

Combustion Kinetics and Emission Characteristics of Polycyclic Aromatic Hydrocarbons from Polylactic Acid Combustion

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ABSTRACT

This study investigates the combustion kinetics and emission factors of 16 U.S. Environmental Protection Agency priority polycyclic aromatic hydrocarbons (PAHs) in polylactic acid (PLA) combustion. Experimentally, two reactions are involved in the PLA combustion process that potentially result in the release of lactide, acetaldehyde, and *n*-hexaldehyde. The products may continuously be oxidized to form carbon dioxide (CO₂) and some PAHs produced because of incomplete combustion. The analytical results indicate that the emission factors for PAHs are in the range of not detectable to 98.04 μg/g. The emission factors are much lower than those of poly(ethylene terephthalate) (PET) and other combustion of plastics. Results from this work suggest that combustion is a good choice for waste PLA disposal.

IMPLICATIONS

PLA is one of the most attractive and useful biodegradable polyesters. Ideally, waste PLA is more suitable for recycling, composting, and landfilling than for incinerating; however, because of an increasing lack of landfill space, it is generally recycled with other plastics, resulting in plastic contamination, or it is collected along with municipal solid wastes and then incinerated. In the work presented here, it is confirmed that incineration with energy recovery is a good alternative to waste PLA disposal. Furthermore, the combustion kinetics of PLA provide essential information concerning reactor sizing and optimized operation conditions.

INTRODUCTION

Biodegradable polymers have environmental advantages over other nondegradable polymers. These include preservation of fossil-based raw materials, complete biological degradability, and reduction of carbon dioxide (CO₂) emissions to the atmosphere. For example, Vink et al.¹ proposed an application of life cycle assessment to polylactic acid (PLA) wherein they found that the reduction of greenhouse gas emission is approximately 3.5 kg CO₂ equivalents/kg PLA. PLA is a biodegradable, thermoplastic, and aliphatic polyester that is principally produced from starch saccharification, lactic acid fermentation, oligomerization, cyclic monomer, and ring-opening polymerization of the cyclic monomer.² It has been proven to be one of the most attractive and useful biodegradable polyesters.³ Similar to poly(ethylene terephthalate) (PET), PLA is resistant to fatty foods and dirty products, has an excellent flavor barrier, and exhibits good heat sealability.⁴ Thus, PLA has many applications including disposable cutlery, plates, cups, lids, and drinking straws; packaging bags and films; and containers for liquid foods.^{5,6} PLA is possibly the most commonly applied biodegradable polymer.⁷

It is estimated that 1300 t/month of PLA are used and need to be disposed of in Taiwan. Ideally, waste PLA is more suitable for recycling, composting, and landfilling than for incinerating; however, PLA is not a regulated recycling waste in Taiwan. PLA has an appearance similar to that of polyvinyl chloride (PVC) or polyolefins, and it is often recycled with other plastics, resulting in contamination of plastics and thus interfering with plastic recycling efforts. Many techniques (e.g., composting, landfill

disposal, incineration, low-level reutilization, and recycling) have been investigated for waste PLA disposal. Most studies of the degradation of PLA have focused on biodegradation in soil⁸ or compost⁹ and thermal degradation in nitrogen¹⁰⁻¹³; however, waste PLA is generally collected along with municipal solid waste and then incinerated. Thus, the thermal degradation behavior of PLA should be investigated. Cornelissen et al.⁷ studied the co-pyrolysis of PLA with biomass. Sivalingam et al.¹⁴ investigated the interaction between PLA and polycaprolactone (PCL) during pyrolytic degradation, wherein they proposed that the two polymers degrade independently of one another. Hideki et al.¹⁵ studied the thermal degradation of PLA in the presence and absence of residual zinc catalyst. The main volatile decomposition products from PLA pyrolysis include cyclic oligomers, lactide, and other gaseous products such as CO₂, acetaldehyde, ethenone, and carbon monoxide (CO).¹³

