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Exploratory study on the pyrolysis and PAH emissions of polylactic acid

Yi-Chi Chien [a,*], Chenju Liang [b], Shu-hua Yang [a]

[a] Department of Environmental Engineering and Science, Fooyin University, Kaohsiung Hsien, Taiwan, ROC
[b] Department of Environmental Engineering, National Chung Hsing University, 250 Kuo-kuang Road, Taichung 402, Taiwan, ROC

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ABSTRACT

The emission factors for 16 U.S. EPA priority polycyclic aromatic hydrocarbons (PAHs) from the polylactic acid (PLA) pyrolysis and the decomposition mechanism were investigated in this study. The fragments and gas compositions using on-line thermogravimetry-mass spectrometry (TG-MS) were determined. A temperature series of 7 fragments was analyzed in helium, and was found to include: $m/z = 16$, which may represent methane; 28, which may be carbon monoxide; 44, which may be acetaldehyde; 56, which may be methylketene, 144, which may be oligomers of lactide. In addition, there are little amount of 100, and 200 which are oligomers of lactides observed in the pyrolysis of PLA. The pyrolysis of PLA is a non-radical, backbiting ester interchange reaction involving the OH chain ends. Depending on the size of the cyclic transition state, the product can be a lactide molecule, an oligomeric ring with more than two repeat units, methylketene, or acetaldehyde. Carbon monoxide and methane are contributions from the decomposition of acetaldehyde.

Experimentally, not detected (n.d.)-40.47 μg of 16 PAH emissions were determined from per gram of PLA pyrolysis. The PAH profiles showed a predominance of naphthalene (58.9%), phenanthrene (12.5%), and fluoranthene (5.9%). The total PAH emissions for PLA pyrolysis is significantly lower than the values associated with PLA combustion. From the viewpoint of air pollution control, this result suggests that pyrolysis seems a better alternative than combustion for the disposal of waste PLA. Also, since pyrolysis is the first step for an incineration process, these results can provide important information on the control of PAHs formation for a commercialized incinerator.

1. Introduction

Biodegradable polymers such as polylactic acid (PLA) have environmental advantages including preservation of fossil-based raw materials, complete biological degradability, and reduction of CO_2 emissions to the atmosphere over other nonbiodegradable polymers. For example, Vink et al. (2003) have conducted a life cycle assessment of PLA and found the reduction of approximately 3.5 kg CO_2 emission per kg PLA usage. To move toward the sustainable society, renewable resources need to be used more effectively. Thus, the production and usage of biodegradable polymers are increasing very fast.

PLA is produced principally from microbial fermentation of sugar feedstock (Garlotta, 2002). PLA has an excellent flavor barrier, and exhibits good heat sealability and resistant to fatty foods (Copient et al., 2004). Thus, PLA is well known as typical biodegradable polymer in practical applications such as disposable cutlery, plates, cups, lids, and drinking straws, packaging bags and films, and containers for liquid foods (Conn et al., 1995). It has been considered as one of the most attractive and useful biodegradable polymer (Kricheldorf, 2001). It is estimated that 1300 tons per month of PLA are used and need to be disposed of in Taiwan. Many techniques such as composting, landfill disposal, incineration, and recycling, have been investigated for waste PLA disposal. However, PLA is not a regulated recycling waste in Taiwan. It has an appearance similar to that of PVC or polyolefins, and it is possibly recycled with other plastics, resulting in contamination of plastics and thus interfering with plastic recycling efforts. It seems that it is more suitable for disposal rather than recycling for waste PLA.

In many studies, kinetics and the products of PLA pyrolysis have been investigated. For example, the Ea value (activation energy) for pyrolysis of PLA in 250–300 °C at a certain fractional weight ratio was 141–176 kJ/mol calculated using Doyle's and Reich's methods (Omura et al., 2006). Aoyagi et al. reported that the Ea of PLA pyrolysis is 80–160 kJ/mol. The Ea decreases with weight loss at initial stage of degradation and then increases remarkably with progress of degradation. The drastic change in the Ea revealed that the reaction mechanism changes with

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[*] Corresponding author. Tel.: +886 7 783 0542; fax: +886 7 782 1221.
E-mail address: PL036@mail.fy.edu.tw (Y.-C. Chien).

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temperature and conversion. In addition, the main volatile decomposition products from PLA pyrolysis include cyclic oligomers, lactide, and other gaseous products, such as carbon dioxide, acetaldehyde, ketene, and carbon monoxide were also determined (Aoyagi et al., 2002). However, the decomposition mechanism of PLA pyrolysis is not well understood.

In recent years, thermal analysis tools such as thermogravimetry (TG) and differential scanning calorimetry (DSC) are becoming important in offering valuable information in terms of kinetic parameters, decomposition mechanism and thermal stability etc (Petrović and Zavargo, 1986; Chihiro et al., 2003; Chien et al., 2005). Continuous real-time information regarding the weight loss and decomposition products can be obtained by coupling a mass spectrometry to the thermogravimetry (TG-MS). It also can offer more detailed information for the decomposition of hydrocarbon compounds by identifying fragments ions from the original compounds with temperature changing (Éhen et al., 2004).

