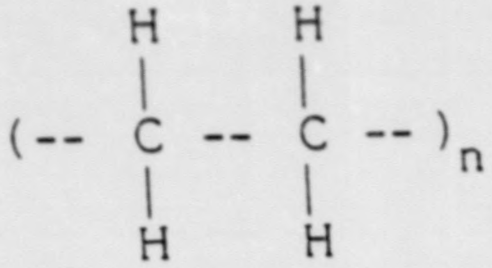
Besides thermal analysis methods, there are ASTM procedures which can be used to determine polymer flammability.(12) Despite this fact, there are several advantages to using thermal analysis methods rather than the standard ASTM evaluation procedures for evaluating polymer flammability.(12) The ASTM procedures often require special equipment, are time consuming, and are empirical in nature. On the other hand, thermal analysis methods are very fast with most being completed in less than one hour. Second, these methods are reproducible and have sensitivities down to milligram quantities. Third, the thermal analysis methods are fundamental meaning they are low in empiricism making the data obtained in the quality control lab useful to the research lab. Finally, thermal analysis is a versatile technique providing multiple information in a single experiment.(12)

C. Structure of Polyethylene

Polyethylene is a polymer which is a member of a group of chemical compounds known as polyolefins. It is one of the most widely used polymers of all of the thermoplastic materials.(33) Polyethylene is formed by addition reactions of olefins, acetylenes, aldehydes, or compounds with unsaturated bonds.(21) The polymer has the basic structure shown in Figure 7. Sometimes the chain exhibits side-branching as shown in Figure 8. There are two basic forms of polyethylene in terms of density. The first is low density polyethylene (LDPE) which has a short chain molecular structure with a high degree of side-branching. The LDPE structure of polyethylene has a 65% crystallinity factor.(33) The other form of polyethylene is high density polyethylene (HDPE). High density polyethylene consists of long molecular chains with very little side-branching. HDPE has a greater density and a crystallinity factor of 85%.(34) Polyethylene is a tough, chemically resistant polymer. It can be shaped into a wide variety of forms including powders, granules, rods, films, and sheets.(33) It is used as a construction material in home furnishings, domestic and industrial buildings, appliances, fabrics, and transportation vehicles.(20)

1. Flammability of Polyethylene

Despite its excellent properties as a construction material, the one drawback to using polyethylene is its flammability. Polyethylene typically burns at temperatures below 400^0C. Because of polyethylene's flammability metals, ceramics, and other materials are often used for construction



$$\left(-\!-\ \overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\ -\!-\ \overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\ -\!-\right)_n$$

Figure 7 Basic Structure of Polyethylene

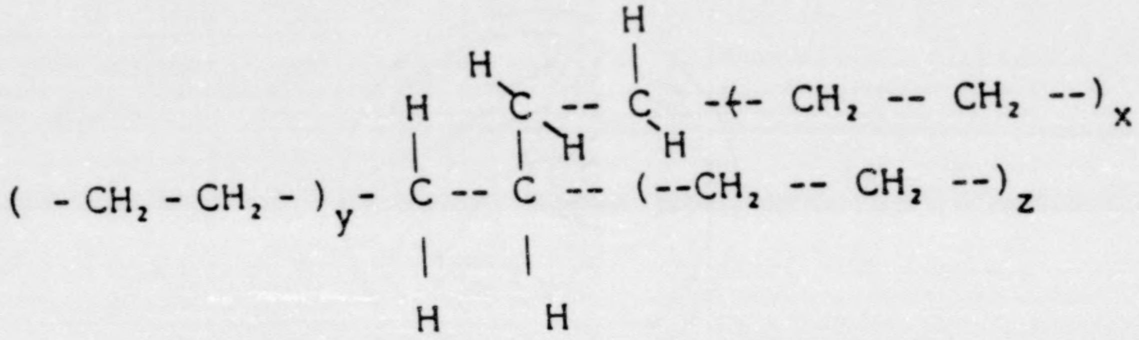


Figure 8 Structure of Polyethylene with Side-Branching

materials even though polyethylene is cheaper and in some cases stronger.(21) Several possible explanations why organic polymers are thermally unstable have been proposed.(21) One explanation is that a lower entropy is desired. An example of a polymer favoring lower entropy occurs when an organic polymer is at a high temperature. At this high temperature it will favor a low molecular weight over a high molecular weight. Other explanations are that carbon-carbon bonds are relatively weak or these bonds are oxidatively unstable. There is also a possibility that the polymer has structural abnormalities, such as branch points, existing along the chain. Another possibility is that terminal catalytic sites may initiate depolymerization. Finally, a long chain of atoms may facilitate decomposition chain reactions.

2. Chlorination of Polyethylene

Polyethylene as has been stated is a highly flammable polymer. Finding a method to reduce this flammability is of great scientific interest to researchers and industry. One possible way of reducing the flammability of polyethylene is through the addition of a halogen such as chlorine.(32) The chlorination of polyethylene occurs as a free radical chain reaction.(35) The reaction occurs as follows:

$$-CH_2- \quad + \quad Cl\cdot \quad \text{----->} \quad -\underset{\cdot}{C}H- \quad + \quad HCl$$

$$-\underset{\cdot}{C}H- \quad + \quad Cl_2 \quad \text{----->} \quad -CHCl- \quad + \quad Cl.$$

This reaction is catalyzed by heat, radical initiators, and UV light. Chlorination can either be carried out in solution or on the solid polymer. The reaction usually only occurs on the outer surface of the polymer.(34) This is usually an advantage because only the surface properties are changed and the bulk mechanical properties of the polymer remain unchanged. Chlorination of the polymer also results in decreased crystallinity of the polyethylene structure. A 25% chlorinated sample has a crystallinity factor of 25% while samples above 36% chlorination have a crystallinity factor less than 2%.(34)

EXPERIMENTAL

This study looks at the effects of various chlorinated samples on the thermal decomposition of HDPE in atmospheres of nitrogen, air, and pure oxygen. Four different samples were used - three containing chlorine and one unchlorinated sample. The experiments were run using various thermal methods such as TGA, DTA, and DSC to study the decomposition of high density polyethylene. Two coupling techniques were also employed to study the gases evolved during a thermal decomposition. These included a TGA linked to an FTIR and a DTA linked to a GC/TCD. The experimental conditions remained relatively constant for all samples run and all methods used. Following is a more detailed description of the experimental methods and conditions used in this study.

A. Materials

For this research four different samples were used. For comparison purposes, one sample used was unchlorinated high density polyethylene (HDPE). It has a basic polyethylene structure with few side branches. Branching inhibits the formation of crystals and results in lowering the density of polyethylene.(34) Therefore, our sample with few side branches does not inhibit the formation of crystals and has a higher density. Our sample had a crystallinity limit ranging from 80-90%.(34) To study the effects of chlorination on the decomposition of HDPE three chlorinated samples were used. Each chlorinated sample had a different percentage of chlorine in order to study the effects of varying the chlorination. Included in this study was a 25% chlorinated sample of HDPE (25% Cl-PE), a 36% chlorinated sample of HDPE (36% Cl-PE), and a 42% chlorinated sample of HDPE (42% Cl-PE). Chlorination of HDPE replaces the backbone hydrogen of polyethylene with chlorine.(34) The result is a chlorinated sample similar in crystal structure to the unchlorinated sample. An attempt was made to chlorinate randomly but because of amorphous and crystalline regions in the polyethylene this is often difficult to accomplish.(34) As a result of chlorination, the crystallinity of the chlorinated samples was decreased. The 25% Cl-PE retained approximately 25% crystallinity while the 36% and the 42% Cl-PE retained less than 2% crystallinity.(34) All four of the high density polyethylene samples used in this study were obtained from Scientific Polymer Products, Inc. The three chlorinated samples used were in granular form and needed no further preparation. The HDPE sample, on the other hand, was in a pellet shape. We were unable to use the sample in this form and therefore we had to have it ground to a granular form. The grinding of the HDPE sample was done by the Central Research Lab of Dow Chemical Company.

Three gases were used in this study - nitrogen, air, and oxygen. These were all obtained from the Southern Welding

Company of Bowling Green, Kentucky and all had a purity of approximately 99.9%

B. Apparatus

Several different instruments were used to study the effects of chlorination and also to study the products formed from the decomposition of the polyethylene samples. To study the thermal decomposition of the samples a DuPont 951 Thermogravimetric Analyzer (TGA) and a DuPont 1090B Thermal Analyzer were employed. A continuous flow of gas was maintained through the thermogravimetric analyzer by the use of 1/4 inch tubing connecting the gas tank and the gas inlet valve on the TGA. A Fischer and Porter Flow meter was connected between the tank and the TGA in order to regulate the amount of gas entering the TGA. For all three gases used -- nitrogen, air, and oxygen -- a flow rate of 50 ml/min was used. To study the change in heat during decomposition a DuPont 910 Differential Scanning Calorimeter (DSC) was used. This was also connected to the flow meter and gas tank as explained above. To study the gases evolved at different temperatures coupling techniques were employed. A Nicolet MX 1 Fourier Transform Infrared Spectrophotometer (FTIR) was coupled to the DuPont 951 TGA and a Shanghai 100 Gas Chromatograph (GC/TCD) was coupled to the TGA/DTA. All TG-FTIR studies were done by Wei-Ping Pan at Wood Research Lab at the University of Montana. The TG/DTA - GC data was obtained from Mr. Gen-cai Cai at East China Institute of Chemical Technology. It should be noted that all three sets of TG data, obtained from three different labs, were identical in content. For the FTIR data, a teflon tube was connected to the outlet valve of the TGA and the inlet valve of the gas cell on the FTIR. The gas flows into the gas cell (10 cm. in length) and flows out an exit valve on the gas cell. This allows for the continuous flow of gas, formed in the TGA, through the FTIR. GC data was obtained by using a teflon tube connected to the outlet valve of the DTA and the injection port of the GC. The GC data was obtained by sampling the gaseous products at various temperatures. This was done to establish what type of products are being formed when different levels of chlorination are employed.

A Sartorius Model 1801 analytical balance was used for all mass measurements, specifically with the DSC and the DTA. This balance has a maximum capacity of 110 grams with an accuracy of ±0.1 milligrams.

C. Conditions for Experiments

In order to get reproducible results and to allow for easier comparisons of data we attempted to hold the experimental conditions constant for all runs. As mentioned earlier, the experiments were carried out in three different atmospheres: nitrogen to study pyrolysis, air to study combustion, and oxygen to study ignition. For the TGA and DSC the gas flow rate was maintained at 50 ml/min. For the DTA, the gas flow rate in nitrogen and air was also maintained at 50 ml/min but for the oxygen atmosphere the flow rate was reduced to 15 ml/min. This was done because the higher concentration interfered with the GC data when the DTA and the GC are linked. For all instruments the heating rate was held constant at 10^0C/min, with an initial temperature of 30^0C and a final temperature of 600^0C. At 600^0C, the furnace maintained isothermal conditions for ten minutes. This enabled the furnace temperature and the sample temperature time to equilibrate.

D. Preliminary Experiments

Before analyzing the samples, certain preliminary experiments were carried out in order to verify sample homogeneity and also to determine appropriate masses to be used for the three different atmospheres. To test sample homogeneity three different masses of the same sample were run in the TGA. We looked for indications that no matter what sample size was used a similar Tmax, reactivity, and residual were obtained. Next, we checked our sample to find the most reproducible mass. This time we ran the same sample size over and over to see if the Tmax, reactivity, and residual were identical. The initial study only looked at nitrogen's most reproducible mass but later encompassed air and oxygen's most reproducible masses also.

1. Sample Homogeneity

Before sample analysis, experimental runs were carried out to determine whether or not the samples were homogeneous. To establish homogeneity, numerous runs for the three different sample sizes - 2.5 mg, 5 mg, and 10 mg, were obtained. To determine sample homogeneity, 42% chlorinated

HDPE in nitrogen was used. Table 1 shows the results obtained on the Thermogravimetric Analyzer. The three kinetic factors-Tmax, reactivity and residual were all considered. The Tmax for peak 1 had similar values ranging from 326-328^{0}C while peak 2 had even closer values of 471-472^{0}C for the three different samples tested. The reactivities were even closer with all runs for peak 1 having a reactivity (%/min.) of 0.10 ± 0.009 and peak 2 having a reactivity (%/min.) of 0.19 ± 0.008 for all runs. The residual (%) ranged from 4.91 for the 10 mg. sample to 6.28 for the 5 mg. sample. When the Tmax is plotted with regard to mass a relatively straight line results (Figure 9). Because the three different sample sizes resulted in similar Tmax's, it was determined that our samples were homogeneous.

2. Reproducibility

Once it was established that the 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-HDPE in nitrogen. All three runs involved the same experimental conditions with a sample mass of 10 mg. All of the Tmax's were in the range of 325 to 328^{0}C for the first peak and 472 to 473^{0}C for the second peak. The reactivities (%/min) were even closer with all peak 1 values being 0.10 ± 0.0062 and all peak 2 values being 0.19 ± 0.002. The residual (%) 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

TABLE 1

SAMPLE HOMOGENEITY FOR 42% CHLORINATED HDPE IN NITROGEN

Mass (mg.)	Peak 1		Peak 2		Residue (%)
	Tmax (^{0}C)	Reactivity (%/min)	Tmax (^{0}C)	Reactivity (%/min)	
10	326.13	0.101	472.47	0.190	4.91
5	327.75	0.103	471.6	0.190	6.28
2.5	328.85	0.110	471.1	0.198	5.51

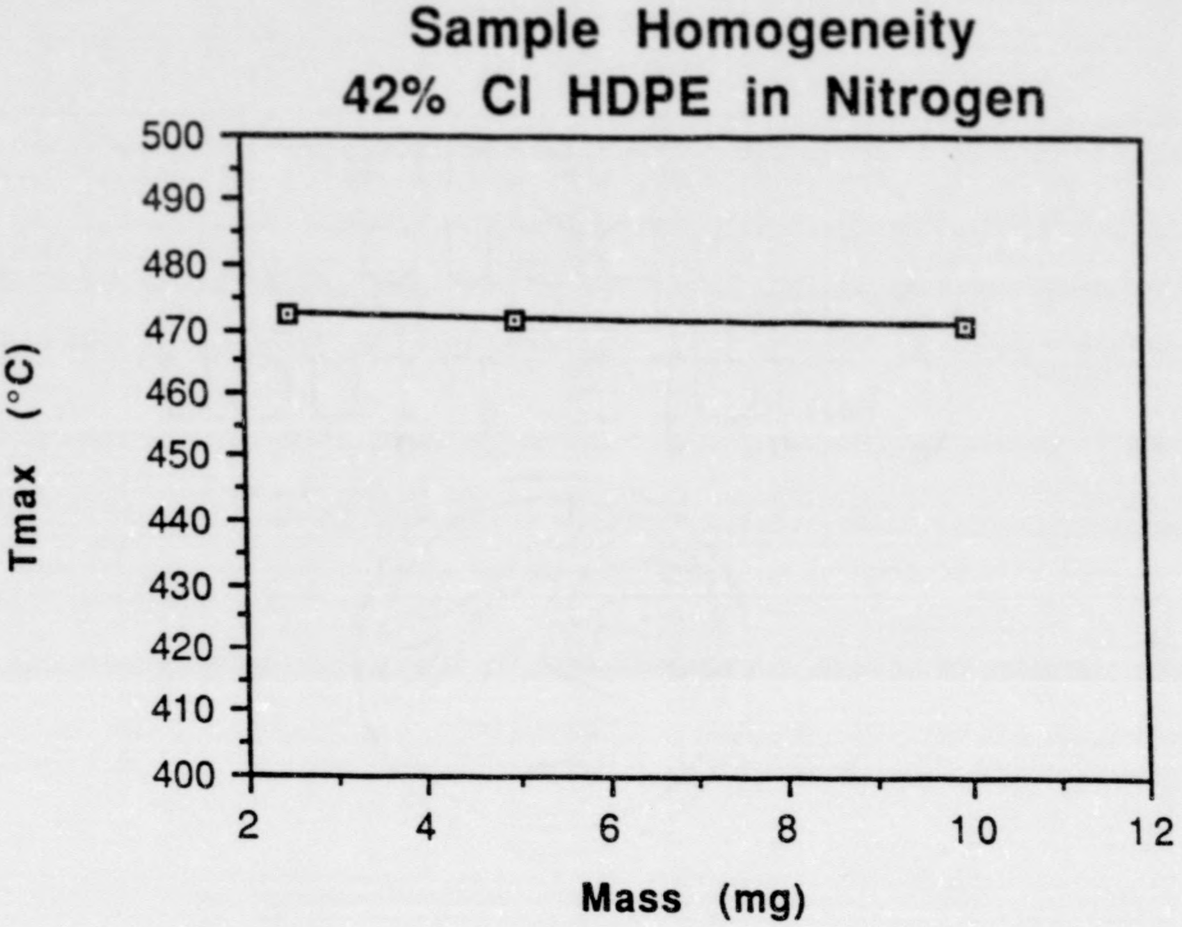


Figure 9 Sample Homogeneity - 42% Cl-PE in Nitrogen

TABLE 2

REPRODUCIBILITY FOR 42% Cl-PE IN NITROGEN
(Mass 10mg.)