Incineration is a widely and successfully applied technique for municipal solid waste disposal. Waste combustion offers several advantages over other disposal techniques, including a reduction of waste mass and volume by more than 90%, the destruction of hazardous materials, and energy recovery; however, the key challenge in waste combustion is to effectively burn wastes while minimizing the emission of hazardous byproducts from incomplete combustion.¹⁴ Because the waste PLA is generally incinerated along with municipal solid wastes, the combustion of waste PLA should be investigated. In general, polycyclic aromatic hydrocarbons (PAHs) are produced in the combustion process and are of special interest because of their toxicity, carcinogenicity, and ubiquitous presence in the environment.¹⁶ PAHs are carcinogenic, making their identification and minimization imperative in the combustion process. The characteristics of PAHs from different sources (e.g., biomass burning,¹⁷ agricultural debris combustion,¹⁸ animal carcass incineration,¹⁹ domestic combustion,^{16,20} and plastic combustion²¹⁻²³) have been reported; however, to the best of the authors' knowledge, no studies have reported on the PAHs formed in the combustion of waste PLA. In addition, the combustion of waste PLA is not thoroughly understood. To better understand how to control and reduce PAH emissions in waste PLA combustion, the presence, concentration, and distribution of PAHs need to be identified. Thus, the objective of this paper is to study the emission factors of 16 U.S. Environmental Protection Agency (EPA) priority PAHs in PLA combustion. In addition, the combustion kinetics of PLA using a thermal gravimetric analyzer (TGA) were calculated.

EXPERIMENTAL PROCEDURES

Kinetics Analysis

PLA was purchased from Aldrich, Inc. and used without further purification. An elementary analyzer (Elementar vario EL III) determined the elemental analyses of the PLA. The PLA contained 49.8 wt % C, 5.6 wt % H, 44.4 wt % O, and 0.2 wt % N. In addition, there was no S or Cl detected. The high heating value of PLA was 4050 kcal/kg.

The preliminary combustion kinetics of PLA were investigated in a TGA (model SDT 2960 and Thermal Analyst 2000; TA Instruments) with temperatures and

sample weights recorded at 2-sec intervals. Approximately 14.3, 5.1, and 8.9 mg of the PLA sample was loaded onto the sample holder and then heated from 25 to 600 °C at heating rates of 5, 10, and 15 °C/min, respectively, at a high-purity air atmosphere flow rate of 100 mL/min. The gravimetric analysis was performed with a sensitivity of 0.1 ± 0.01 μg. At the same time, the computer recorded the thermogravimetry (TG) and differential thermal analysis (DTA) profiles. Aluminum oxide was used as a reference in all of the conducted TGA experiments.

The overall rate equation for the conversion x is expressed in the Arrhenius form as

$$\frac{dx}{dt} = A \cdot \exp\left\{-\frac{Ea}{R \cdot T}\right\} \cdot (1-x)^n \cdot [O_2]^m \quad (1)$$

where $x = \frac{W_0 - W}{W_0 - W_f}$ and t is time (min); A is a pre-exponential factor (1/min); Ea is the activation energy (kcal/mol); T is the temperature of reaction (°C); R is the universal gas constant (1.987 kcal/mol °C); $[O_2]$ is the oxygen concentration in the carrier gas; W is the mass of the sample at time t ; and W_0 and W_f are the initial and final masses of the sample, respectively. The kinetic parameters (i.e., the activation energy, pre-exponential constant, and reaction order) were calculated from TGA weight loss data at heating rates of 5, 10, and 15 °C min⁻¹ according to Friedman's method.^{24,25}

The natural logarithm of eq 1 gives

$$\begin{aligned} \ln\left[\frac{dx}{dt}\right] &= -\frac{Ea}{R \cdot T} + \ln\{A \cdot (1-x)^n \cdot [O_2]^m\} \\ &= -\frac{Ea}{R \cdot T} + (\ln A + m \ln[O_2]) + n \ln(1-x) \end{aligned} \quad (2)$$

