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STUDY OF PYROLYSIS AND INCINERATION OF DISPOSABLE PLASTICS USING COMBINED TG/FT-IR TECHNIQUE

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Abstract

Thermogravimetric analysis (TG) provides information regarding mass changes in the sample resulting from heat treatment under controlled environment. However, it does not provide any chemical information regarding the gases evolved during the thermal degradation. Using FT-IR spectrometry in combination with TG, it is often possible to identify the evolved gases, and also monitor their evolution profiles during thermal degradation. In this study, we present the TG/FT-IR combined analysis of incineration and pyrolysis of some common plastics such as high density polyethylene (HDPE), polyvinyl chloride (PVC), polyethylene terephthalate (PET), and polystyrene (PS). This study demonstrates the utility of such combined analysis in providing useful information regarding the use of thermal treatment for recycling or incineration.

Keywords: disposable, evolved gases, FT-IR spectroscopy, polymers, TG

Introduction

Presently, plastics occupy about 20% by volume of municipal solid waste [1]. The amount of plastics products has been increasing and their disposal has become an important environmental concern. The following polymers materials constitute a large portion of the solid wastes: high density polyethylene (HDPE) used in milk containers and disposable bags, polyvinyl chloride (PVC) used in shampoo bottles, polyethylene terephthalate (PET) used in 1/2 gallon soda bottles and polystyrene (PS) used in cups and hamburger containers. Modern day plastic disposal techniques include land filling, incineration and recycling using thermal treatment. Due to increased landfill crisis, the other disposal techniques are preferred. Plastics disposal using incineration involves high temperature treatment of plastics using excess air. Plastics recycling processes often go through a pyrolysis step, which involves heat treatment without oxygen. Both incineration and pyrolysis techniques produce: i) gaseous products which could be potential health hazards, and therefore, should be treated carefully, and ii) residual solid products, which need further disposal [2–4]. Therefore, the primary objective of this investigation was to analyze and compare both the gases evolved as well as changes in the mass of disposable plastics samples during thermal degradation under nitrogen and air atmospheres.

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Experimental

Apparatus

Bio-Rad FTS 165 FT-IR spectrometer interfaced with TA Instruments model TA 2050 Thermogravimetric analyzer was used for data acquisition. The TG unit was equipped with an evolved gas analysis furnace. The gases evolved were lead into a special TG interface accessory consisting of a transmission gas cell through a transfer line. Temperatures of both the gas cell and the transfer line were controlled at 523 K during data acquisition using Bio-Rad Win-IR Sequence software.

Materials and methods

The polymeric materials analyzed using the TG/FT-IR combined technique included: HDPE, PVC, PET, and PS. Typical size of samples used in the experiments was about 3 mg. Temperature programming of the TG furnace was as follows: Ramp at 30 K min^{-1} from room temperature (about 300 K) to 1273 K. The furnace was purged with nitrogen at 90 cm^3 min^{-1} for pyrolysis experiments and with air for incineration. For spectral data acquisition, a room temperature DTGS detector was used. The spectral resolution was set at 4 cm^{-1}. Spectra of evolved gases were acquired continuously and every 6 s interval data were co-added to produce a representative scan set.

Data analysis

Thermogravimetric analysis was used to provide information regarding mass loss of the sample in two different forms: i) mass loss as a function of either the temperature or time, and ii) derivative of mass loss as a function of temperature or time.

The spectra of gases evolved during thermal degradation was processed to provide the following three types of information: i) Evolved gas profile or the Gram Schmidt chromatogram shows the variation in total absorbance intensity during the thermal degradation. This variation in the total absorbance could result from changes in absorptivity as well as concentration of the gases evolved during the mass loss. ii) Specific gas profile or functional group profile shows the variation in absorbance intensity over a specific spectral region as a function of time. iii) Absorbance spectra averaged over specified time durations show representative spectra of gases evolved over the time durations.

Results

High density polyethylene (HDPE) and polystyrene (PS)

In this paper, the analysis of recycled HDPE homopolymer are presented. The mass loss profile and its derivative during pyrolysis are shown in Fig. la and 1b. Thermal degradation of HDPE began around 643 K and showed maximum mass loss around 737 K (15.9 min). Above 873 K, HDPE degraded completely, leaving no residue.