Run	Peak 1		Peak 2		Residue
	Tmax $(^{0}\mathrm{C})$	Reactivity (%/min)	Tmax $(^{0}\mathrm{C})$	Reactivity (%/min)	(%)
1	325.2	0.103	472.0	0.190	4.51
2	324.7	0.102	472.0	0.189	4.71
3	328.5	0.097	473.4	0.191	5.50
Average	326.13	0.101	472.47	0.190	4.91

mass for pyrolysis. All subsequent runs for pyrolysis and combustion used a sample size of 10 mg. For ignition it was found that a smaller sample size (less than 5 mg.) gives better reproducibility.

RESULTS AND DISCUSSION

The four HDPE samples were exposed to several thermal techniques under the three different atmospheres - nitrogen, air, and oxygen. Thermal techniques employed included TGA, DTA-TG, DSC, and TG-DTG while several analytical techniques such as GC and FTIR were employed. The thermal techniques were used along with several analytical techniques in order to correlate the data among the different methods. Several important conclusions were drawn from the data obtained. The data for pyrolysis (nitrogen) conditions will be considered first followed by the data for combustion (air) and ignition (oxygen) conditions.

A. Pyrolysis

After it had been established that the test samples were homogeneous and had verified a sample weight that allowed for high reproducibility it was desired to study the effects of chlorination on the thermal decomposition of HDPE under pyrolysis conditions. Pyrolysis involves a chemical change when a material is heated in the presence of pure nitrogen. Pyrolysis is involved in the process of combustion but is not easily distinguished from this process.(22) Therefore, it was necessary to run the HDPE in pure nitrogen to obtain a clearer view of the pyrolysis decomposition.

1. Thermogravimetric Analysis for Pyrolysis

First the decomposition of the chlorinated and unchlorinated samples was considered using the Thermogravimetric Analyzer (TGA). A typical thermogravimetric heating curve (TG heating curve) can be seen in Figure 10. This shows a curve of the 42% chlorinated high density polyethylene in nitrogen. It plots percent weight loss on the Y axis versus temperature on the X axis. The dotted line shows the Differential thermogravimetric curve (DTG heating curve) for the 42% chlorinated sample. The DTG curve plots the rate of weight loss against the temperature. The DTG curve is often presented in thermal analysis work because it is more sensitive than a TG curve.(3) Two different thermodecomposition stages are seen for the 42% chlorinated sample on the TG curve 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 thermodecomposition stage which is present from 280-350^{0}C is believed to be due to the loss of HCl. Peak 2, the second thermodecomposition stage, is present from 350-500^{0}C and is believed to be 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 as Tmax. The second kinetic factor is the reactivity (Rmax, %/min.) at Tmax and the third kinetic factor is the residue (%) or char left after heating to 600^{0}C.

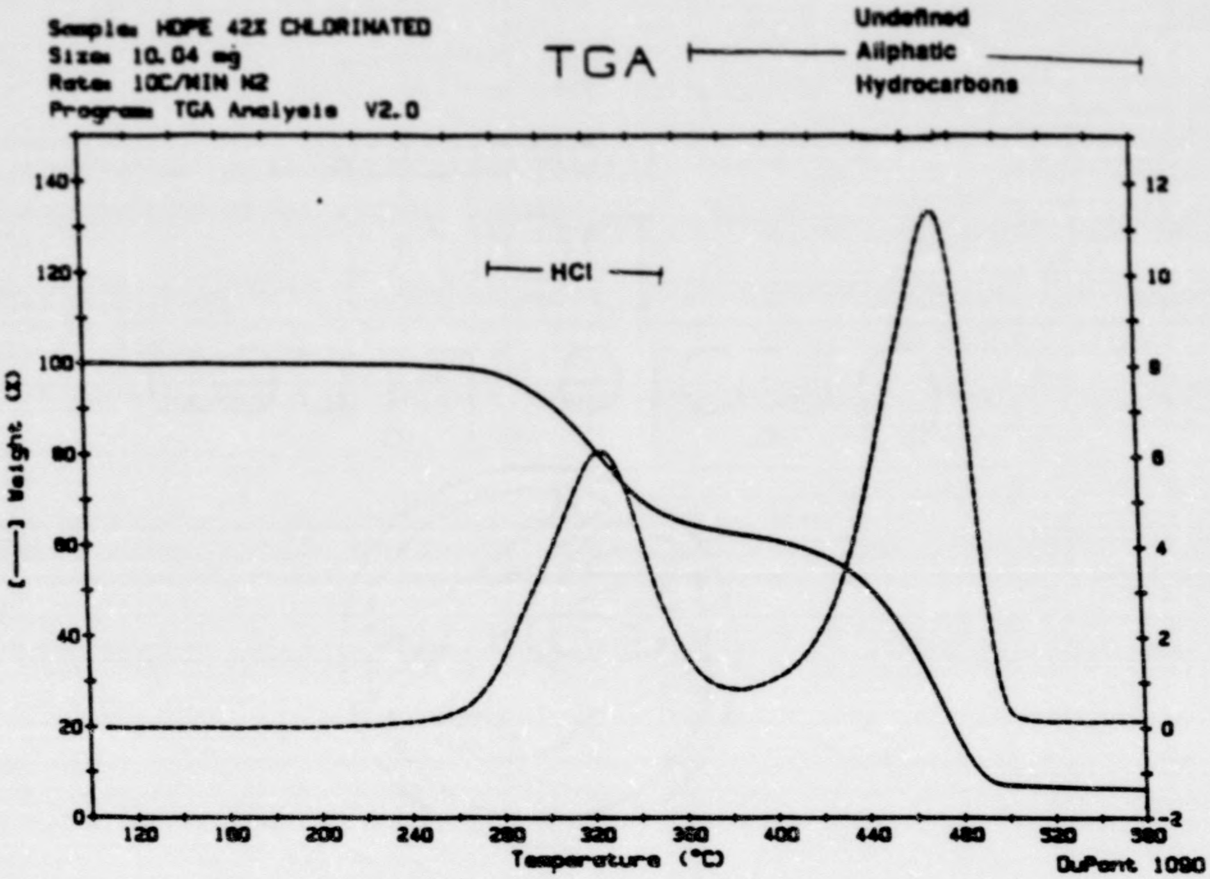


Figure 10 TG Heating Curve - 42% Cl-PE in Nitrogen

To compare the difference between chlorinated and unchlorinated samples next the TG curve for high density polyethylene was considered (Figure 11). This shows an HDPE sample under pyrolysis conditions. If this is compared to the TG curve for the chlorinated sample, obvious differences are apparent. One difference is that only one decomposition stage is present (440-510^{0}C). This peak corresponds to the loss of aliphatic hydrocarbons similar to those found for the 42% chlorinated HDPE in the second thermodecomposition stage. Since no chlorine is present there should be no stage corresponding to the loss of HCl. Therefore, for simplicity, we will label HDPE's single peak as Peak 2.

The Tmax, reactivity, and residual for all four samples in nitrogen are shown in Table 3. Several general differences are apparent at first glance. One difference involves the Tmax for the two different samples. The Tmax for the unchlorinated sample is slightly higher than 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 residual. For the unchlorinated sample the residual is slightly greater than 1% meaning that only a very small percentage of the polymer did not decompose. The chlorinated sample had a higher residual anywhere from 4-5%.

Recall that polymer flammability is a complex process which is believed to contain two different phases.(23) The first is the vapor phase where a flame retardant, such as

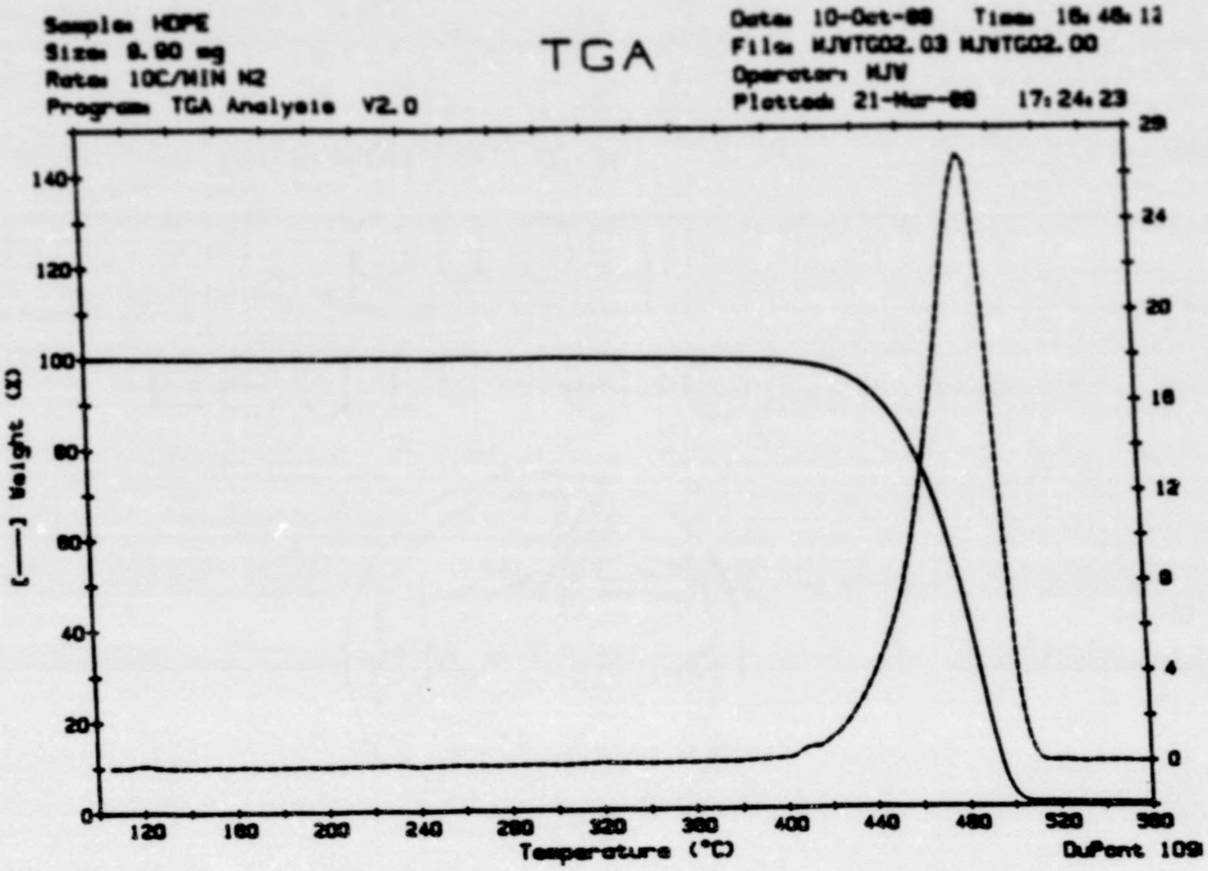


Figure 11 TG Heating Curve - HDPE in Nitrogen

TABLE 3

COMPARISON OF HDPE AND CHLORINATED SAMPLES IN NITROGEN

% Chlorination	Mass		Peak 1	Peak 2		Residue
		Tmax	Reactivity	Tmax	Reactivity	
(%)	mg.	(⁰C)	(%/min)	(⁰C)	(%/min)	(%)
0	10	----	----	486.75	0.451	1.11
25	10	339.53	0.058	490.8	0.261	5.40
36	10	335.8	0.087	472.9	0.190	5.14
42	10	326.13	0.101	472.47	0.190	4.91

chlorine, reduces free radical reactions which are involved in flame formation and propagation. Second is the condensed phase. If the material studied has a flame retardant that modifies its thermodecomposition and enhances char formation then the flame retardant is working in the condensed phase.

A trend can be seen in the data obtained in nitrogen. For the first peak, correlating to the loss of HCl, as the chlorination increases the Tmax decreases and the reactivity increases. For the second peak, correlating to the loss of aliphatic hydrocarbons, a similar trend occurs. Once again as the chlorination increases the Tmax decreases but in this case the reactivity decreases. Also if the residue is considered, there is a significant difference between the HDPE and the chlorinated samples. The HDPE had a residual (char) of about 1% ranging from 0.737% to 1.49%. While the chlorinated samples had a residual of anywhere from 4% to 5%. Flame retardants have the characteristics that our data proposes. A high flame retardant, such as chlorine, results in a lower Tmax and a higher residue. A significant similarity was found between the 36% chlorinated HDPE and the 42% chlorinated HDPE. If Tmax is compared to the amount of chlorination (Figure 12), it is found that increasing chlorination tends to decrease the Tmax. Above 36% chlorination, it is found that Tmax levels off and the 42% chlorinated sample is similar to the 36% chlorinated sample. Next reactivity was compared to percent chlorination (Figure 13). As the chlorination increases the reactivity decreases.