For a fixed $[O_2]$ and x , a plot of $\ln(dx/dt)$ versus $1/T$ for various heating rates should yield a straight line, the slope of which is $-Ea/R$. For a given $[O_2]$, the activation energy can be obtained from the average value of the activation energy for a different x . For a given x , a plot of $[\ln(dx/dt) + Ea/RT]$ versus $\ln(1-x)$ for various heating rates should yield a straight line with slope n and intercept $(\ln A + m \ln[O_2])$. When $[O_2] = 0$, A is obtained. If oxygen is present, $(\ln A + m \ln[O_2])$ can be plotted against $\ln[O_2]$ to yield a straight line with slope m and intercept $\ln A$.

EXPERIMENTAL PROCEDURES

The PLA combustion experiments were conducted in a fixed bed reactor (SS 316 tube, inner diameter = 2.54 cm, and length = 45 cm). The schematic diagram in Figure 1 shows the laboratory setup for the PLA combustion experiments. Approximately 3 g of PLA was placed in a quartz container wherein they were positioned to the middle of the reactor. The sample was heated from room temperature to 450 °C. A K-type thermocouple was inserted to monitor the temperature profile where the reaction occurred. The combustion-supporting gas was high-purity air that passed through the reactor at a flow rate of 50 mL/min.

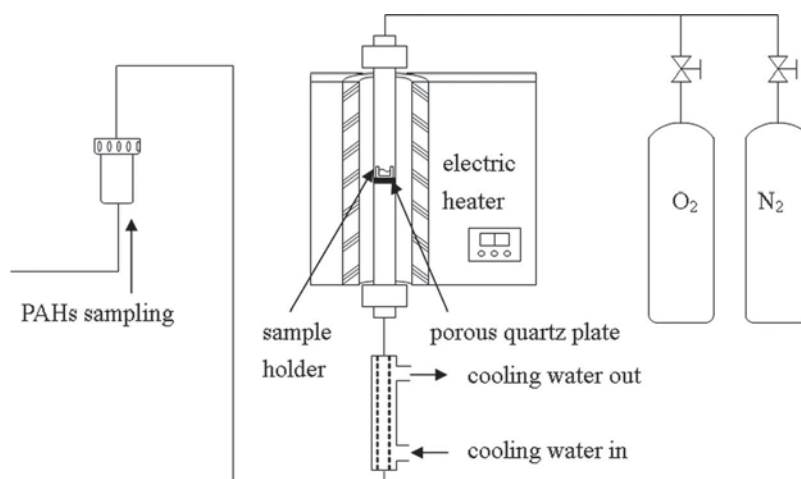


Figure 1. Schematic of the reaction apparatus.

TG-Mass Spectroscopy Analysis

TG-mass spectrometry (MS) experiments were conducted simultaneously using a TG (STA 409 CD; Netzsch Instruments, Inc.) and a quadrupole MS (QMA 400; Balzers Instruments, Inc.) system. A Skimmer Coupling System (Netzsch Instruments, Inc.) was used to combine these two instruments. Approximately 3 mg of PLA was combusted by TG, and the fragments and gas products were then introduced to the MS system to obtain evolution curves. The sample was heated from room temperature to 450 °C at a heating rate of 10 °C·min⁻¹ in 50-mL·min⁻¹ high-purity air.