The IR spectrum of the evolved gases at 737 K (maximum mass loss temperature) is shown in Fig. 2a. This spectrum shows strong C–H stretching peaks (aliphatic single bonds: 2928 and 2857 cm^{-1}) and the C–H bending peak (1450 cm^{-1}) indicating presence of short chain aliphatic hydrocarbons of long chain HDPE thermal degradation products (oligomers). In addition, the spectrum of evolved gases includes aliphatic –C=C–H stretching (3084 cm^{-1}), –C=C– bending peak (1638 cm^{-1}), and –C=C– *trans* (970 cm^{-1}), vinyl (910 cm^{-1}), and *cis* (720 cm^{-1}) peaks. These peaks indicate that pyrolysis products of HDPE include saturated and unsaturated hydrocarbons.

Figure 1c and 1d show mass loss profile and its derivative for HDPE under air purge. In contrast with the single step pyrolysis, these profiles show significantly more complex patterns demonstrating a multi-step reaction.

Figure 2b shows a typical IR spectrum of gases evolved at 621 K, the temperature at which maximum mass loss occurred. The IR spectrum clearly indicates presence of carboxylic acids (broad bands between 3000–2650 cm^{-1}), and aldehydes (2770–2700 cm^{-1}). These are further confirmed by carbonyl stretching bands between 1800–1600 cm^{-1}. Other gaseous components evolved were easily identified as carbon dioxide (2400–2200 cm^{-1}), carbon monoxide (2200–2050 cm^{-1}), and water vapor (3700–35550, 1550–1350 cm^{-1}). Short chain saturated or unsaturated hy-

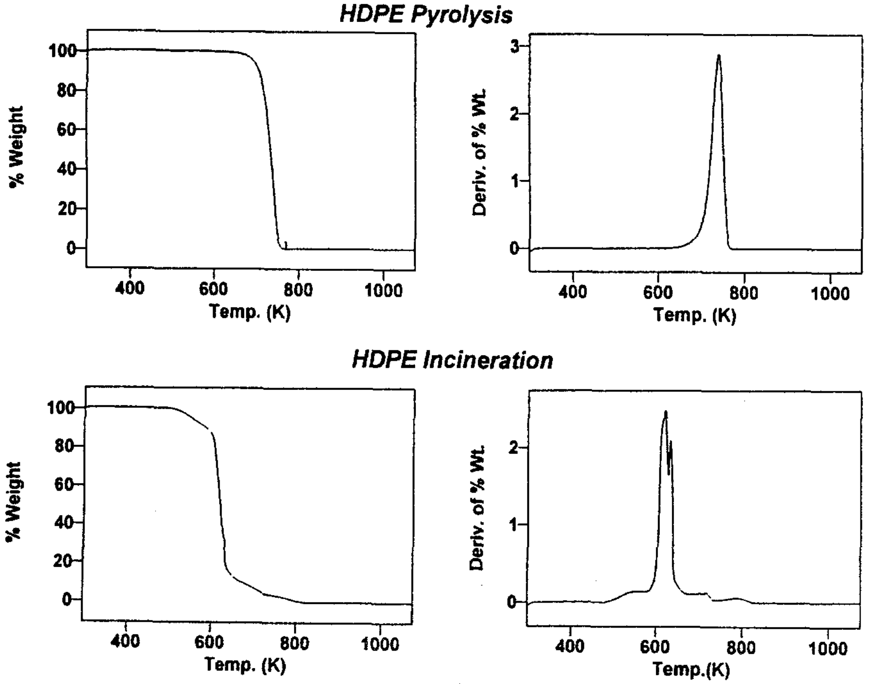

Fig. 1 Thermal degradation of HDPE under nitrogen (pyrolysis) (a), derivatized mass loss of HDPE during pyrolysis (b), thermal degradation of HDPE under air (incineration) (c), derivatized mass loss of HDPE during incineration (d)

drocarbons (which were the major pyrolysis products) were minor products of incineration.

The results from pyrolysis and incineration study of PS were somewhat similar to the HDPE results. Although the early part of incineration produced a significant amount of gaseous styrene (a result similar to pyrolysis), a large portion of the mass loss was dominated by release of oxidized gaseous products such as CO_2, CO, and aldehydes.