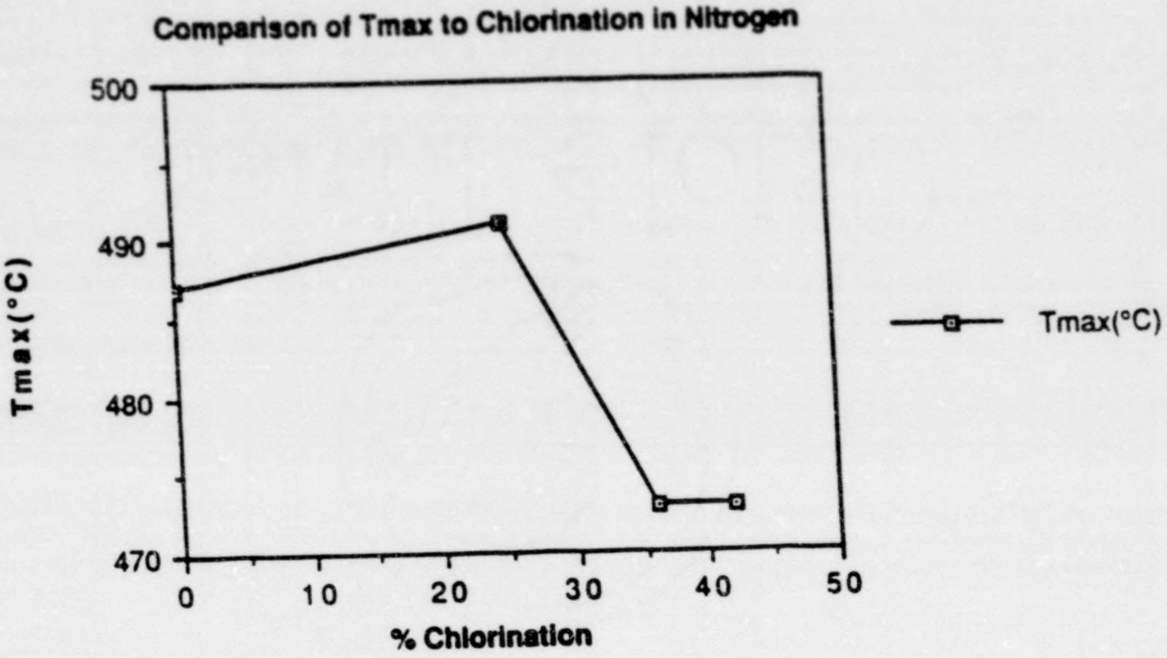


Figure 12   Comparison of Tmax and %Cl in Nitrogen

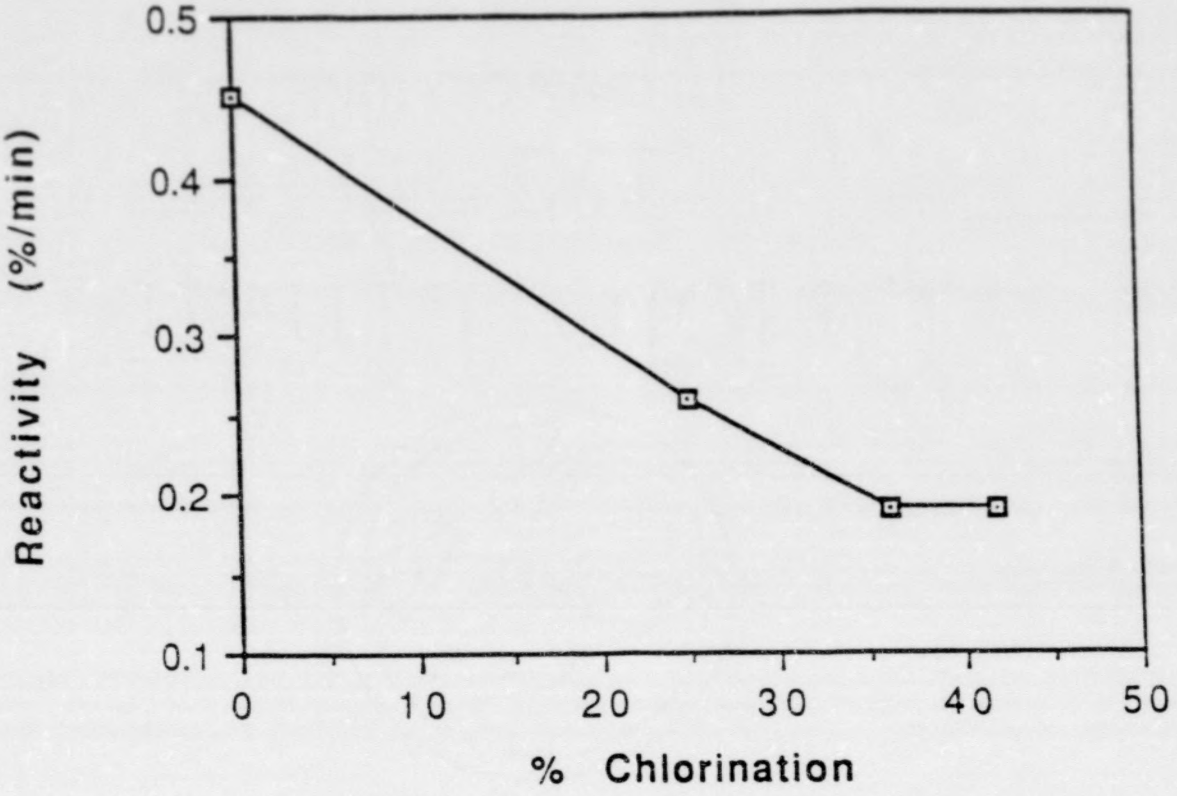


Figure 13 Comparison of Reactivity and %Cl in Nitrogen

Once again small differences are found above 36% chlorination. Therefore it can be concluded that increasing the chlorination above 36% has little effect on the thermal decomposition of the polymer.

2. FTIR and GC Data for Pyrolysis

If the FTIR or Gas Chromatograph is linked with the TGA as mentioned in the instrumental section, the gaseous products evolved during the thermal decomposition of the polymer can be studied. Three different aliphatic hydrocarbon peaks were studied 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 wavenumbers.(36) The second is a set of peaks at 3188 and 2788 wavenumbers which correlates to the C-H stretching of a saturated hydrocarbon unit (SHU).(36) Third is another set of peaks at 2400 and 2240 wavenumbers represented by the C-H stretching of ethylene or acetylenic C-H unit (CHE).(36) Finally, the loss of the HCl was studied for the chlorinated samples. Table 4 gives the FTIR data obtained for the HDPE sample in nitrogen. Figure 14 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^{0}C it is noted that no decomposition of the polymer has occurred. Figure 10, the 42% Cl-PE sample, supports the FTIR data that the polymer has not decomposed before 375^{0}C. Above 375^{0}C, we

TABLE 4

FTIR DATA FOR HDPE SAMPLE IN NITROGEN

Temperature (^{0}C)	Peak Height*	Peak Area*	
	OOP	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

* Arbitrary Units for Peak Height and Peak Area

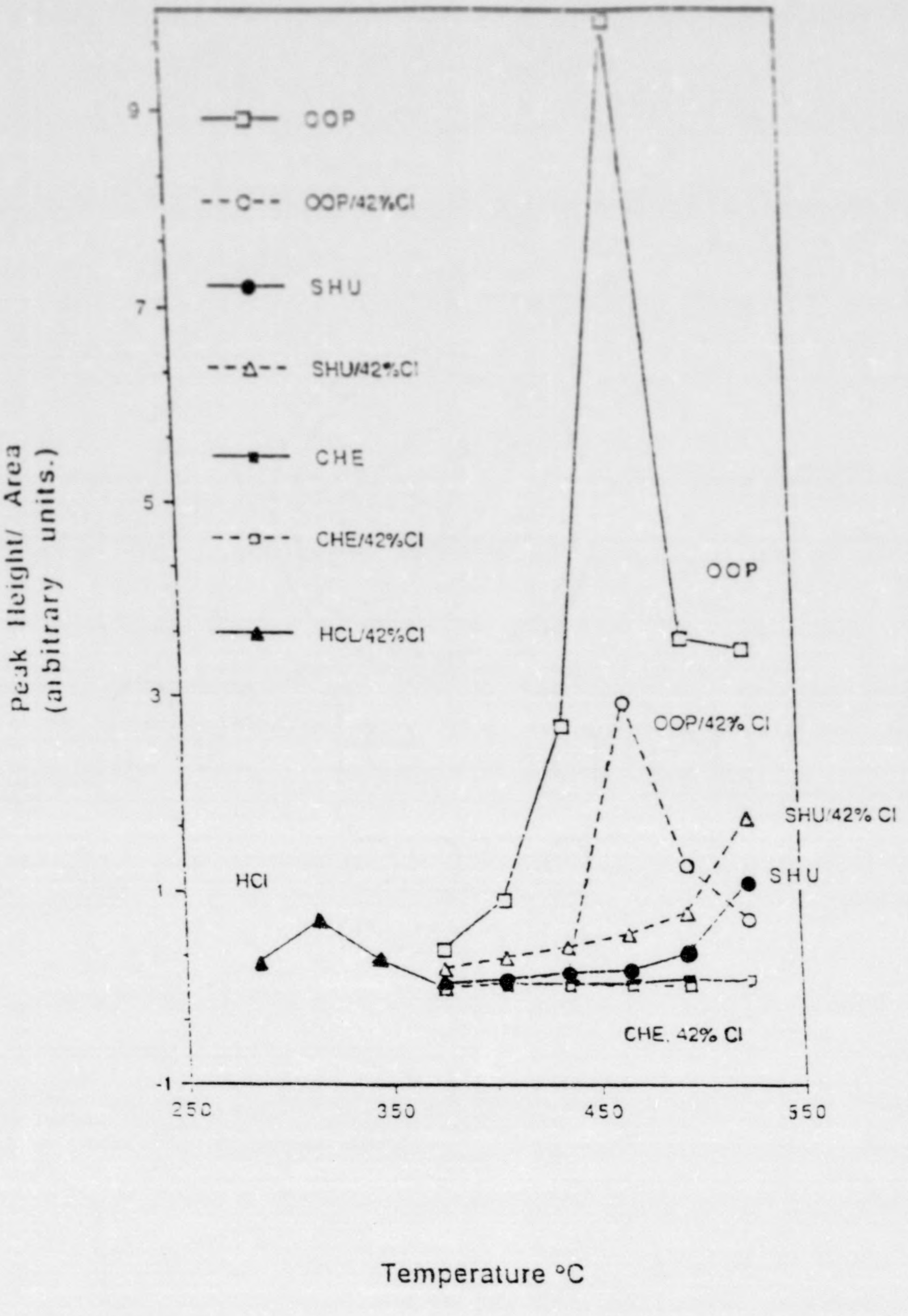


Figure 14 FTIR Data for 42% Cl-PE and HDPE in Nitrogen

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 the HCl. Before 375^{0}C only HCl is given off as product, but after 375^{0}C the C-H units begin to break off. After 375^{0}C no HCl gas is detected giving strength to the belief that peak 1 is strictly due to the loss of HCl. If the FTIR spectra for 42% Cl-PE (Figures 15 and 16) are considered there are two areas of the spectra to consider. First are the two sharp well-defined peaks at 3200 wavenumbers that came off first. These correspond to the loss of HCl at peak 1 on the thermogravimetric curve (Refer to Figure 10). Next, the numerous peaks occurring at temperatures above 350^{0}C on the FTIR spectra (Figure 16) should be considered. The other large peak shown at approximately 2800 wavenumbers is due to the presence of alkenes such as ethylene and propylene stretching. Smaller peaks occur at 1463 cm and 908 cm these are also due to alkane units such as -CH breaking off. Another sharp peak found below 800 cm is possibly due to the C-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.

If we consider the GC data, we find that various aliphatic hydrocarbons including hydrogen, methane, ethylene, and propylene were given off due to the thermal decomposition of the polymer at the temperature range between 360^{0}C and 490^{0}C in all four samples (Table 6). After about 490^{0}C only

TABLE 5

FTIR FOR 42% CHLORINATED HDPE IN NITROGEN

Temperature (^{0}C)	Peak Height*	Peak Area*		
	OOP	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

* Arbitrary Units for Peak Height (Area)

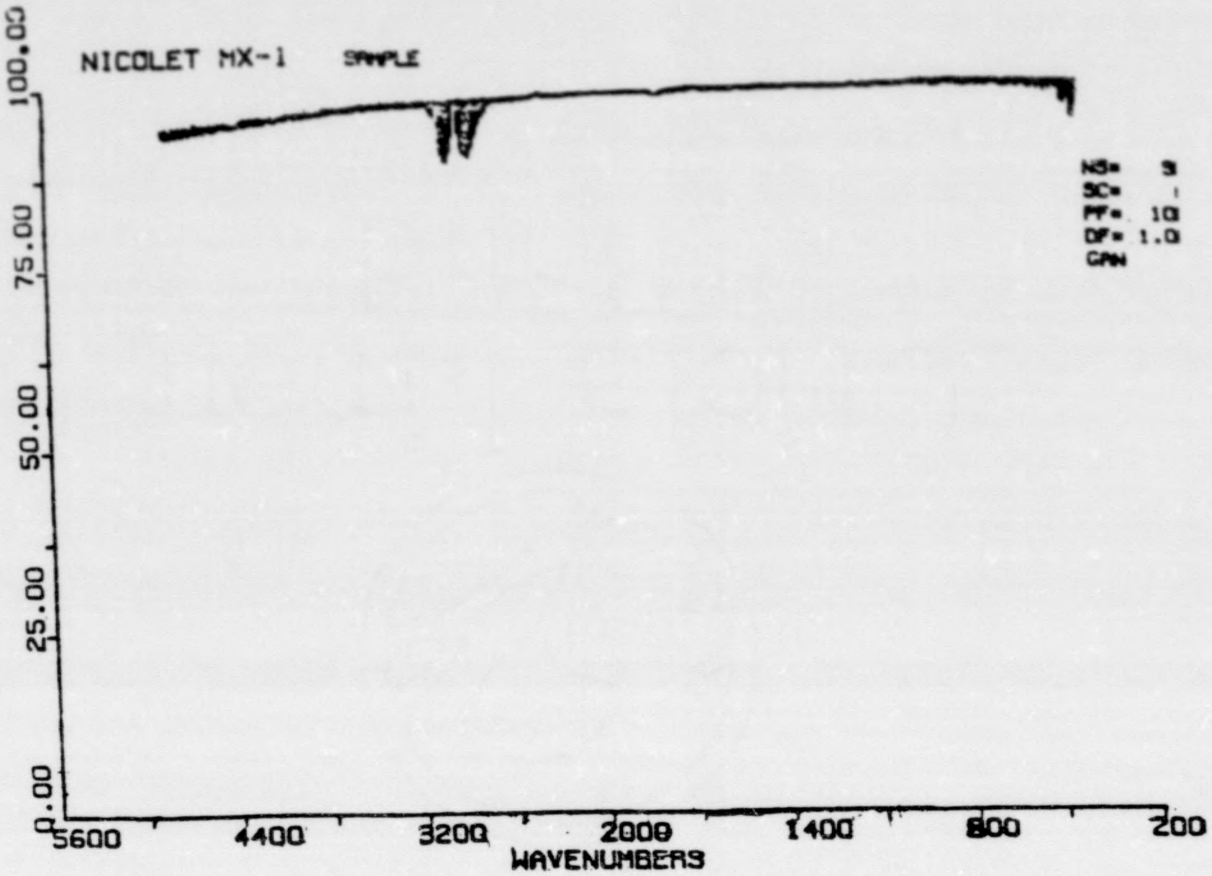


Figure 15 HCl Peaks on FTIR in Nitrogen (Temperature Range 280-380)

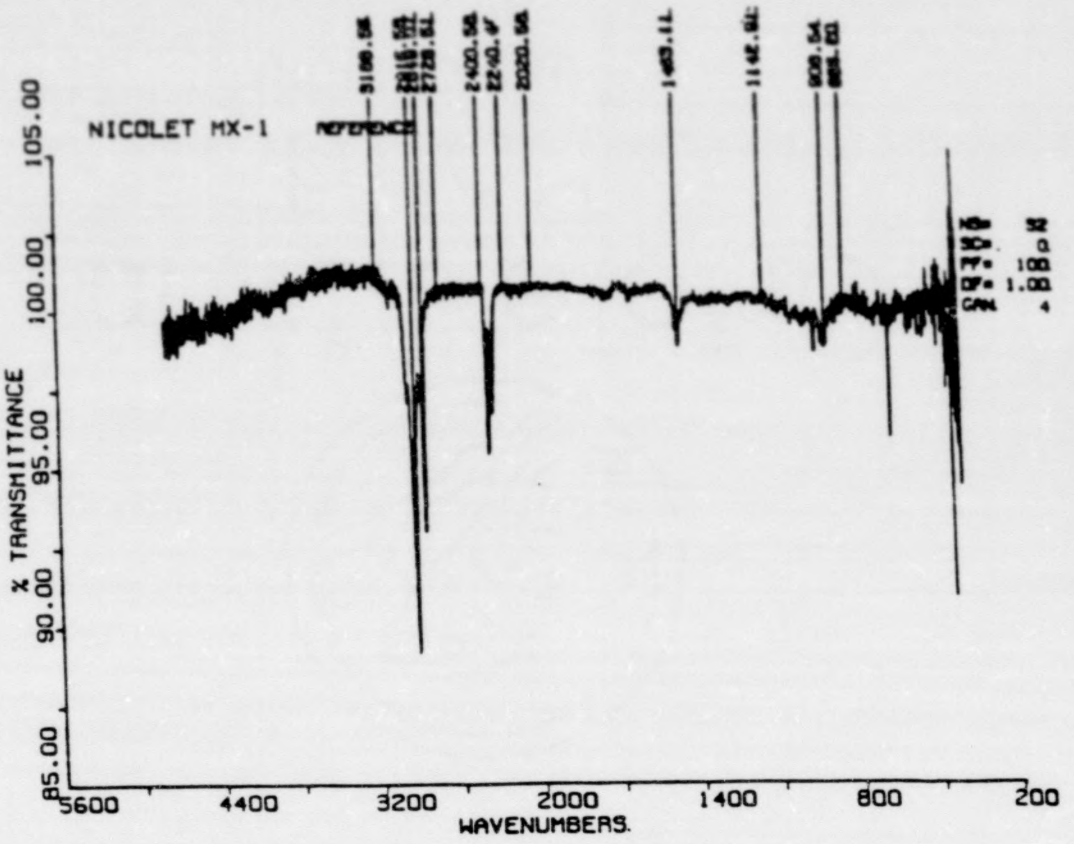


Figure 16   Aliphatic Hydrocarbons on FTIR in Nitrogen
(Temperature Range 380-520)