PAHs Measurements

As shown in Figure 1, combustion product gases passed through a water cooler. Glass fiber filters (MF-Millipore; 0.45 μm) and XAD-2 resins (Supelco) were used for the adsorption of particulate- and gas-phase PAHs, respectively, at a temperature below 50 °C. Before the experiments, glass fiber filters and XAD-2 resins were precleaned by Soxhlet extraction for 24 hr in methylene chloride. After completion of the combustion run, filters and resins were removed and placed in separate glass bottles with Teflon-lined caps and stored at 5 °C. The filters and resins were placed in the precleaned Soxhlet apparatus again and extracted for 24 hr in methylene chloride. The extract liquid was subsequently concentrated to a volume of 1 mL using a high-purity nitrogen purge and transferred to a Teflon-sealed screw-cap vial for storage and analysis. The concentrations of PAH compounds were measured by gas chromatography (GC)/MS using a Shimadzu GC QP 2010 equipped with a Shimadzu MS QP 2010 mass selective detector. A GC was fitted with a DB-5 (30 m × 0.25 mm) column and helium gas was used as the carrier gas at a flow rate of 1.66 mL/min. PAHs were confirmed and quantified using the retention times and calibration curves from standard PAH solutions (Dr. Ehrenstorfer GmbH PAH-Mix 25). Analysis was conducted using a 1-μL injection and the following temperature program: injection port, 290 °C; transfer line, 250 °C; initial temperature, 70 °C; initial hold, 1 min; ramp rate, 15 °C min⁻¹; final temperature, 280 °C; and final hold, 15 min. The MS was operated in the selected ion monitoring (SIM) mode at an electron energy of 70 eV.

To ensure the purity of the XAD-2 resins and glass fiber filters, blanks of XAD-2 resins and glass fiber filters were also extracted and analyzed. No PAHs were detected in plain XAD-2 and glass fiber filter extracts. For the solution blank test, 250 mL of methylene chloride were concentrated to 1 mL, which was analyzed to ensure that there were no detectable PAHs in the used solvent. In addition, PAHs were also not detected from the sampling of reactor exhaust in the absence of PLA (combustion blank).

Recovery tests of PAHs for the XAD-2 resins and glass fiber filters were also conducted. The recoveries (in duplicate repetitions) of the 16 PAHs for the XAD-2 resins and glass fiber filters were 78.2–101.5% and 82.4–93.2%, respectively. Duplicate analysis was performed for assessing the reproducibility of the PAH analysis.

RESULTS AND DISCUSSION

TG Analysis

To develop a better understanding of PLA combustion, the oxidation behavior of fresh PLA was investigated. Figure 2 depicts the results of TGA-DTA analysis of PLA combustion. Experimentally, the TGA curves exhibited two phases, whereas the DTA curves demonstrated broad, small shoulders at approximately 300 °C and sharp, large peaks at 380–407 °C. The TGA curves suggested that the decomposition started at 200 °C and ended at 430–455 °C with no residue left. The derivative TG (DTG) curve indicates at least two reactions involved in the combustion process, possibly corresponding to the release of lactide and methyl ketene (CH₃CHCO), which were then oxidized to CO₂.

The heating rate is an important factor that affects TGA results, because a higher heating rate may decrease the heat distribution in the investigated PLA samples and make the decomposition start at higher temperature. Thus, the shape of the TG curves, the initial decomposition temperature, and the temperature for a given weight loss increase with increasing heating rate (shown in Figure 2a).

KINETICS ANALYSIS

Because the DTG curve indicates that two reactions are involved in PLA combustion, the rate equations can be expressed as

