Journal of Analytical and Applied Pyrolysis 105 (2014) 14–22

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Characterisation of gas evolution and char structural change during pyrolysis of waste CDs

Ravindra Rajarao*, Irshad Mansuri, Renu Dhunna, Rita Khanna, Veena Sahajwalla

Centre for Sustainable Materials Research and Technology (SMaRT), School of Materials Science and Engineering, University of New South Wales, Sydney, NSW 2052, Australia

ARTICLE INFO

Article history:
Received 10 August 2013
Accepted 26 September 2013
Available online 18 October 2013

Keywords:
Waste compact disc
Pyrolysis
Gas evolution
Char characteristics
TG-FTIR
TG-GCMS

ABSTRACT

The purpose of this study is to determine the characteristics of gas evolution and char structural change during pyrolysis of waste compact disc (CD). A combination of Thermogravimtetry-Fourier Transform Infrared spectroscopy (TG-FTIR) and Thermogravimtetry-Gas Chromatography/Mass Spectrometry (TG-GCMS) techniques are employed for this study. The thermal characteristics, temperature trend of evolving gas species and gas characteristics are investigated by TG-FTIR and TG-GCMS techniques. From the results, the waste CD degradation is divided into three stages (a) main gaseous compounds in first stage (<500 °C) are CO_2, CO, CH_4 and H_2O (b) organic species including aromatic hydrocarbons, phenols and its derivatives are evolved between 500 and 600 °C. (c) Temperature above 600 °C, carbonisation and char formation occurred. The char chemical structure and physical characteristics are investigated by Scanning Electron Microscopy, FTIR spectroscopy, Raman spectroscopy and X-ray diffraction techniques. This fundamental study provides basic insight of waste CD pyrolysis and also indicates that very high valuable carbon product (90% carbon in residue) with good crystallinity is achievable.

1. Introduction

In early 1980s, the Philips and Sony industries collaboratively introduced the compact disc's (CDs) to the world. Since then, the demand for discs and their uses have expanded into the fields of text, motion pictures, data storage and programming. The worldwide production of CDs was 400 million in 1991 [1] and has increased significantly in recent years. In 2003, 12 billion units of CDs and Digital Versatile Discs (DVDs) were produced for audio, video and data storage around the world [2]. Each year millions of waste CDs and DVDs are dumped in landfills and it has become serious environmental issue due to increased usage in daily life and improper method of disposal. CDs are largely rich with polycarbonate polymer with 55–70 nm thick metal coating. Polycarbonate (PC) is a commercially important engineering thermoplastic, that possess several distinct properties including transparency, dimensional stability, flame resistance, high heat distortion temperature, high impact strength and moisture insensitivity, and can maintain rigidity up to 140 °C and decomposition starts above 350 °C [3–5]. Bisphenol A is a monomer used in the production of polycarbonate, which is endocrine disruptor and has adverse effect on human health [6,7], and United States Food and Development Authority (USFDA) has banned the use of Bisphenol derived products in baby bottles and cups [8]. Various recycling technologies such as physical, chemical and pyrolytic processes have been adopted by the previous researchers to treat waste CDs due to its complexity [9–11]. Among these methods, pyrolysis has been recognised as a promising process because during pyrolysis, waste CD is decomposed to gases and carbon residue, which can be used as fuels or chemical feedstock. The pyrolysis of polycarbonate yields 10–25% solid residue which includes value added materials such as potential carbon black and activated carbon [12,13]. Recently, Mansuri and Sahajwalla used PC char as carburiser material in alloy making [14] and also Linan et al. used PC char as carbon adsorbent in methane and hydrogen storage applications [13]. In this aspect, it is very significant to study the thermal degradation and gas evolved characteristics of waste CDs for both the design and the operation of waste CDs thermal treatment facility.

Thermogravimetric analysis (TGA) is a well-established and widely used technique in which the mass of a sample is monitored as a function of temperature or time. Pyrolysis TGA involves the thermal degradation of the sample in an inert atmosphere with uniform heating rate and simultaneous recording the mass loss of a sample with temperature. TGA is inherently quantitative, and therefore an extremely powerful thermal technique, but gives no direct information of chemical or evolved species during thermal degradation. To understand the thermal decomposition process, the information of gas evolved is very important. Thus hyphenated thermal analytical technique has attracted significant

* Corresponding author. Tel.: +61 2 9385 9934; fax: +61 2 9385 4292.
E-mail address: r.rajarao@unsw.edu.au (R. Rajarao).

0165-2370/$ – see front matter
http://dx.doi.org/10.1016/j.jaap.2013.09.014

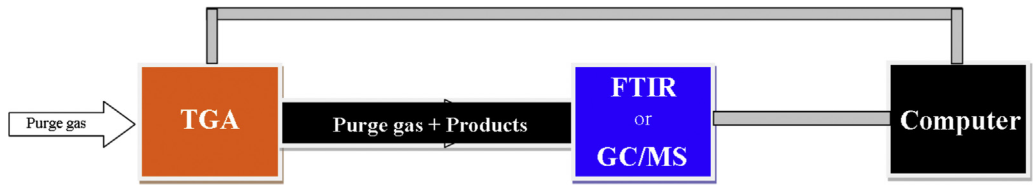

Fig. 1. Illustration of TGA-FTIR and TGA-GC/MS experimental system.