TABLE 6

GC DATA FOR ALL FOUR SAMPLES IN NITROGEN

Temperature (^{0}C) Range	HDPE	25%Cl-PE	36%Cl-PE	42%Cl-PE
120 240 360		HCl	HCl	HCl
360 460		H_2, CH_4 $C_2^=$, $C_3^=$ HCl	H_2, CH_4 $C_2^=$, $C_3^=$ HCl	H_2, CH_4 $C_2^=$, $C_3^=$ HCl
460 504	H_2, CH_4 $C_2^=$, $C_3^=$	H_2, CH_4 $C_2^=$, $C_3^=$	H_2, CH_4 $C_2^=$, $C_3^=$	H_2, CH_4 $C_2^=$, $C_3^=$
504 600	H_2, $C_2^=$	H_2, CH_4 $C_2^=$, $C_3^=$	H_2	H_2, $C_2^=$
% Weight Loss	100%	94.99%	95.39%	95.34%

hydrogen and ethylene were given off as gaseous products. The GC results are similar to those obtained by Miller and Martin.(37)

3. DSC for Pyrolysis

Next the effects of chlorination on the polymer using Differential Scanning Calorimetry (DSC) were considered. A TG-DTA was also run which gives identical results to the DSC. Because of this only the DSC data will be discussed. Using the DSC data, it could be established whether an endothermic or exothermic reaction was occurring and also to compare this to the results on the TGA. DSC shows endothermic peaks where sublimation and decomposition are occurring and exothermic peaks where decomposition is occurring. Figure 17 shows a typical DSC curve for high density polyethylene in nitrogen. This curve shows two endothermic peaks one at 130^0C (peak maximum) and the other is a broad peak starting at about 180^0C and ending at about 500^0C. From the TG data we would expect only one peak, the one occurring at 465^0C (See Figure 11). The peak at 138^0C is a sharp well-defined peak which correlates to the heat of melting. If we also consider the GC data at this temperature we see that no gaseous products are given off. On this basis it can be deduced that nothing is decomposed to form products therefore a phase transition of a solid to a liquid has occurred. The second broad endothermic peak was due to the heat loss from the decompostion of HDPE. The three chlorinated samples in nitrogen give similar curves with three endothermic peaks.

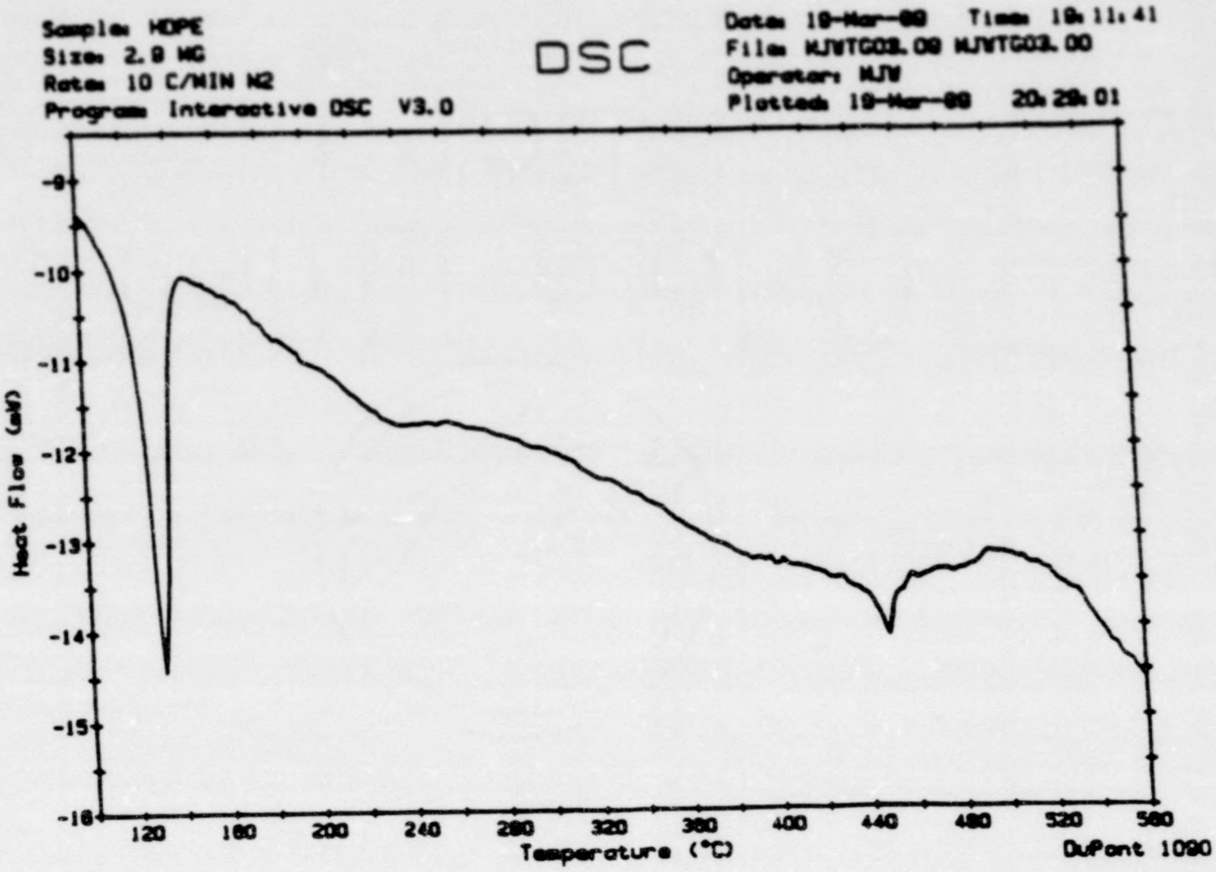


Figure 17 DSC Peak for HDPE in Nitrogen

Figure 18 shows the DSC curve for 42% Cl-PE. The first peak is due to the heat of melting. It should be noted that the intensity of this peak is decreased with increased chlorination (See Figure 19). It may indicate that the crystallinity of the polymer samples is decreased with increased chlorination. Recall that according to Vanzo, the high density polyethylene has a crystallinity limit of 80-90%.(34) The product with 25% chlorine retains approximately 25% crystallinity, while the 36% and 42% chlorinated products have less than 2% crystallinity.(34) The second endothermic peak is due to the heat release that corresponds to the loss of HCl on the TG curve (See Figure 10). This peak starts at a temperature of 260^{0}C and ends at about 360^{0}C. The third peak which goes from approximately 360-520^{0}C is due to the heat loss of HDPE. The heat release of the HDPE for the unchlorinated sample shows a more gradual loss of HDPE over a wider range of temperatures. The chlorinated samples, on the other hand, lose their HCl and possibly some of their HDPE at the second endothermic peak with the majority of the HDPE coming off in the temperatures encompassed by the third endothermic peak.

B. Combustion

Next, the combustion process for the thermal decomposition of high density polyethylene was considered. Combustion involves a chemical change when a material is heated in the presence of air. The combustion process involves four basic steps (1) preheating, (2) decomposition,

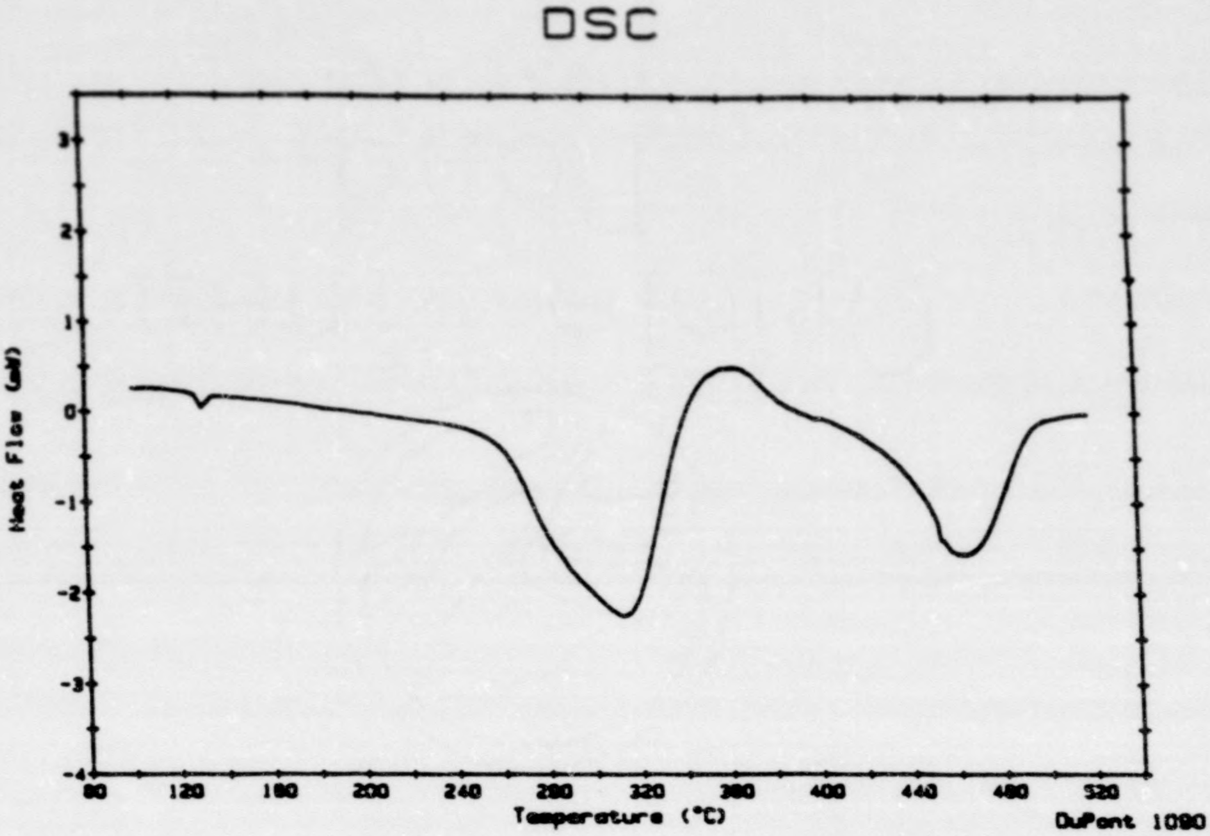


Figure 18 DSC Peak for 42% Cl-PE in Nitrogen

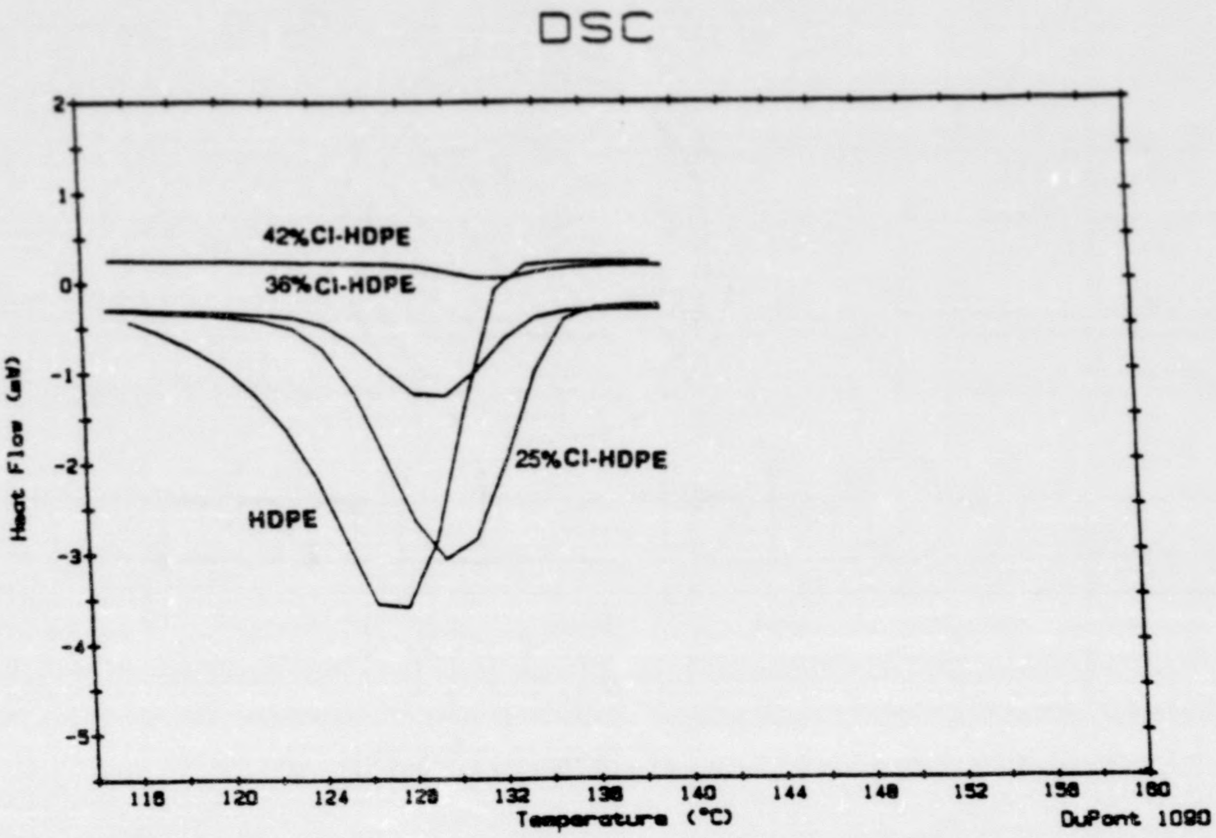


Figure 19 DSC Peak at 120°C for All Samples in Nitrogen

(3) ignition, and (4) combustion and propagation.(22) Preheating involves raising the temperature of the polymer at a specific rate to a specific temperature. As the sample is heated, a temperature is reached where the sample begins to degrade. This is the decomposition stage of the combustion process. Flammable gases are then formed which begin to concentrate and eventually bring about sustained oxidation in the presence of the ignition source. Finally, the combustion process becomes self generated if enough heat is present to bring about decomposition of the polymer.

For combustion the three kinetic factors; Tmax, Rmax, and residual; were considered for all data obtained.