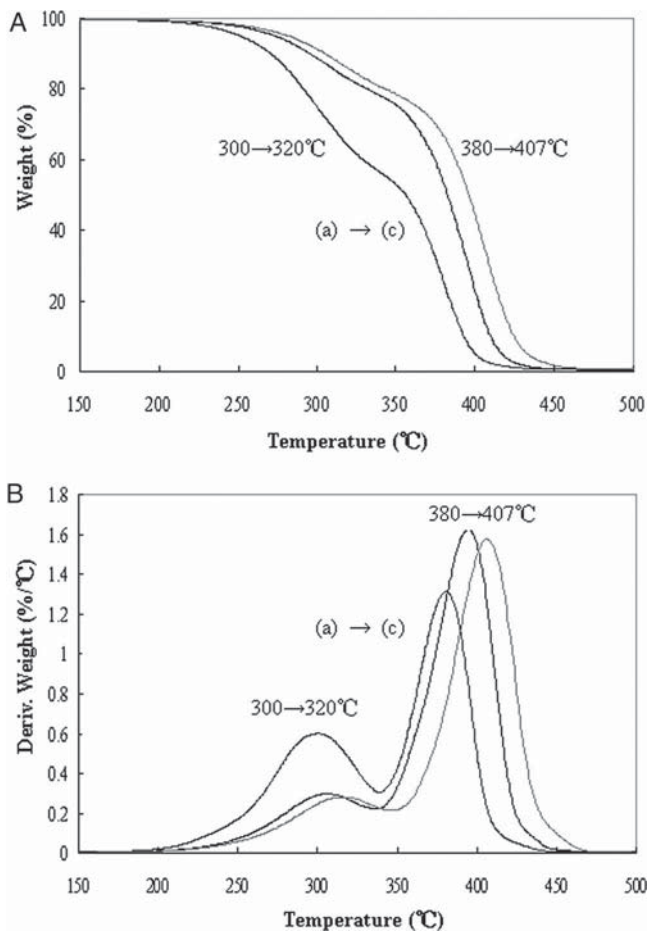


Figure 2. The TGA (A) and DTA (B) curve of PLA combustion at a heating rate of (a) 5, (b) 10, and (c) 15 K/min, respectively, in flowing high-purity air 100-mL/min.

$$\frac{dx_1}{dt} = 9.4 \times 10^6 \cdot \exp\left\{-\frac{-15.2}{8.314 \times 10^{-3} \cdot T}\right\} \cdot (1 - x_1)^{2.99} \cdot [O_2]^{-2.12} \quad (3)$$

$$\frac{dx_2}{dt} = 6.4 \times 10^{13} \cdot \exp\left\{-\frac{-22.5}{8.314 \times 10^{-3} \cdot T}\right\} \cdot (1 - x_2)^{2.79} \cdot [O_2]^{-2.08} \quad (4)$$

where x is the conversion of PLA, T is the combustion temperature ($^{\circ}\text{C}$), and t is the combustion time (min). Here, subscripts 1 and 2 denote the first and the second reactions, respectively. Approximately 15–33% of the total mass is lost at the end of the first reaction, with the remainder being combusted in the second reaction. In Table 1, the activation energies are 15.2 and 22.5 kcal/mol for the first- and second-stage reactions, respectively. The reaction order is not substantially altered for the first and second reactions. Table 1 also suggests the amount of oxygen that would decrease the activation energy and enhance the reaction rate. It is noted that the complete rate equation for the two stages of reaction can be calculated by summing the individual weighted rate equations according to

Table 1. Kinetic parameters for the combustion of PLA and a comparison of the activation energy of PLA combustion in this work to those of PLA pyrolysis from other studies.^{11–13}

	<i>E_a</i> (Kcal/mol)	<i>n</i>	<i>A</i> (L/min)	<i>m</i>
Oxidation (first stage)	15.2	2.99	9.4×10^6	-2.12
Oxidation (second stage)	22.5	2.79	6.4×10^{13}	-2.08
Thermal degradation	28.5 ¹¹			
Thermal degradation	26.3 ¹²			
Thermal degradation	19.1–38.2 ¹³			

$$\frac{dx}{dt} = x_c \cdot \frac{dx_1}{dt} + (1 - x_c) \cdot \frac{dx_2}{dt} \quad (5)$$

In eq 5, x_c is the fraction conversion factor at the end of the first reaction and can be obtained from the average value of the TG or DTG curve for different heating rates. The combustion process may be affected by several factors, including molecular weight, stereoregularity, the presence of additives, and experimental conditions such as heating rate and atmosphere. Table 1 compares the activation energy of PLA combustion in this work to that of PLA pyrolysis from the literature. As expected, lower activation energy was obtained for PLA combustion as compared with that for PLA pyrolysis. Generally, a fundamental understanding of the reaction kinetics and thermal properties of the combustion reaction is essential for advancement in the development of technically and economically feasible systems. The conversion and reaction times are the significant engineering design information used in sizing the reactor and optimizing the operation conditions. On the other hand, the combustion temperature is the key factor for determining the desired product distribution.