attention to extract information of evolved gas species to study the characteristics of pyrolysis. Thermogravimetric analyser coupled with Fourier transform infrared spectrometer (TGA-FTIR) is a valuable technique to determine continuously both the mass loss and the volatile species evolved during pyrolysis of materials in a TGA furnace. Due to the advantage of real-time gas analysis, the hyphenated technology of TGA-FTIR has been used to analyse the products from the pyrolysis of waste glass substrate, pine saw waste, poplar wood [15–17], etc. During thermal decomposition, many organic products will be released at the same time. So in order to separate and identify various molecules, an advanced hyphenated technique, Thermogravimetric analyser coupled with gas chromatography/mass spectrometry (TGA-GC/MS) is used. TGA-GC/MS has been used due to its high sensitive, rapid, effective separation and detect very low levels of material in complex mixtures; hence it is used to evaluate the mechanism of degradation of polymers. The combination of TGA-FTIR and TGA-GC/MS gives the real time analysis and in detail characterisation of gas molecules evolved during pyrolysis [18], which is beneficial in understanding thermal degradation characteristics. In addition to the study of gas evolution during pyrolysis, chars are used as fuels, carburiser material, hydrogen storage material, mixed with water or oil to form slurries to give more useful and valuable chemical products, etc. [19]. Therefore it is very significant to determine the evolution of char structural features during pyrolysis of waste CD.

In this present study, the combined TGA-FTIR and TGA-GC/MS techniques are employed for the first time to study the gas evolution during pyrolysis of waste CD. The weight loss of waste CD is measured in TGA, and evolved gases were detected by FTIR. In addition, TGA-GC/MS analysis is performed to separate and identify the major volatile products produced during pyrolysis of waste CD. The information obtained is used to interpret the possible mechanism of thermal decomposition of waste CD. Furthermore, the evolution of char structural features during pyrolysis of waste CD was also investigated by Scanning Electron microscope (SEM), X-ray diffraction (XRD), Raman and FTIR spectroscopy techniques.

2. Experimental

2.1. Materials

The material used is a typical waste CDs. Prior to experiments, the sample was dried in an oven at 105 °C for 3 h, the CD materials were crushed and pulverised before they were analysed.

2.2. Composition analysis of waste CDs

The polymer composition in waste CD was identified by FTIR spectroscopy. The FTIR measurement was carried out with Spectrum 100 PerkinElmer and also compared to virgin material to verify the attribution of FTIR peaks. The X-ray fluorescence spectrometry measurements were performed on a PANalytical PW2400 Sequential Wavelength Dispersive X-ray fluorescence spectrometry (WDXRF) to find out various elements in waste CDs.

2.3. Study of gas evolution during pyrolysis

2.3.1. TGA-FTIR technique

The real time analysis of gas evolved during pyrolysis of waste CDs was performed using PerkinElmer TGA-FTIR system, which consists of Thermogravimetric analyser (STA 6000) coupled to a FTIR spectrophotometer (Spectrum 100). In this study, approximately 10 mg of sample is heated from 50 °C to 1000 °C at a rate of 40 °C/min in a dry nitrogen atmosphere. The flow rate of nitrogen into the cell for TGA/IR experiments was approximately 60 mL/min. The heated lines were maintained at 250 °C to prevent the condensation of the produced gases. IR spectra were recorded in the spectral range of 4000–450 cm^{-1} with a 4 cm^{-1} resolution.

2.3.2. TGA-GC/MS technique

Thermogravimetric analyser (Pyris 1, TGA) coupled with gas chromatography/mass spectrometry (Clarus 600, GC/MS) was used to analyse evolved gas during pyrolysis of waste CD. Sample on heating by TGA released volatile materials, which were transferred to GC by heat transfer line maintained at 250 °C. In GC, components were collected on a trapping media and deposited on the head of a column. The sample was run by GC to separate the gas molecules, and the peaks were identified by the MS system. Helium was used as carrier gas for at constant flow of 1.0 mL/min. The mass detector identified the characteristic fragment ion intensity of the volatiles according to their respective mass to charge ratios. The decomposition products were identified by means of the comparison between the experimental mass spectrum and the mass spectrum library attached to GC/MS system. Fig. 1 illustrates the experimental system for both TGA-FTIR and TGA-GC/MS.

2.4. Study of char structural change

2.4.1. SEM

Scanning electron microscopy (SEM) is often used to describe the physical structure of char. A coating of Au film was applied to the sample using a Cressington 208 HR Sputter Coater. The coated samples were then examined and imaged using a Topcon SM720 Field Emission Scanning Electron Microscope.

2.4.2. FTIR technique

Chars were mixed with KBr in a mass ratio of 1:100, and then the samples were compressed into films and scanned by a Fourier transform infrared spectroscopy (FTIR, Spectrum 100, PerkinElmer) in wavenumber range of 4000–500 cm^{-1} to analyse the functional groups in chars.

2.4.3. XRD technique

The crystalline components of the char were determined by X-ray diffraction. The samples were analysed in a PANalytical X'Pert Pro multipurpose X-ray diffractometer operating at 40 kV and 40 mA. Measurements were recorded from a start angle $2\theta = 10°$ to an end angle of 80°.