1. Thermogravimetric Analysis for Combustion

First the TGA was used to study the decomposition of the four samples. Table 7 shows the Tmax, reactivity, and residual for all four samples in air. As in the nitrogen atmosphere, peak 1 is due to the loss of HCl and is not present for HDPE. Peak 2 is due to the loss of aliphatic hydrocarbons both for the chlorinated and unchlorinated samples. A trend can be seen for the combustion data obtained. For the first peak, correlating to the loss of HCl, as the chlorination increases the Tmax increases and the reactivity increases up to 36% chlorination and then both decrease. For the second peak, correlating to the loss of aliphatic hydrocarbons, as the chlorination increases the Tmax increases but the reactivity decreases. Figure 20 compares Tmax to percent chlorination in air. There is a large

TABLE 7

COMPARISON OF HDPE AND CHLORINATED SAMPLES IN AIR

Chlorination (%)	Mass (mg)	Peak 1		Peak 2		Residue
		Tmax (°C)	React (%/min)	Tmax (°C)	React (%/min)	(%)
0	10	-----	-----	387.4	0.906	0.455
25	10	326.65	0.0645	453.6	0.586	4.125
36	10	333.65	0.1024	454.5	0.358	3.980
42	10	321.15	0.0980	455.7	0.326	4.45

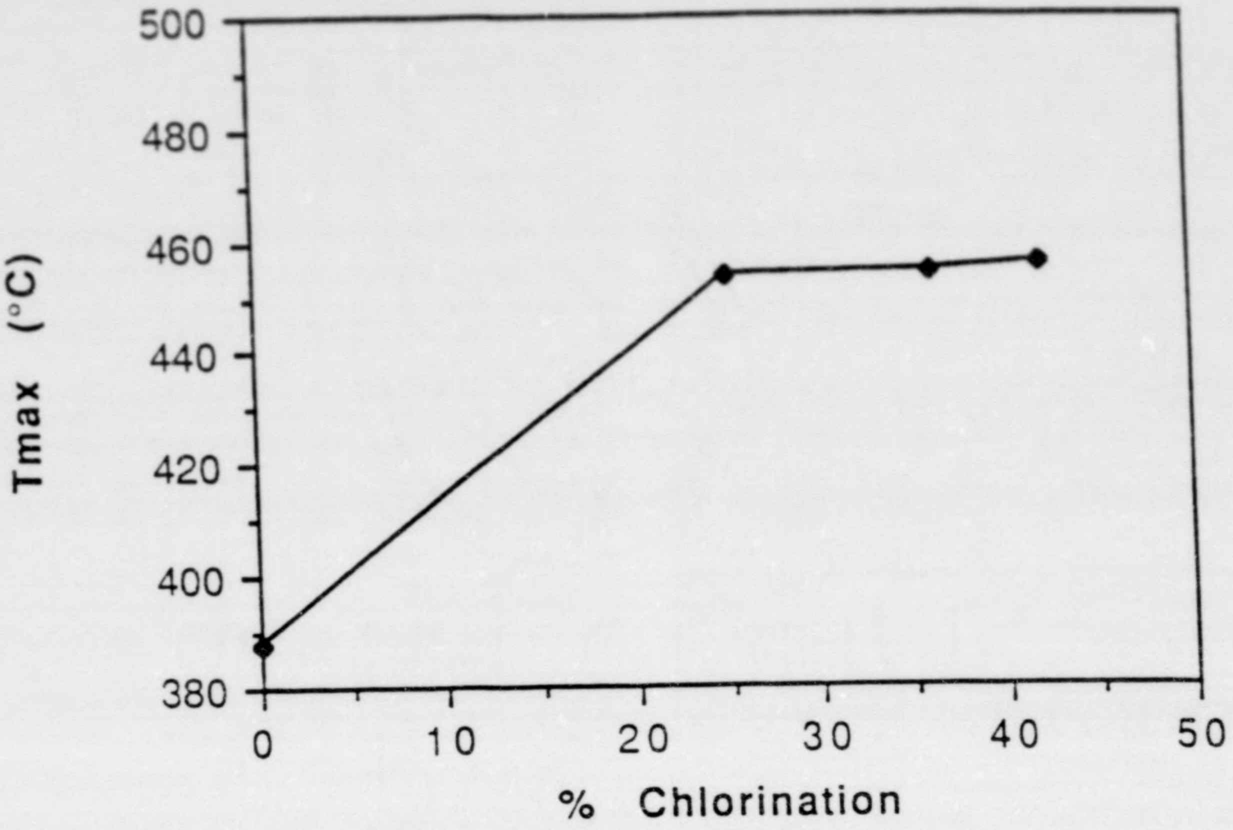


Figure 20 Comparison of Tmax to %Cl in Air

difference between the Tmax for the HDPE and the Tmax for the chlorinated samples. HDPE had a Tmax of around 387°C while the chlorinated samples had a Tmax of between 453-456°C. Figure 21 compares the percent chlorination to the reactivity in air. There is a steep decrease in reactivity going from the HDPE sample all the way to 42% chlorinated HDPE. The HDPE had a reactivity (%/min) of 0.906 while the chlorinated samples had reactivities ranging from 0.586 down to 0.326. If the residue is also considered, there is a significant difference between the HDPE and the chlorinated samples. The HDPE had a residual (char) of less than 1%. While the chlorinated samples had a residual of about 4%. A possible explanation for this phenomenon could be that a certain percentage of chlorine, as a flame retardant, attaches to the polymer and is not decomposed but instead left as residual. This results in increased char formation and points to a condensed phase mechanism when only the TG data is considered.(27)

For simplicity, 3 thermogravimetric curves (HDPE, 25% Cl-PE, and 36% Cl-PE) were placed on the same figure (Figure 22). This allowed for easier comparison of percent weight loss at different temperatures along the curves (Table 8). The HDPE curve shows one distinctive decomposition peak followed by several minor decompositions. These minor decompositions starting about 400°C are due to the effect of air on the polymer which allows for rearrangement of its structure and secondary reactions.(20) The chlorinated samples show two

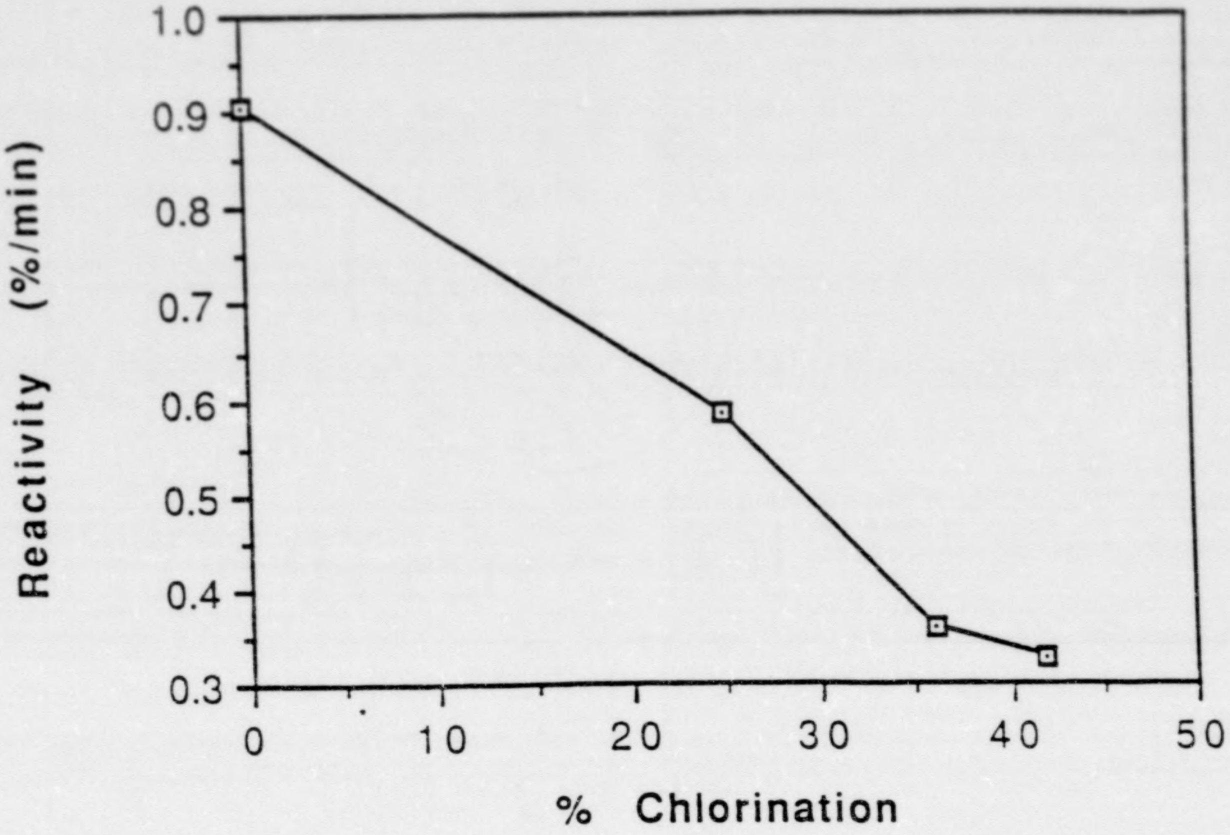


Figure 21 Comparison of Reactivity to %Cl in Air

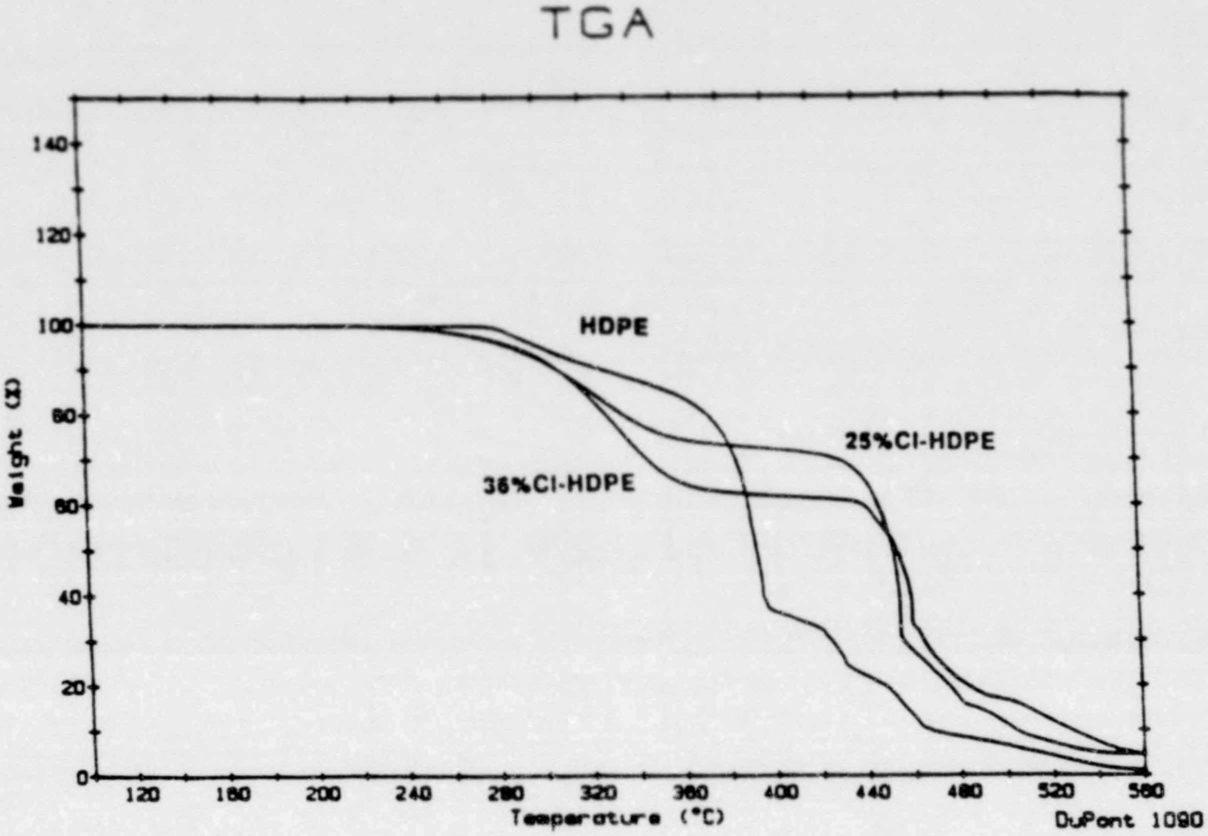


Figure 22 TG Heating Curves: HDPE, 25%Cl-PE, 36%Cl-PE in Air

TABLE 8

PERCENT WEIGHT LOSS IN AIR AT VARIOUS TEMPERATURES

Chlorination (%)	% Wt. Loss at 360^{0}C	% Wt. Loss at 440^{0}C	% Wt. Loss at 466^{0}C*
0	15.022	77.779	90
25	25.316	33.619	50
36	35.084	40.008	34
42	35.717	42.454	31

* Based on HDPE Loss Only

distinctive decompositions before their secondary decompositions occur at approximately 460^{0}C. If the weight loss of the chlorinated samples is compared to the unchlorinated sample at 360^{0}C, several interesting trends can be seen. At 360^{0}C, the unchlorinated HDPE had already started to decompose and had lost 15.0% of its total weight. At this same point the chlorinated samples have finished their first decomposition which is dechlorination. An interesting factor at this point is the correlation between percent weight loss and percent chlorination for the 25% Cl-PE and the 36% Cl-PE. Also at 360^{0}C, the 42% Cl-PE is strikingly similar to the 36% Cl-PE. The identical nature in which these two samples decompose (Figure 23) points to the fact that increasing chlorination above 36% chlorination has little effect on the decomposition of the polymer. If we look further along the TG curve (Figure 22) at 440^{0}C we see that most of the HDPE has decomposed and the chlorinated samples are beginning their second decomposition. At this temperature, almost 80% of the HDPE has decomposed while only about half that amount of the chlorinated samples has decomposed. Finally, if we look at the percent weight loss at 466^{0}C we find that all the samples have for the most part completed their decomposition. The data was adjusted taking into account the percent chlorination. The percent chlorination was subtracted out so that we could compare the percent weight loss of the HDPE only. The 36% Cl-PE and the 42% Cl-PE are once again similar for percent weight loss, both having values from 31-34% range.

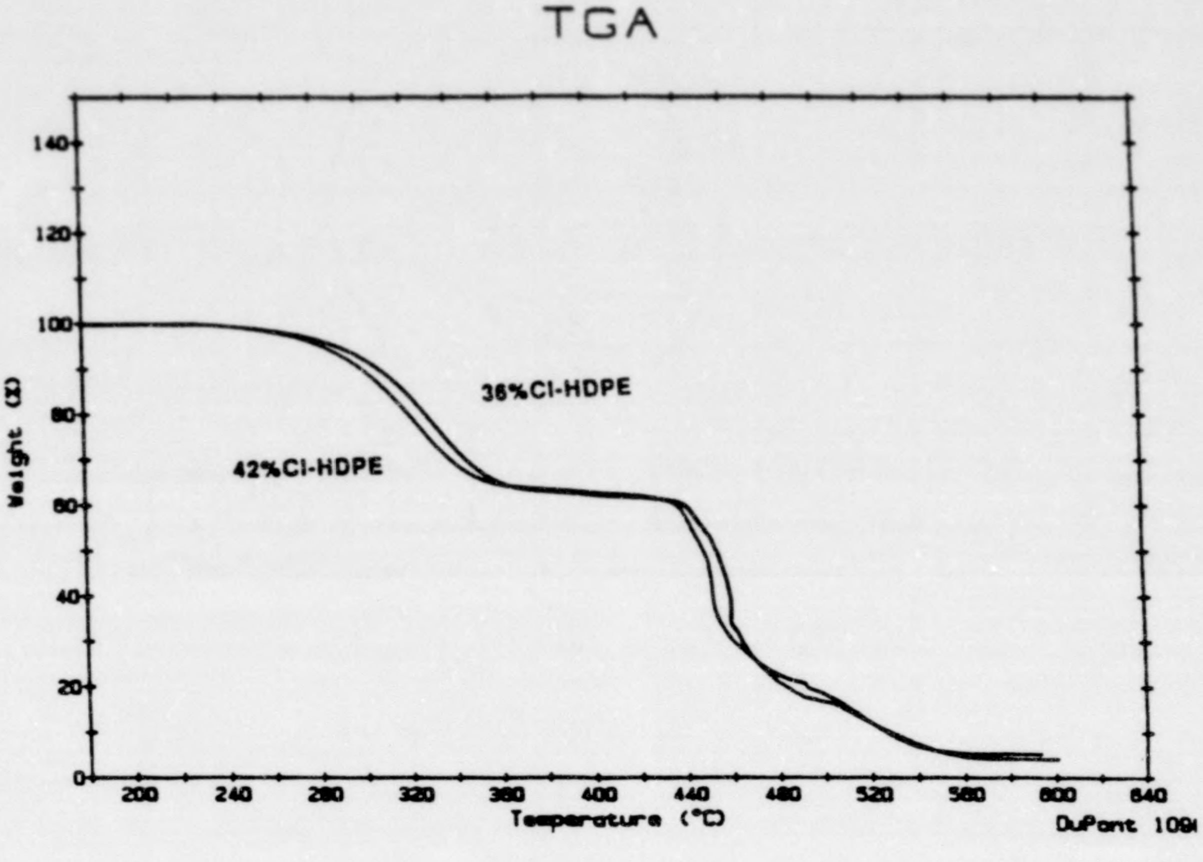


Figure 23 TG Heating Curves - 36% Cl-PE & 42% Cl-PE

We believe that the 42% Cl-PE value of 31% is slightly lower than it should be due to the fact that only 35-36% weight loss occurred after the first peak and we subtracted out according to a 42% weight loss. This would lead us to believe that there is little difference between 36% Cl-PE and 42% Cl-PE (See Figure 23). If the curves are compared it can be noted that the Tmax for the chlorinated samples are higher than the Tmax for the HDPE. All of this leads us to believe that increasing chlorination retards the thermal decomposition of HDPE.