Three regions can be identified in the Arrhenius plots of PLA combustion depicted in Figure 3. For region I, at low temperatures nearly straight lines of the reaction rate can be observed. The combustion rate increases with increased heating rate and temperature. For region II, at higher temperatures all plots show a straight-line profile with parallel lines. The combustion rates increase with increasing temperature. For region III, at high temperatures the Arrhenius plots depart from the straight-line

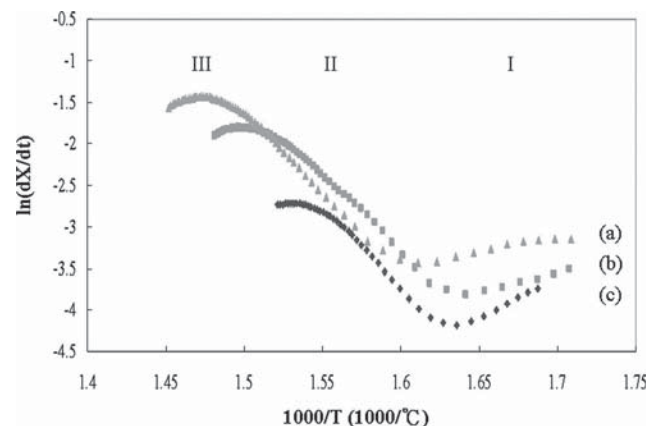


Figure 3. The Arrhenius plots of PLA combustion at heating rates of (a) 5, (b) 10, and (c) 15 K/min, respectively, in a 100-mL/min flow of high-purity air.

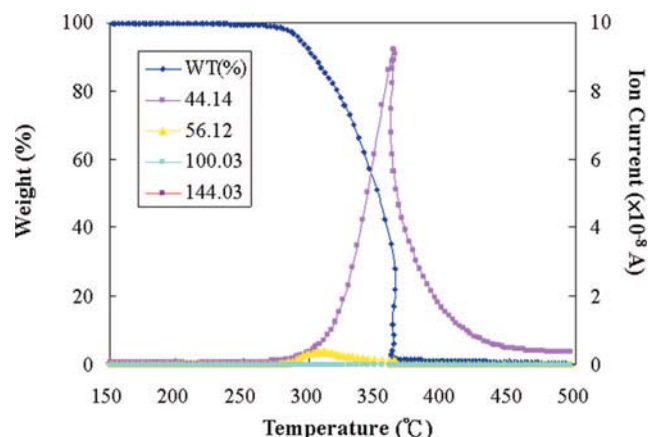


Figure 4. MS intensity curves of $m/z = 44, 56, 100,$ and 144 for PLA combustion.

shape, whereas the combustion rate is observed to decay with increasing temperature. A parallel shift to lower temperatures can be observed in the Arrhenius plots, as shown in Figure 3. This is consistent with an n th order kinetic model ($n > 1$) that is equivalent to a Gaussian distribution of reactivity.²⁶ This suggests that the heating rate affects the combustion rate at the same time as the intrinsic kinetics of bond dissociation.²⁷