Pyrolysis of organic wastes can recover high-value petrochemical or fuel feedstocks that has been used an effective resource recovery alternatives. Cornelissen et al. (2008) have investigated that the pyrolysis of PLA can produce 40.6% of bio-oil, 1.5% of char and 57.9% of gases. The PLA contained 49.8 wt% of C, 5.6 wt% of H, 44.4 wt% of O, and 0.2 wt% of N. In addition, there was no sulfur and chlorine detected. The high heating value of the PLA was 4050 kcal/kg. It has a high potential energy content that makes it suitable for thermal processes. It seems that pyrolysis of waste PLA may be economically and environmentally attractive. However, in general, PAHs are produced in the thermal process and are of special interest because of their toxicity, carcinogenicity, and ubiquitous presence in the environment (Oanh et al., 1999). Since, PAHs are undesirable air pollutants, making their identification and minimization in the thermal process is imperative. The characteristics of PAHs from different sources including biomass burning (Jenkins et al., 1996), agricultural debris combustion (Kakareka and Kukharchyk, 2003), animal carcass incineration (Chen et al., 2003), and plastic combustion (Wheatley et al., 1993; Li et al., 1995; Durlak and Biswas, 1998; Wang et al., 2001) have been reported; however, to the best of our knowledge, no studies have reported on the PAHs formed in the pyrolysis of waste PLA. Since pyrolysis may offer an alternative waste treatment option. Furthermore, in order to better understand how to control and reduce PAH emissions in waste PLA pyrolysis, 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 US EPA priority PAHs in PLA pyrolysis. In addition, the decomposition mechanism of PLA pyrolysis was also investigated by TG-MS.

2. Experiment

2.1. Experimental procedure

PLA (ALDRICH Inc.) was used without further purification in the experiments. The PLA pyrolysis experiments were conducted in a fixed bed reactor (SS 316 tube, ID = 2.54 cm, and L = 45 cm). The diagram of experiment setup was reported elsewhere (Chien and Shih, 2006). About 3 grams of PLA was placed in a quartz container, wherein they were positioned to the middle of the reactor that heated from room temperature to 450 °C at a N_2 flow rate of 50 mL/min. The product gases of PLA pyrolysis 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 at a temperature below 50 °C, respectively, before emission.

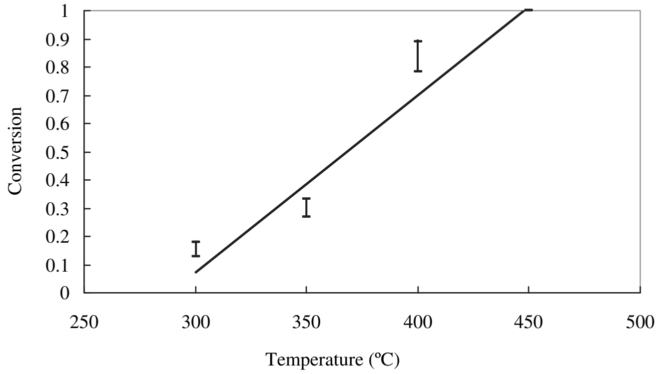

Fig. 1. Effect of temperature on the conversion of the pyrolysis for PLA in the fixed-bed reaction system.

2.2. Thermogravimetry-mass spectroscopy (TG-MS) analysis

TG-MS experiments were conducted using a TG (STA 409 CD, Netzsch Instruments, Inc.) and a quadrupole mass spectroscopy (QMA 400, Balzers Instruments, Inc.) system simultaneously. A Skimmer Coupling System (Netzsch Instruments, Inc.) was used to combine these two instruments. Approximately 3.0 mg of PLA was heated from room temperature to 450 °C at a heating rate of 10 °C min^{-1} in 50 mL min^{-1} high-purity helium by TG, and the fragments and gas products were then introduced to the mass spectroscopy to obtain evolution curves.

2.3. PAHs measurements

The concentrations of the following PAHs were determined: naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (Acp), fluorine (Flu), phenanthrene (PA), anthracene (Ant), fluoranthene (FL), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (CHR), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), Indeo[1,2,3,-*cd*]pyrne (IND), Dibenz[*a,h*]anthracene (DBA), Benezo[*ghi*]perylene (BghiP). Glass fiber filters and XAD-2 resins were used for the adsorption of particulate and gas phase PAHs, respectively. Glass fiber filters and XAD-2 resins were precleaned by Soxhlet extraction for 24 h in methylene chloride prior to the

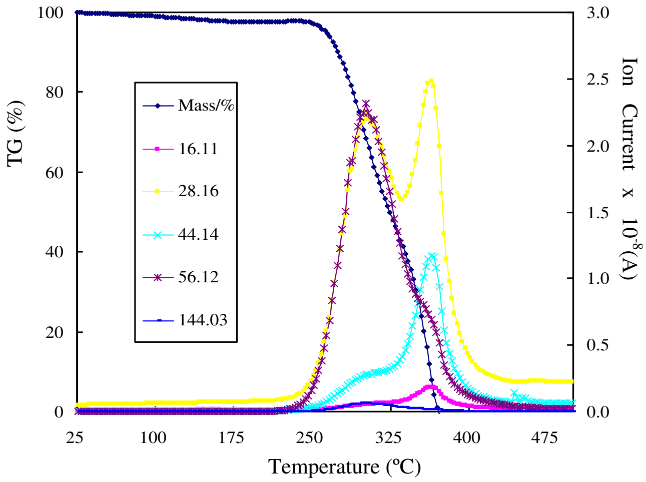

Fig. 2. Mass spectroscopy intensity curves of $m/z = 16$, 44, 56, 100, 132, 144, and 200 from PLA pyrolysis.