2. FTIR and GC Data for Combustion

Once again the Fourier Transform Infrared Spectrophotometer (FTIR) is linked with the TGA to study the decomposition of the polymer in air. Because of the presence of oxygen we get very different results on the FTIR. The HDPE-FTIR data is tabulated in Table 9. Five gaseous products were studied to see how their peak area (peak height), calculated in arbitrary units, changes when the temperature is increased. The five products studied were CH_3OH, HCOOH, CO_2, CO, and H_2O. The peaks are all relatively small below 385^{0}C. At 385^{0}C the majority of the carbon monoxide comes off. The rest of the products are largely decomposed at 425^{0}C. Next, we considered the FTIR data for the 42% Cl-PE in air (Table 10). Figure 24 A and 24 B shows the FTIR data comparing the 42% Cl-PE and HDPE in air. For the chlorinated sample only four products were considered. These were CH_3OH, CO_2, CO, and H_2O. It is hard to distinguish the HCl as a

TABLE 9

FTIR DATA FOR HDPE IN AIR

Row	Temp. (^{0}C)	Peak Height*			Peak Area*	
		CH_3OH	HCOOH	H_2O	CO_2	CO
1	275	0.10	0.12	0.3	0.681	0.19
2	315	0.08	0.07	0.3	1.202	0.28
3	345	0.12	0.10	0.6	1.870	0.49
4	385	0.17	0.08	1.1	3.400	2.16
5	425	0.34	0.16	2.2	4.700	1.89
6	465	0.24	0.08	0.5	2.900	0.33
7	525	0.30	0.00	0.0	5.200	0.48

* Arbitrary Units

TABLE 10

FTIR DATA FOR 42% CHLORINATED HDPE IN AIR

Row	Temp. (^0C)	Peak Height*		Peak Area*	
		CH_3OH & HCl	H_2O	CO_2	CO
1	245	2.2	0.0	0.22	0.0
2	285	6.6	0.1	0.47	0.0
3	325	7.9	0.1	0.59	0.0
4	375	8.1	0.1	0.72	0.0
5	405	7.2	0.1	1.08	0.1
6	435	11.0	0.2	1.94	0.1
7	465	11.4	1.8	5.11	0.4
8	495	6.0	0.8	7.76	0.4
9	525	3.1	0.5	12.00	0.7
10	555	2.3	0.3	9.54	0.5

* Arbitrary Units

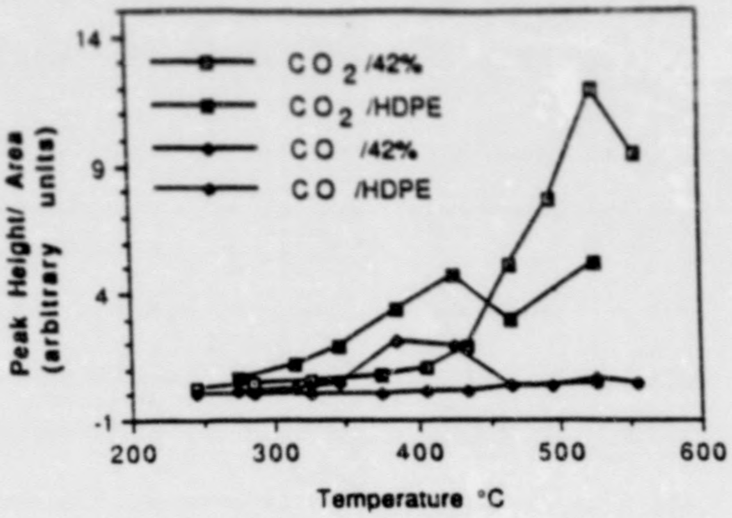
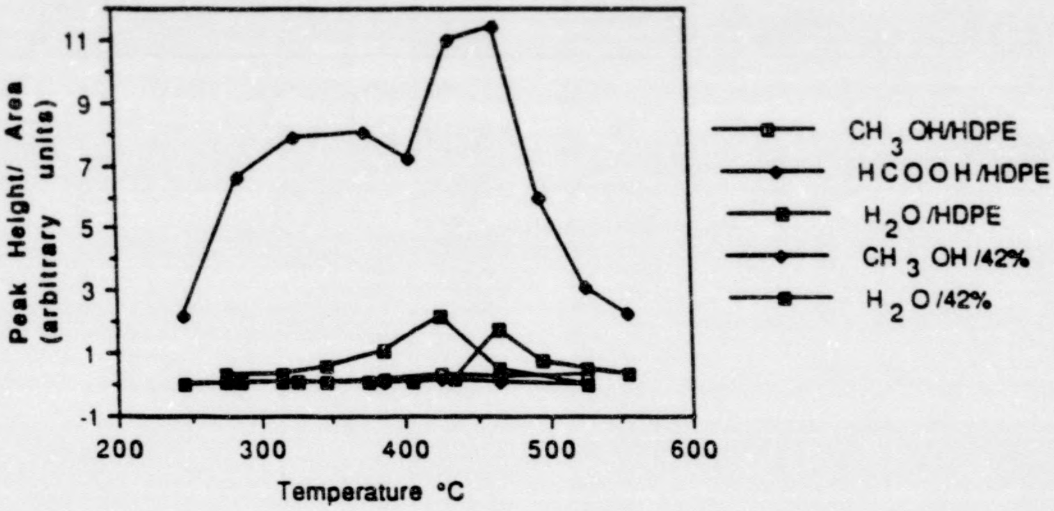


Figure 24 A. FTIR Data for 42% Cl-PE and HDPE in Air



B. FTIR Data for 42% Cl-PE and HDPE in Air separate entity for the chlorinated data because it is masked by CH_3OH. The HCOOH which was found in HDPE is also not a significant part of the chlorinated samples decomposition. Most of the methanol has not been given off as a decomposition product until 465^0C and most of the CO_2 does not appear as a decomposition product until about 525^0C. Decomposition of products occurred at higher temperatures for the chlorinated sample pointing to the retardation of the flammability because of the chlorination.

The results from the Gas Chromatograph (GC) are quite similar for the HDPE and the chlorinated samples. Table 11 gives the GC products for the thermal decomposition of all four samples studied. All four samples experience a phase change at 120^0C. The chlorinated samples gave off HCl from approximately $250\text{-}426^0C$. After that it was found that various aliphatic hydrocarbons including methane, ethylene, and propylene were given off between 426^0C and 600^0C due to the thermal decomposition of the polymer. The GC results point to the flame retardant working by a vapor phase mechanism because the chlorinated HDPE did not alter the volatile products but instead produced the actual flame inhibiting species (HCl).(27)

A more detailed discussion of how the GC and FTIR data correlates to the thermal data is included in the following section on Differential Scanning Calorimetry.

3. <u>Differential Scanning Calorimetry for Combustion</u>

The next step was study the decomposition of the polymer using the Differential Scanning Calorimeter (DSC) under conditions of air. Figure 25 shows a typical DSC curve for high density polyethylene in air. The GC data for specific temperatures is shown in Table 11. The DSC curve for HDPE in air shows one endothermic peak at 120^0C and a broad area of exothermic peaks from 250^0C to 480^0C. The peak around 120^0C is a sharp peak which correlates to the heat of melting. If the GC data is then considered for the peak it is found that no gaseous products are given off. It is on this basis that we deduce nothing is decomposed to form products; therefore, a phase transition of a solid to a liquid has occurred. The second set of broad exothermic peaks is due to the decomposition and gaseous rearrangements of HDPE. Recall that the HDPE sample in nitrogen only gave endothermic peaks and the products lost were various aliphatic hydrocarbons (H_2, CH_4, $C_2^=$, $C_3^=$). In air, because of the presence of oxygen, we obtain exothermic peaks and several different products (CO_2, CO, H_2O, $C_2^=$, $C_3^=$, C_4). The presence of oxygen results in reactions and rearrangements that were not possible in an atmosphere of pure nitrogen. All these reactions that occur in oxygen lead to decompositions that are exothermic in nature. The three chlorinated samples give very different results. The 42% chlorinated sample is seen in Figure 26. The GC data for the three chlorinated samples in air is seen in Table 11. Figure 27 shows the DSC curve for the 25% chlorinated sample enlarged. By enlarging the curve two things can be distinguished. The first thing noted is the

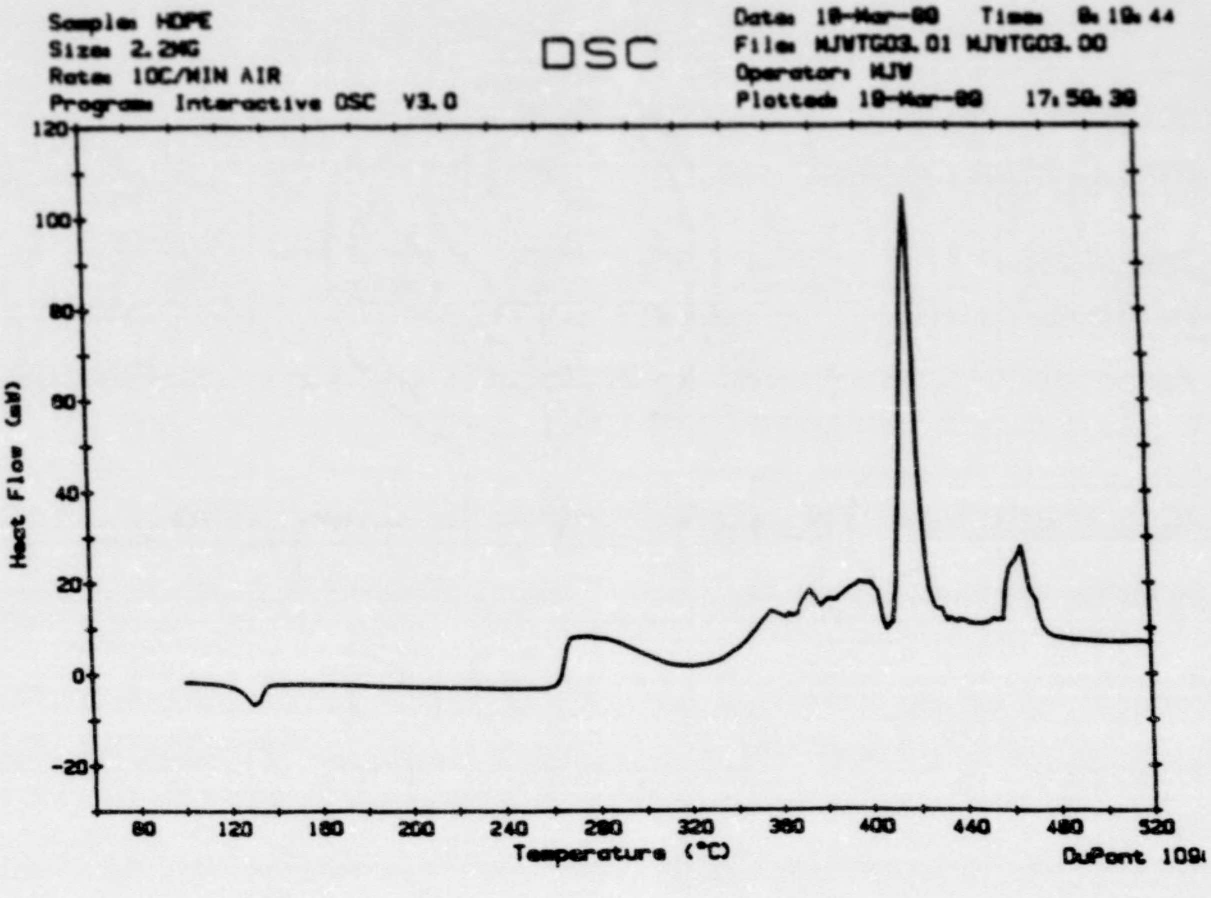


Figure 25 DSC Curve for HDPE in Air

TABLE 11

GC DATA FOR HDPE AND CHLORINATED SAMPLES IN AIR

Temp. (^0C)	HDPE	25%Cl-PE	36%Cl-PE	42%Cl-PE
120 130	H_2O	H_2O	H_2O	H_2O
200 212	H_2O			
212 420	CO_2 $C_2^=$, H_2O	CO_2 H_2O HCl	CO_2 H_2O HCl	CO_2 H_2O HCl
420 465	CO_2 $C_2^=$, $C_3^=$ C_3^0, C_4 H_2O	CO_2 $C_2^=$, $C_3^=$ C_3^0, H_2O	CO_2 $C_2^=$, $C_3^=$ C_3^0, H_2O	CO_2 $C_2^=$, $C_3^=$ H_2O
465	CO_2 H_2O	CO_2 H_2O, $C_2^=$ C_3^0, $C_3^=$	CO_2 H_2O, $C_2^=$ $C_3^=$	CO_2 H_2O
% Weight Loss	100%	97.07%	96.70%	96.52%