Polyethylene terephthalate (PET) and polyvinyl chloride (PVC)

The mass loss and derivatized mass loss of PET under pyrolysis condition is shown in Figs 3a and 3b. A single mass loss was observed between 603–823 K. About 9.5% of the recycled PET remained as a residue after pyrolysis.

The IR spectrum of gases evolved during the mass loss is fairly complex indicating a mixture of several different products. Although it would be very difficult to determine the identity of all the individual gaseous products evolved using IR spectroscopy, the characteristic peak locations indicated presence of benzoic acid, terephthalic acids or their derivatives, and CO_2 (Fig. 4a).

The mass loss and derivatized mass loss of PET under incineration condition is shown in Figs 3c and 3d respectively. The mass loss profile shows 2 major steps between 623–873 K. No residue was left behind after incineration of PET.

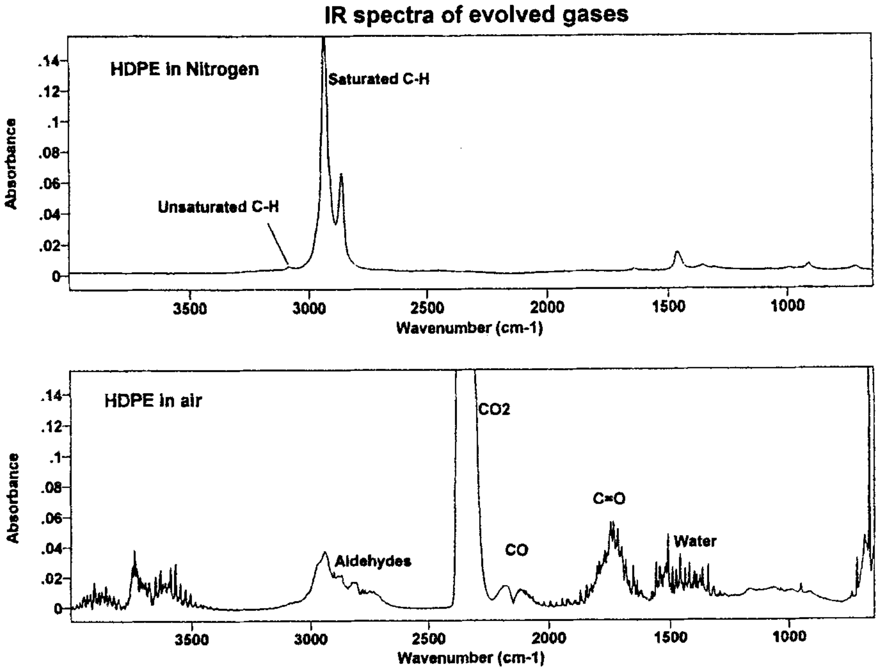

Fig. 2 IR spectrum of gases evolved during pyrolysis of HDPE (a), IR spectrum of gases evolved during incineration of HDPE (b)

The IR spectra of gases evolved at different times during incineration are shown in Fig. 4b. These spectra show that other than CO_2, the gases evolved during the first mass loss of incineration are similar to those evolved during the only mass loss in pyrolysis. The second mass loss during pyrolysis primarily resulted in evolution of CO_2 and CO. The results from pyrolysis and incineration study of PVC were similar to those of PET. Pyrolysis resulted in a three-step mass loss process leaving 8% residue. Incineration occurred with one additional mass loss step (total four steps), leaving negligible residue. During the first three mass loss steps of incineration, thermal decomposition products (Benzene, HCl, CO_2, and hydrocarbons which were the only products INpyrolysis) contributed significantly to evolved gases. The final mass loss during incineration eliminated any residue and resulted in evolution of primarily CO_2 and CO.

Discussion

The mass loss profiles HDPE during pyrolysis and incineration follow completely different patterns. The evolved gases during pyrolysis consist of thermal decomposition products such as saturated and unsaturated hydrocarbons. The evolved gases during incineration consist mainly of the oxidative products with small contributions from hydrocarbons. This may indicate that HDPE follows very different