TG-MS Analysis

The following m/z ratio (mass-to-charge ratio) analyses were obtained from online TG-MS to better understand the combustion mechanisms of PLA: 44, 56, 100, and 144. The temperature series of selected MS fragments are shown in Figure 4. Peaks at $m/z = 56, 100,$ and 144 represent acetaldehyde, n -hexaldehyde, and lactide, respectively. It is obvious that only small amounts of n -hexaldehyde and lactide are produced in the combustion process. Because the main component of PLA is lactic acid, it is reasonably expected that acetaldehyde, n -hexaldehyde, and lactide would be produced in the combustion process. These fragments may be produced from C–C or C = C bond cleavage of the long carbon chain of PLA, depending on the numbers and locations of the C = C double bonds of the original PLA. As expected, in addition to hydrocarbon fragments, the temperature series of CO₂ ($m/z = 44$) can also be observed in Figure 4. An increase in the combustion temperature leads to an increase in CO₂ at less than 350 °C; however, because the TG-MS experiments were conducted under an air atmosphere, the m/z ratio of CO was unable to be tracked.

In addition, PAHs are generally produced from the combustion process. However, it is worth noting that no PAHs were observed by TG-MS. The TG-MS information may be helpful for understanding the combustion mechanisms of PLA and the potential byproducts; however, the concentrations and emission factors cannot be determined by TG-MS analysis.

PAHs Analysis Results

PAH emission from PLA combustion was also investigated on a fixed-bed reactor. PLA was completely combusted at approximately 450 °C; hence, PAH emissions from the PLA combustion experiment were conducted

at 450 °C for 10 min. In addition, the sampling geometry had the potential to cause sampling artifacts, including “blow-off” and “blow-on.” The particulate-phase PAHs that affect the filter are blown off by the air passing the filter and then are captured in the resin. The gas-phase PAHs that adsorbed on the filter or on accumulated particulate and/or organic matter on the surface of the filter are blown on.²⁸ These would result in bias of the PAH measurements. Thus, the PAHs in the particulate and gas phases are summed to “total PAHs” in this study. Emission factors are expressed as the mass of PAHs emitted per gram of PLA combustion. According to their molecular weight, PAH contents were also classified into three categories, including low molecular weight PAHs (LM-PAHs; containing two- to three-ring PAHs), middle molecular weight PAHs (MM-PAHs; containing four-ring PAHs), and high molecular weight PAHs (HM-PAHs; containing five- to six-ring PAHs). In addition, the carcinogenic potency of a given PAH compound can be expressed in terms of its benz[*a*]pyrene equivalent concentration (BaP_{eq}). The toxic equivalent factor (TEF) for a given PAH compound has been proposed by Nisbet and LaGoy.²⁹ As shown in Table 2, the emission factors for 16 PAHs were nondetectable to 94.08 μg/g. The total PAH emissions for the sum of 16 species were 121.06 μg/g. Table 2 also shows the trend of LM-PAHs > MM-PAHs > HM-PAHs in the PLA combustion process. Clearly, naphthalene was the most dominant species in the PLA combustion. This is because naphthalene has the lowest boiling point and the highest stability of the 16 PAHs. It is known that a higher molecular weight corresponds to a higher carcinogenic potency. Because the naphthalene has been observed to constitute a major share of the

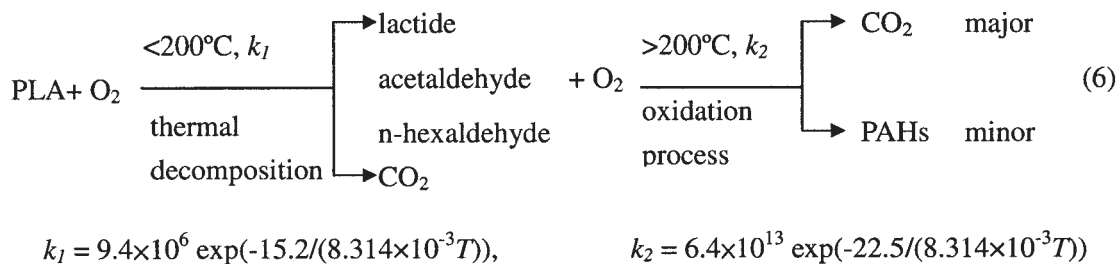
Table 2. The emission factors for 16 EPA priority PAHs from PLA, used polyester fabrics,³⁰ and PE bag³¹ combustion.