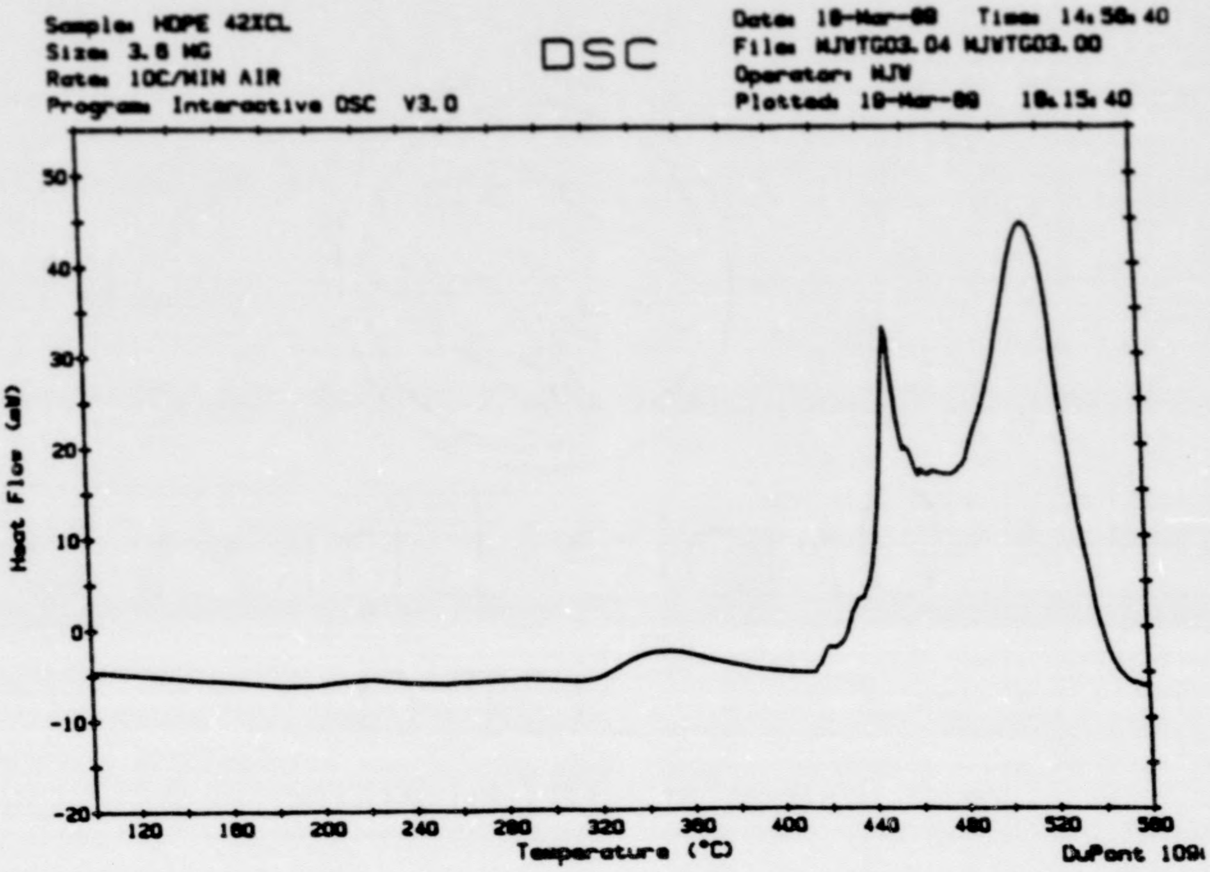


Figure 26 DSC Curve for 42% Cl-PE

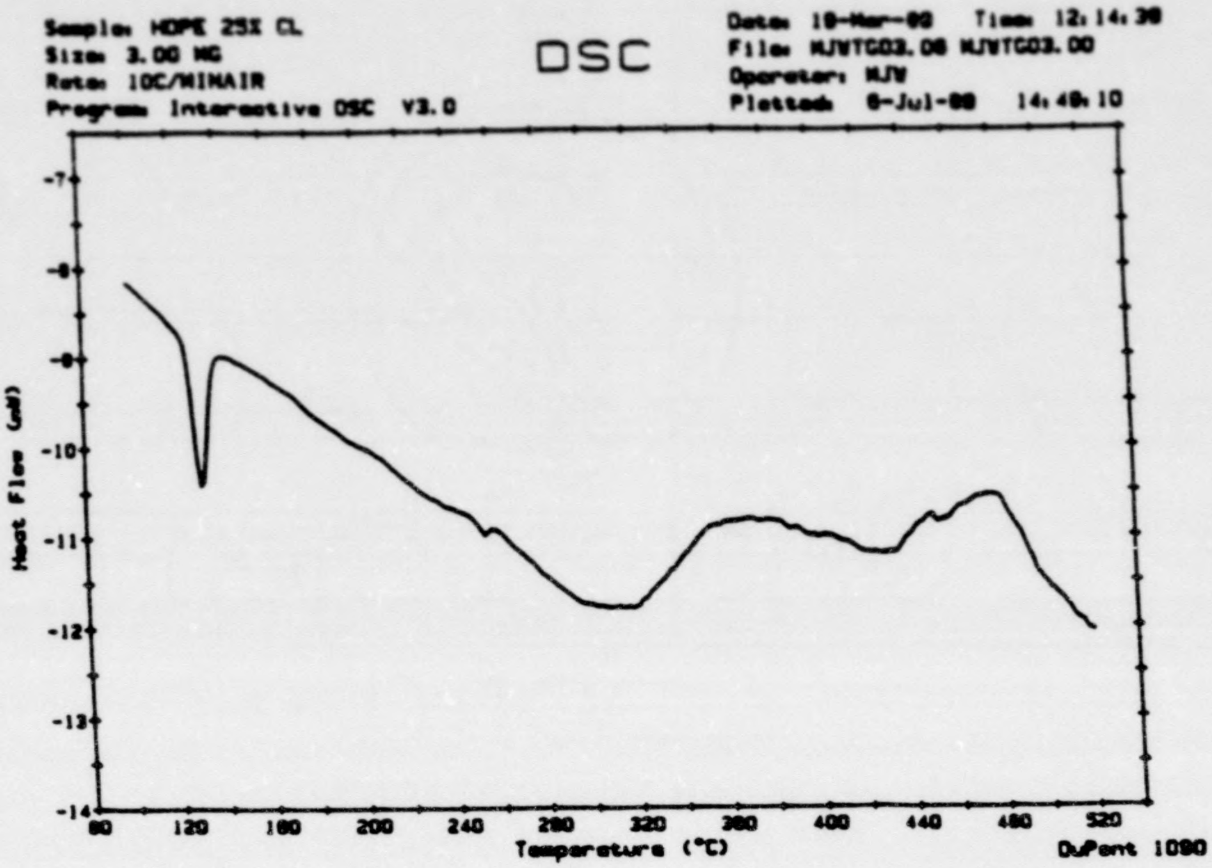


Figure 27 Enlarged DSC Curve for Chlorinated HDPE

sharp peak at 120^{0}C similar to the unchlorinated sample. This sharp endothermic peak is due to a phase transition of a solid to a liquid. It should be noted that the intensity of this peak is decreased with increased chlorination just like the results found for nitrogen. (See Figure 19). This is possibly due to the decrease in the crystallinity factor with increasing chlorination. The second thing found by enlarging the curve is that the DSC curve has a broad endothermic area starting at 160^{0}C and continuing to around 350^{0}C. This is due to the loss of HCl and is similar to the data obtained in nitrogen. Starting at 360^{0}C we find two overlapping exothermic peaks for the chlorinated sample. These are similar in nature to those found for HDPE with several significant differences. First, if we correlate the FTIR products given off for these two exothermic peaks we see that the results are similar for the HDPE and chlorinated samples. The differences occur in the intensity of the heat peaks and the maximum temperatures at which decomposition occurs. The HDPE sample shows a gradual decomposition with the maximum heat peak occurring at 420^{0}C (Note the intensity of the peak at 420^{0}C, Figure 25). At 440^{0}C almost 80% of the HDPE had decomposed. The percent weight loss data was obtained from the TG data. The FTIR data correlates to the maximum decomposition with the majority of products (specifically CO_2) being given off at 420^{0}C (See Figures 24A & B). The chlorinated samples point to a less gradual heat release. At 440^{0}C, where we found almost 80% weight loss, in the TG data, for the unchlorinated sample we find that only about 31% of the chlorinated samples have decomposed. Therefore, almost 70% of the HDPE is still present in the chlorinated samples while almost all of the HDPE has decomposed in the unchlorinated sample. The maximum heat peak for chlorinated samples occur at approximately 520^0C (Note the intensity of this peak, See Figure 26). This correlates to the FTIR data with the majority of products (CO_2) being given off at 520^0C (See Figures 24A & B). The GC data supports the loss of CO_2 for the maximum peak in both chlorinated and unchlorinated samples. The major significance in comparing the chlorinated and unchlorinated samples is that the samples with chlorination tend to have significantly higher T maximum. This indicates retardation of flammability when chlorine is present.(38) From the GC and FTIR results, we propose that the chlorinated HDPE did not alter the composition of volatiles (CO_2, 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.(27) However, the chlorination also results in enhanced char formation from the TG data. This indicates a condensed phase operation for a flame-retardant.(27) Therefore the chlorination of the HDPE may operate by more than one mechanism.

C. Ignition

Finally, the effects of chlorination on the decomposition of high density polyethylene under ignition conditions was considered. The ignition process involves a chemical change when a material is heated in the presence of pure oxygen. Ignition is believed to be a step in the combustion process for studies involving polymer flammability.(22) Therefore a closer look at the ignition process could possibly lead to a better understanding of the combustion process. A sample mass of 5 mg. was used for the ignition process instead of the 10 mg. that was used for combustion and pyrolysis. A smaller sample was used for ignition to minimize or eliminate the possibility of losing some of the sample.(32) The sample may be lost when it ignites if there is enough force to cause the sample to jump from the sample pan. This would lead to inaccuracies in the weight loss and therefore give poor results and poor reproducibility.

1. <u>TGA for Ignition</u>

First the samples were run on the TGA in an atmosphere of pure oxygen (ignition conditions). Figure 28 gives the TG curve for the 36% chlorinated HDPE sample. Table 12 shows the Tmax, reactivity, and residual for all four samples. A trend can be seen in the data obtained in oxygen. For the first peak, correlating to the loss of HCl, as the chlorination increases the reactivity increases. The Tmax, on the other hand, stays almost constant for all three chlorinated samples with a value of about $305^0C \pm 0.7$. For the second peak the Tmax increases as the chlorination increases. A plot of the Tmax versus the percent chlorination

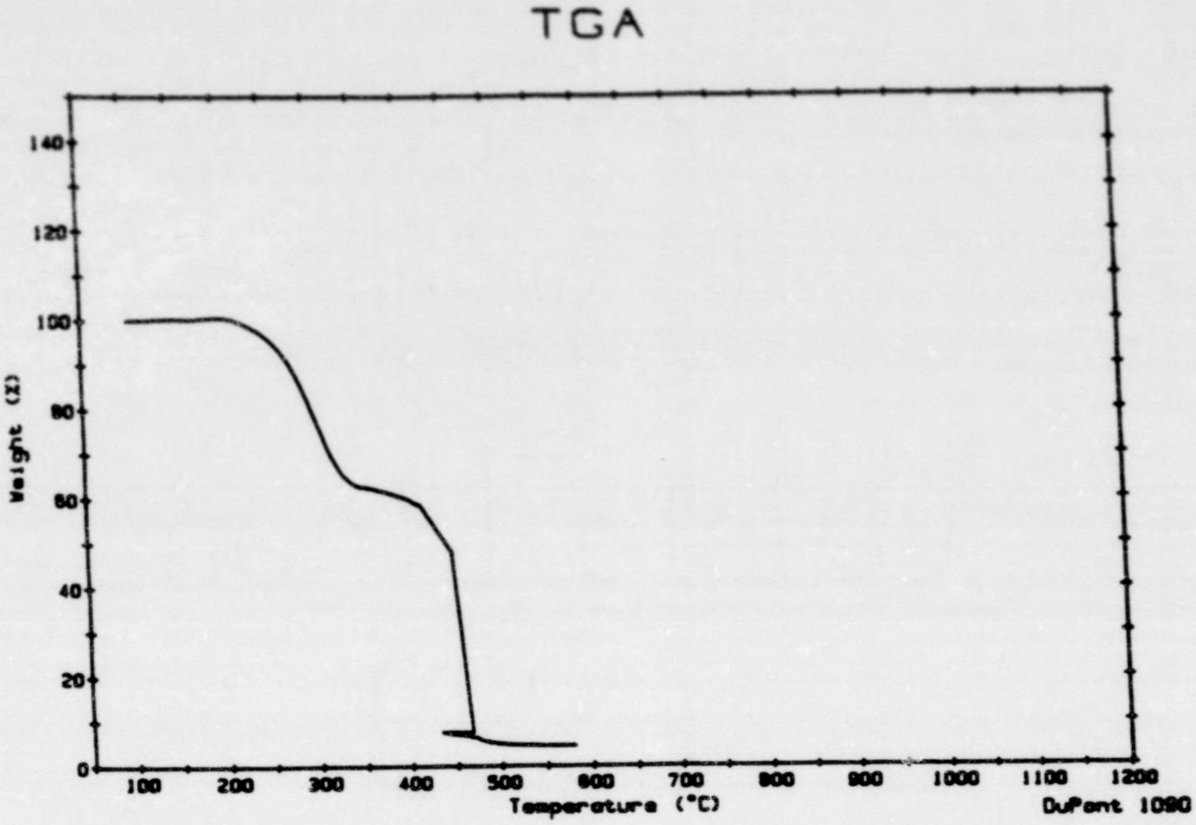


Figure 28 TG Curve for 36% Cl-PE in Oxygen

TABLE 12

COMPARISON OF HDPE AND CHLORINATED SAMPLES IN OXYGEN

Chlorination (%)	Peak 1		Peak 2		Residue (%)
	Tmax (^{0}C)	Reactivity (%/min)	Tmax (^{0}C)	Reactivity (%/min)	
0	-----	-----	396.4	0.001	0.721
25	305.1	0.06	443.8	1.1	3.46
36	305.8	0.09	498.0	1.1	3.74
42	305.7	0.10	502.5	1.1	6.51

can be seen in Figure 29. The reactivity increases moving from the unchlorinated to the 25% Cl-PE then levels off as we increase chlorination. Figure 30 shows a plot of the reactivity relative to the percent chlorination. Also if the residue is considered, there is a significant difference between the HDPE and the chlorinated samples. The HDPE had a residual (char) of less than 1% while the chlorinated samples had a residual(%) anywhere from 3.46 to 6.5. If the curve in Figure 28 is considered an irregularity in the curve at about 430^0C is apparent. This is due to the sample igniting and causing a jump to a higher temperature followed by a return to the temperature of the furnace. When the samples reached a temperature of about 430^0C (395^0C for HDPE), a loud pop was heard and a flash of light was given off by the sample on the balance pan. The noise and light support the idea that ignition of the sample occurred. Flame retardants have the characteristics found in our data. A high flame retardant, such as chlorine, results in a higher Tmax and a higher residue.(20,39) A similarity can once again be found between the decomposition of the 36% Cl-PE and the 42% Cl-PE. Both, the Tmax and the reactivity start to level off above 36% Cl-PE (See Figures 29 & 30). This supports the belief that increasing chlorination above 36% has little or no effect on the thermal decomposition of the polymer.