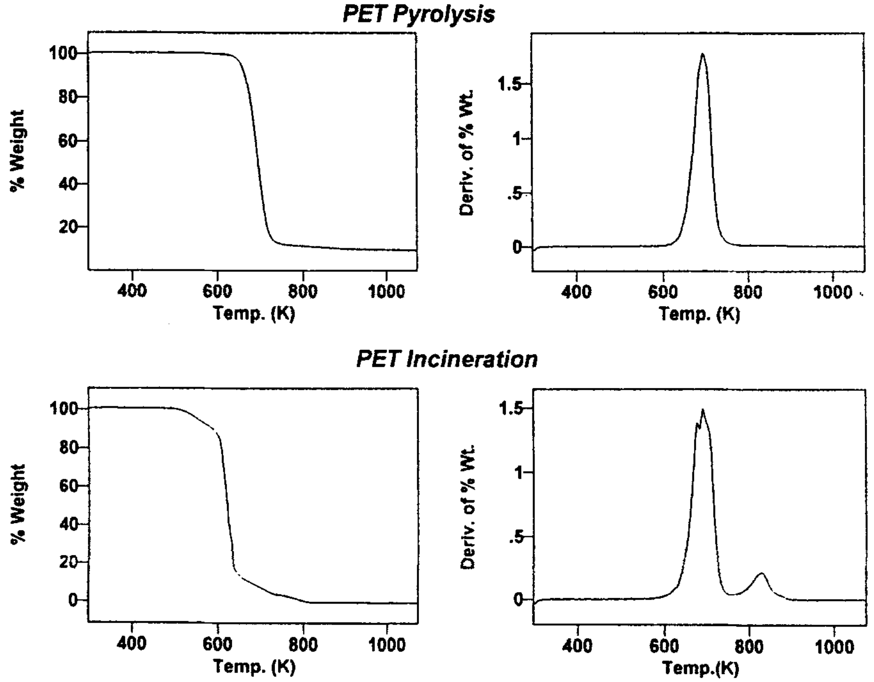

Fig. 3 Thermal degradation of PET under nitrogen (pyrolysis) (a), derivatized mass loss of PET during pyrolysis (b), thermal degradation of PET under air (incineration) (c), derivatized mass loss of PET during incineration (d)

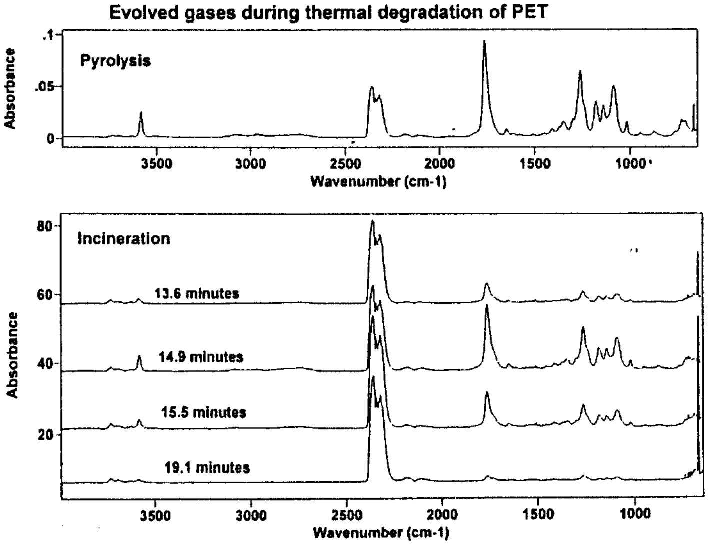

Fig. 4 IR spectrum of gases evolved during pyrolysis of PET (a), comparison of IR spectra of gases evolved during incineration of PET (b)

thermal degradation mechanisms depending on presence of oxidative atmosphere. Both pyrolysis and incineration of PS produced styrene. However, during incineration, oxygenated products seem to account for a large portion of mass loss.

For PVC and PET, the early parts of incineration produced significant amounts of products similar to that in pyrolysis The latter part of incineration produced CO_2 and CO, resulting from oxidation of products which were left behind as residue in pyrolysis.

In the plastics we studied, pyrolysis produced significant residue production for PET and PVC. In contrast, incineration studies virtually left no residue. Also, incineration typically accelerated the mass losses at lower temperatures. Therefore, as a means of disposal, incineration is probably more economically attractive.

Finally, both pyrolysis and incineration of PET produced aromatic acids as gaseous products, whereas PVC produced benzene, and HCl. This demonstrates that efforts to dispose solid plastics waste using these techniques would produce evolved gases which are hazardous and result in air pollution. Therefore, it is important to incorporate air pollution control devices at the disposal facilities.

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