PAH Compound	Total PAHs ^a	Total PAHs ^b	PPAHs ^c
Naphthalene	98.04	—	—
Acenaphthylene	1.55	1320	—
Acenaphthene	0.75	—	1.1
Fluorene	2.04	1240	—
Phenanthrene	9.79	—	19.8
Anthracene	1.03	260	—
Fluoranthene	3.08	480	17.3
Pyrene	1.92	230	10.4
Benz[<i>a</i>]anthracene	0.17	110	—
Chrysene	0.31	440	62.8
Benz[<i>b</i>]fluoranthene	0.17	320	—
Benz[<i>k</i>]fluoranthene	0.58	90	—
Benz[<i>a</i>]pyrene	0.38	60	42.9
Indeo[1,2,3- <i>cd</i>]pyrene	0.25	40	—
Dibenz[<i>a,h</i>]anthracene	0.85	50	—
Benz[<i>ghi</i>]perylene	0.17	30	90.3
total-PAHs	121.06	4670	244.6
LM-PAHs	113.20	2820	20.9
MM-PAHs	5.47	1260	90.5
HM-PAHs	2.39	590	133.2
total BaP _{eq}	1.48	176.57	44.5

Notes: ^aIndicates total PAHs detected in this study; ^bIndicates total PAHs detected from used polyester fabric combustion at 850 °C³⁰; ^cIndicates particulate-phase PAHs detected from open burn of PE bags.³¹ — = not detected in the literature studies; PPAHs = particulate-phase PAHs.

total PAHs, it is reasonable that the total BaP_{eq} content for PAHs is very low.

It should be noted that the contents of the feedstock are one of the major factors affecting the emission of PAHs from the combustion process. For example, in this study, the total PAH emissions (121.06 µg/g) from PLA combustion were significantly lower than that of used polyester fabric combustion (4670 µg/g) at 450 °C³⁰ or PE bags from open burning (244.6 µg/g).³¹ PLA combustion emitted significantly lower carcinogenic PAHs compared with other plastics, such as polystyrene (PS), polyethylene (PE), and PVC combustion.³²



CONCLUSIONS

The level of PAH emissions from the combustion of PLA was determined. Additionally, the fragments and gas compositions of the combustion process were also investigated by online TG-MS. The temperature series of four fragments were analyzed in air, including *m/z* ratios of 44, 56, 100, and 144. The fragment at an *m/z* of 44 is CO₂. The fragments at *m/z* ratios of 56, 100, and 144 represent acetaldehyde, *n*-hexaldehyde, and lactide, respectively, all of which may be fragments of PLA. The TG-MS analysis above can offer a better understanding of the mechanisms of byproduct formation in PLA combustion.

The combustion of PLA in two stages was observed in the combustion process by TGA. The kinetic data may provide essential information about reactor sizing and operation condition optimization.

The amount and distribution of PAHs emitted from the PLA combustion process have been proposed. The amounts of PAHs emitted from PLA combustion are significantly lower than those associated with combustion of other plastics. In addition, PLA can be combusted with no remaining residue. These results suggest that incineration is a suitable approach for the environmentally friendly disposal of waste PLA.

ACKNOWLEDGMENTS

The authors acknowledge the financial support of the Taiwan National Science Council and the help provided by Professors Soo-Fin Cheng and Chung-Shen Kao of Taiwan University in the TG-MS analysis.

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Summarizing the TGA, TG/MS, and PAHs data, eq 6 describes the combustion of PLA. The decomposition of PLA occurs in the early stage of the combustion process (at <200 °C). The PLA molecules may be partially cracked by chain scission to smaller molecules or unstable fragments. These molecules and fragments might be highly reactive free radicals with a very short lifetime that are oxidized by air to form CO₂ (major) or recombined to form more stable PAHs (minor). These PAHs may exist in particulate or gas phases depending on the reaction temperature and their molecular weight.

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