2. <u>GC Data for Ignition</u>

Under ignition conditions only the GC data was used to study the gaseous products formed from the decomposition

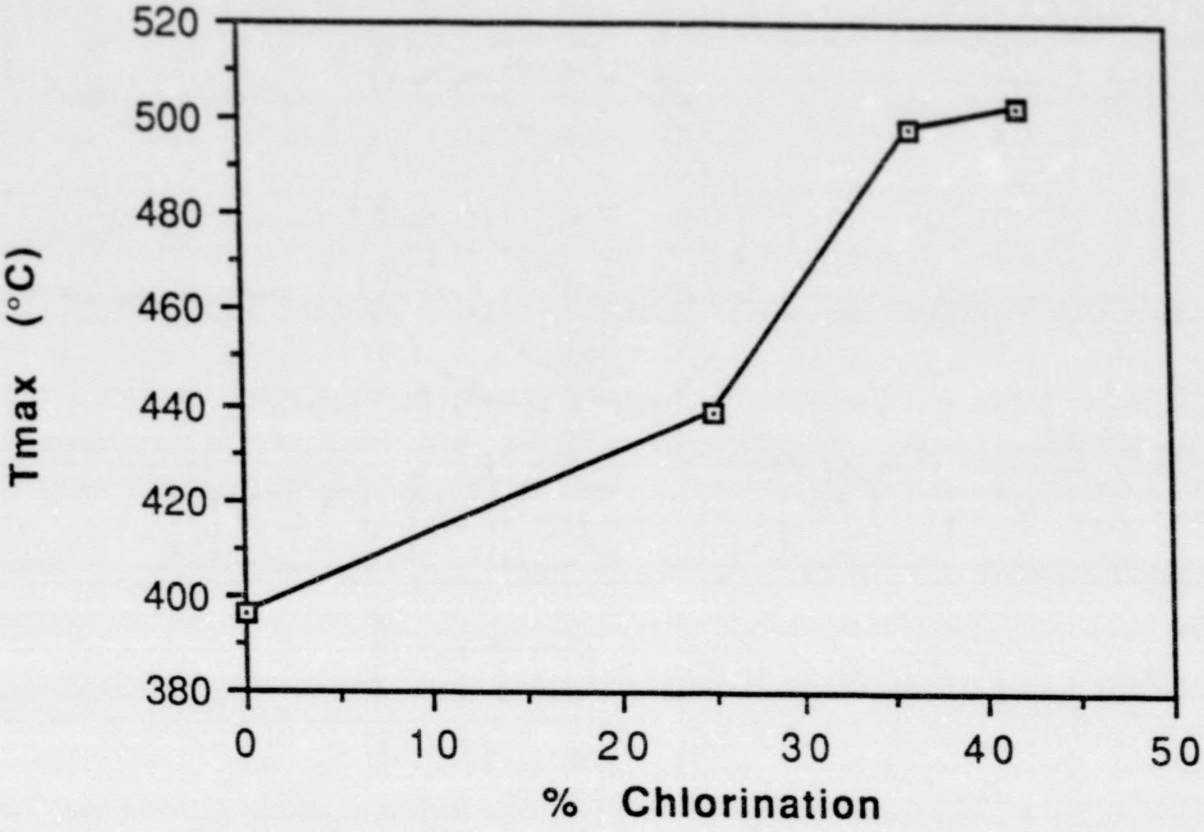


Figure 29 Comparison of Tmax and %Cl in Oxygen

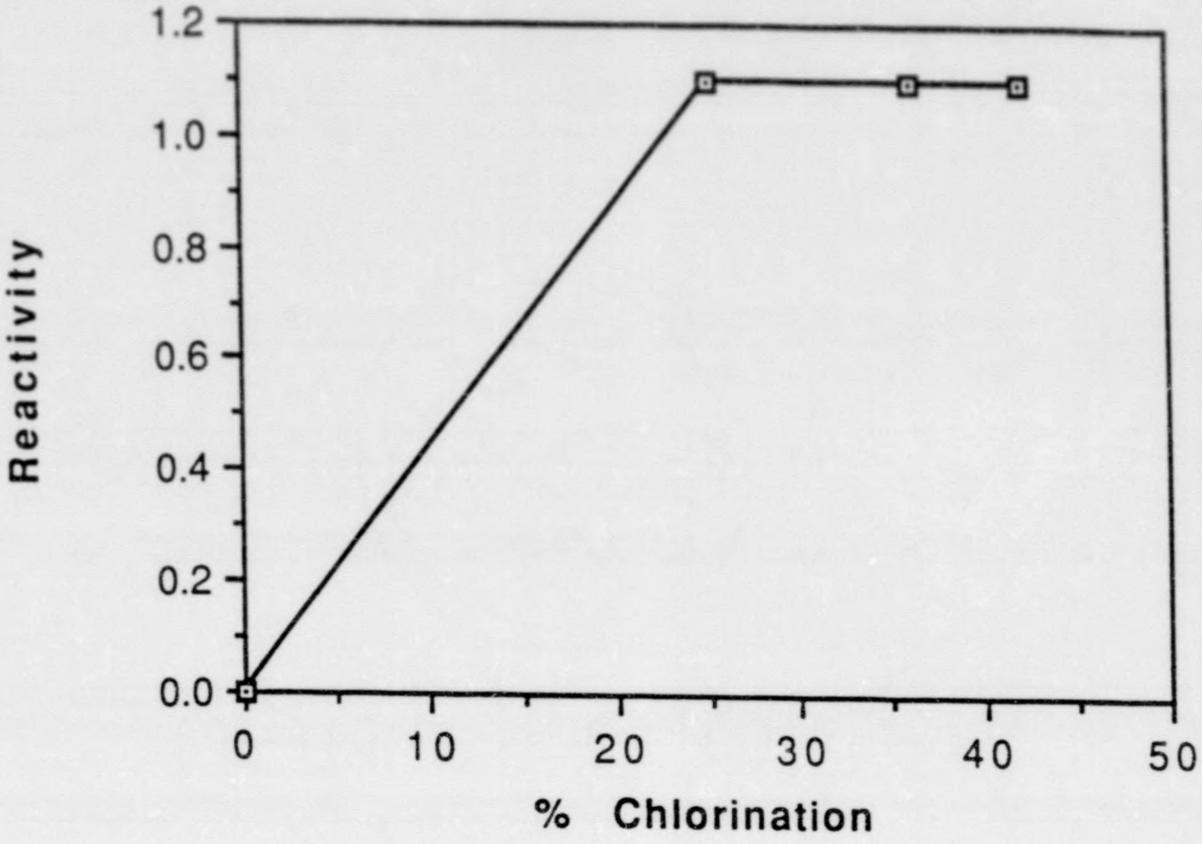


Figure 30 Comparison of Reactivity and %Cl in Oxygen

of the polymer samples. The gas flow rate for the data was modified from 50 ml/min to 15 ml/min so as to avoid interference with the GC results.(40) Table 13 shows the GC data for all four of the HDPE samples under ignition conditions. From 180 to 230^{0}C the only major decomposition product for all four samples is trace amounts of water. From 230-310^{0}C the HDPE sample decomposes and gives off carbon dioxide as its gaseous product (TG data). No carbon monoxide is present because if it was present it would react with the oxygen in the atmosphere to form carbon dioxide. The chlorinated samples continue to give off trace amounts of water until they reach a temperature of between 402-480^{0}C. At this temperature range the chlorinated samples undergo their major decomposition (See TG Curve Figure 28) giving off carbon dioxide and water as gaseous products. At 402-480^{0}C, the HDPE sample gives off CO_2 as a product of thermodecomposition. After 480^{0}C, the only product detected is trace amounts of water.

3. DSC for Ignition

The DSC data under ignition conditions was considered last. The DSC curve for the HDPE sample can be seen in Figure 31. The DSC curve for HDPE in oxygen shows an endothermic peak at about 130^{0}C and a range of exothermic peaks from 240-480^{0}C. We believe the peak at 130^{0}C is due to the heat of melting. If we also correlate the GC data to this peak on the DSC we find that no gaseous products are formed. Therefore, since no products are formed a phase transition of a solid to

TABLE 13

GC DATA FOR HDPE AND CHLORINATED SAMPLES IN OXYGEN

Temp. (^{0}C)	HDPE	25%Cl-PE	36%Cl-PE	42%Cl-PE
180 230	H_2O	H_2O	H_2O	H_2O
230 310	CO_2	H_2O HCl	H_2O HCl	H_2O HCl
310 402	H_2O	H_2O	H_2O	H_2O
402 480	CO_2,H_2O	CO_2,H_2O	CO_2,H_2O	CO_2,H_2O
480 600	H_2O	H_2O	H_2O	H_2O
% Weight Loss	100%	96.66%	95.29%	96.08%

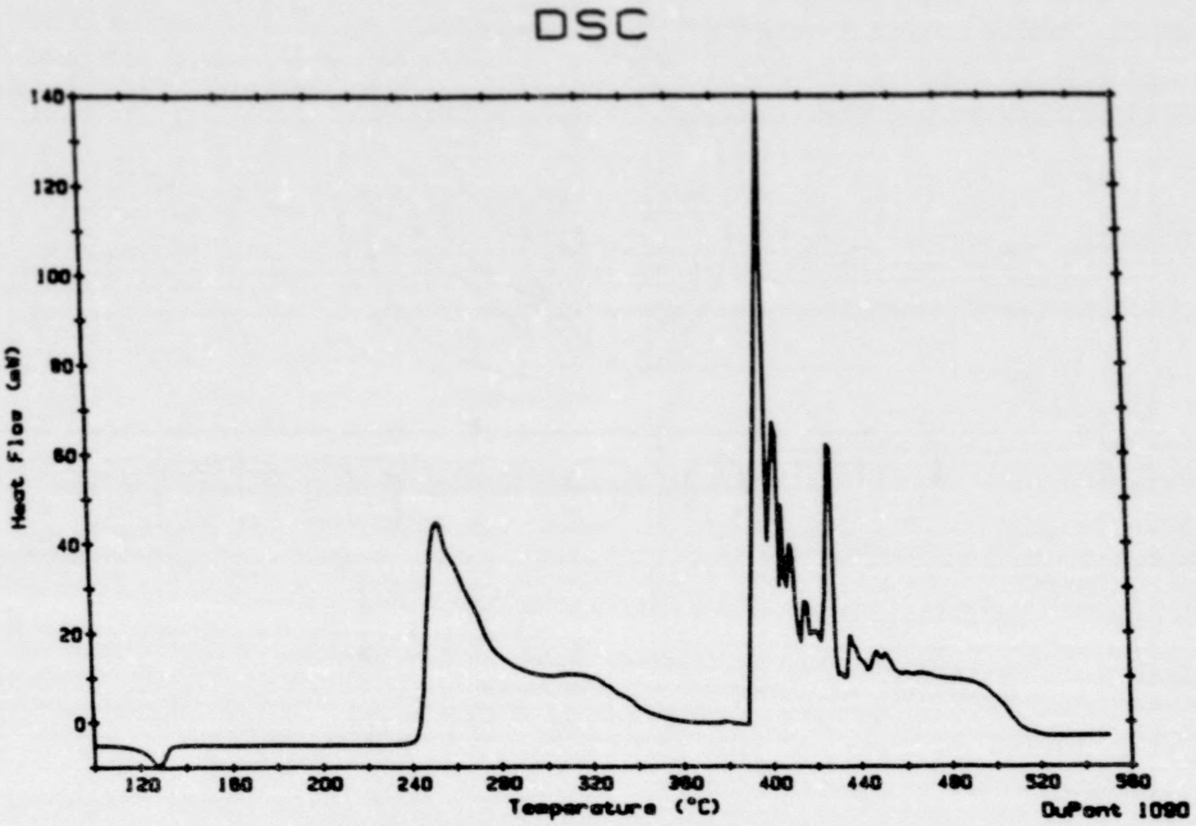


Figure 31 DSC Curve for HDPE in Oxygen

a liquid must be occurring. The exothermic heat peak at 240°C is very large for the HDPE and is due to the decomposition of HDPE (TG data) to form CO_2. Recall that gaseous products such as CO_2 were obtained from the GC data (Table 13). Finally, we looked at the broad range of sharp peaks from 390-480°C. These are due to the heat release from the decomposition of HDPE in the TG data. The GC data for this area on the DSC curve shows the loss of carbon dioxide and water as gaseous products. At 395°C, the sample ignites which results in the very sharp peak at this temperature. Most of the heat release (sharper peaks) occur before 440°C. After 480°C, water is the only product detected by the GC. Figure 32 shows the DSC curve for the 36% Cl-PE sample. Once again we see the phase transition occurring at about 136°C. If we compare this to the HDPE phase transition (Figure 31), we see that increasing chlorination decreases this peaks intensity. This is possibly due to a decrease in crystallinity as chlorination increases. For the chlorinated samples the sharp exothermic peak found for the HDPE sample is not apparent. According to GC results, a decrease in oxygen at this point is only found in the unchlorinated sample. We believe that the oxygen reacted with the HDPE as it decomposed to form the carbon dioxide and water which was detected by the GC. To make this type of assumption we had to use data from three different instruments - TGA, DSC, and TG/DTA-GC. This shows the strong correlation between all the data we collected. The chlorinated samples did not show a significant decrease in oxygen at this point and

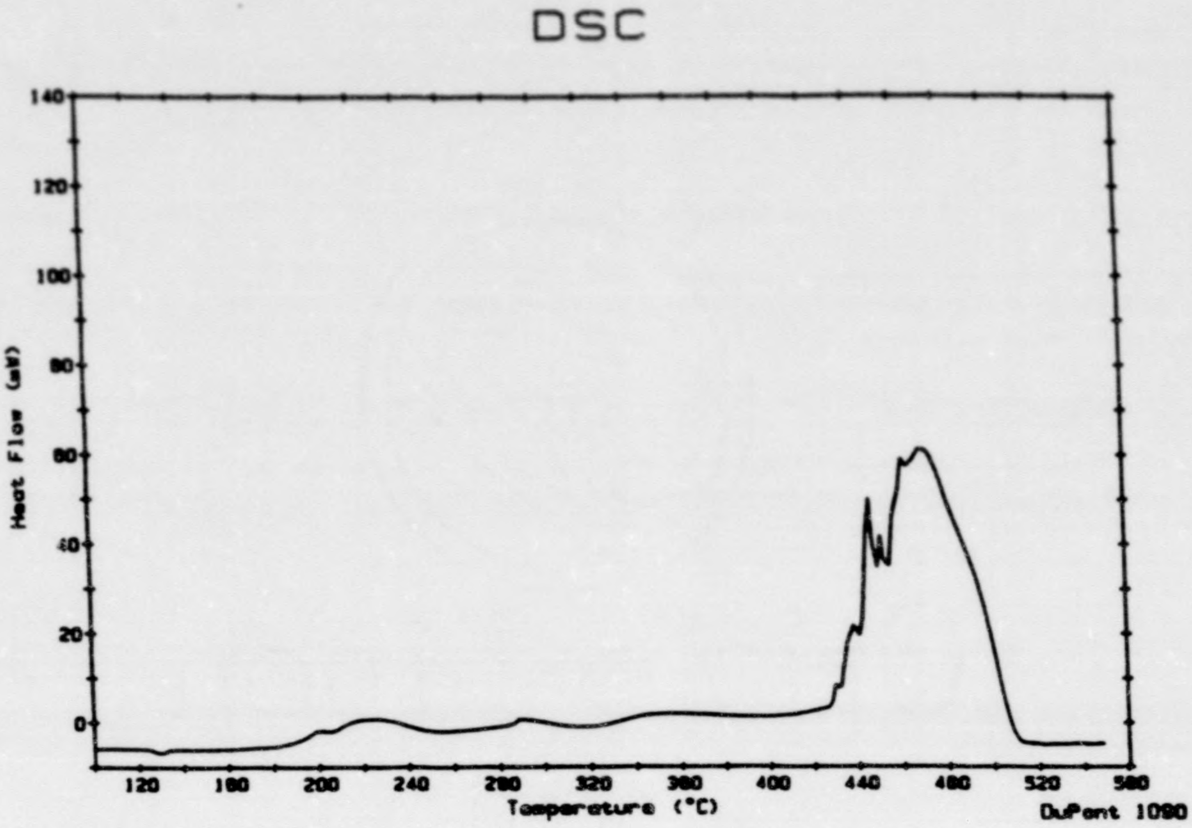


Figure 32 DSC Curve for 36% Cl-PE in Oxygen

therefore carbon dioxide was not given off. Instead only traces of water were obtained as product. From 220-320^{0}C we found that there was a slight endothermic area. This correlates to the loss of HCl on the TGA. This is the only major product at this temperature range with traces of water given off as a minor product (GC data See Table 12). For the chlorinated samples we see a gradual heat release at 440^{0}C resulting in the release of carbon dioxide and traces of water (GC data, Table 13). Most of the HDPE has already decomposed in the unchlorinated sample before the chlorinated samples even begin to decompose. This can be backed up by the DSC data because the major heat release for the unchlorinated samples occurs at 400^{0}C while the major heat release for the chlorinated samples occurs at about 480^{0}C. Also note the intensity of the heat peaks when comparing the chlorinated samples to the unchlorinated samples. The unchlorinated sample shows very intense peaks while the chlorinated samples show heat peaks that are less than half the intensity of the unchlorinated sample. Finally, after 520^{0}C the chlorinated sample only lost trace amounts of water (See GC data, Table 13). All this data points to the retardation of flammability when chlorine is present.

CONCLUSIONS

1. Increasing chlorination will retard the decomposition of HDPE.
2. Increasing the percentage of chlorination above 36% does not have significant effects on the thermal decomposition of HDPE.

RECOMMENDATIONS FOR FURTHER STUDY

1. To obtain quantitative results of the gaseous products evolved.
2. To study the residual (char) at different temperatures along the heating range (30^0C-600^0C) to see what is retained by the sample and what is in the final residual.

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