



Pyrolysis study of waste phenolic fibre-reinforced plastic by thermogravimetry/Fourier transform infrared/mass spectrometry analysis



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ABSTRACT

Pyrolysis is considered to be a promising method to dispose waste plastics by thermal cracking into chemicals. Previous studies focus on pyrolysis recycling of waste thermoplastics. The pyrolysis of waste thermosetting plastics, which may be different from that of waste thermoplastics, receives little attention. In order to provide guidance for reactor design and thermo-chemical process management for the pyrolysis recycling of waste thermosetting plastics, the pyrolysis kinetics, volatile products and reaction mechanisms of one typical waste thermosetting plastics namely phenolic fibre-reinforced plastic (phenolic FRP) are studied in the present study. Thermogravimetric analysis (TGA), in situ Fourier transform infrared (FTIR) and online TGA-FTIR-mass spectra (MS) analyses are employed. Results indicate that the pyrolysis of waste phenolic FRP in inert atmosphere may be divided into two stages with the threshold conversion rate of 0.2. The average values of activation energy in the first, second and whole pyrolysis process were 174.66 kJ/mol, 233.62 kJ/mol and 223.22 kJ/mol, respectively. The crosslinking between phenol derivatives and breakage of branched chain may result in the occurrence of the first stage, while the occurrence of the second stage may be due to the breakage of chain backbone and oxidation of methylene and hydroxymethyl. Four kinds of gases including H₂O, alcohols, aliphatic compounds and carboxylic acids mainly constitute the volatile products in the first stage. The volatile products in the second stage mainly consist of CO, CO₂, carboxylic acids and aromatic compounds. The amount of the volatile products in the second stage is much larger than that in the first stage. The maximum amount of these seven gases in the order of most to least is CO₂ > CO > alcohols > carboxylic acids > aliphatic compounds > water vapour > aromatic compounds. It may be better to recover the waste phenolic FRP for valuable gases either as fuel or chemical feedstock in the first stage than the second stage.

1. Introduction

As a typical thermosetting plastics, fibre-reinforced plastic (FRP) is increasingly used as interior materials for buildings, aircrafts, ships and automobiles with prominent thermal insulation, outstanding impact resistance and sound absorption characteristics [1]. According to the different resin type, FRP can be mainly divided into phenolic FRP and polyester FRP. The market size of FRP increased by approximately 29.4 billion dollars in 2013 and is still under continuous increase in recent years owing to its multi-purpose and cost-effective properties [1]. However, the continuous increasing demand leads to rapid growth in waste FRP accumulation in the meantime. FRP materials are generally compounded from polymers, monomers and glass/carbon fibre, which are considerably difficult to be separated and returned to their original

states [1,2]. Therefore, disposal of waste FRP remains a considerable challenging problem.

Landfill, incineration and pyrolysis are the major methods to dispose waste plastics [2–7]. It was reported that landfill and incineration had great disadvantages in dealing with waste plastics. For example, Sharuddin et al. [2] pointed out that landfill occupied a huge space and the degradation of the waste plastics was quite slow. Environmental problems would be definitely caused. In addition, accumulation of waste plastics by landfill may cause a fire hazard due to their flammable feature [7]. Thus, the percentage of the waste plastics ended up in the landfill is under decrease in the EU in recent years [3]. As to incineration, Kunwar et al. [4] pointed out that incineration could contribute to environment pollution with harmful and toxic emissions. Besides, owing to the existence of glass/carbon fibre components in

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FRP, incineration may trigger agglomeration and plugging inside the reactor [1]. Pyrolysis is able to effectively convert the raw heterogeneous feedstock into homogeneous and more energy dense products in the absence of oxygen without pollution to environment [5]. In the pyrolysis process, higher temperature reactors with higher efficiency are employed compared with those in the incineration process. The synthetic gases/liquids from pyrolysis can be used for high efficiency gas turbines, hydrogen production, and as a feedstock for various chemicals, etc. [1]. Furthermore, the product yield may be optimized by flexibly manipulating the pyrolysis process parameters based on preferences [2,6]. Therefore, pyrolysis may be a promising method for recycling waste thermosetting plastics, which can address both of environment, energy and feedstock concerns. In order to effectively utilize waste FRP for recycling energy and chemical feedstock by pyrolysis, it is important to investigate the pyrolysis kinetics of waste FRP. Besides, understanding the volatile products and reaction mechanisms in the pyrolysis process may contribute to the reactor design for the pyrolysis recycling of waste FRP.

Few studies were reported on the pyrolysis kinetics of waste FRP. With assumption of different reaction order, the pre-exponential factor and activation energy of polyester FRP were calculated by Yun et al. [1] using Friedman method [8]. Besides, four famous kinetic methods including Friedman method [8], Kissinger method [9,10], Ozawa method [11] and modified Coats-Redfern method [12,13] were adopted to calculate the pre-exponential factor, activation energy and reaction order of polyester FRP by Yu et al. [14]. It is worth noting that the values of the pre-exponential factor and activation energy obtained in the research of Yun et al. [1] and Yu et al. [14] differ greatly. In addition, the above two studies focus on the pyrolysis kinetics of polyester FRP instead of phenolic FRP. In fact, the fire performance of phenolic FRP is much better than that of polyester FRP. More widespread application of phenolic FRP may occur compared with that of polyester FRP in the future. Therefore, it is necessary to investigate the pyrolysis kinetics of phenolic FRP, which receives little attention to date. As to the volatile products and reaction mechanisms in the pyrolysis of waste FRP, Yun et al. [1] used gas chromatography (GC) to analyze the volatile products of polyester FRP at different heating rates. However, the analyzed volatile products in the research of Yun et al. [1] only contained H₂, CH₄, CO and CO₂. Besides, in situ Fourier transform infrared (FTIR) was employed to monitor the variations of the major functional groups of the polyester FRP under different temperatures. However, detailed reaction mechanisms during pyrolysis were not discussed. Except for the research of Yun et al. [1], no studies concerning the volatile products and reaction mechanisms in the pyrolysis of waste FRP are reported to the best knowledge of the authors.

The pyrolysis recycling of waste thermoplastics such as polyethylene terephthalate (PET), polyethylene (PE), polyvinyl chloride (PVC), polypropylene (PP) and polystyrene (PS) has been widely studied [2–7]. Many pyrolysis technologies such as fixed bed reactor [15–18], fluidized bed reactor [19–21], spouted bed reactor [22,23], rotary kiln reactor [24,25], plasma reactor [26,27] and autoclave reactor [28–30] have been proposed to recycle the abovementioned waste thermoplastics, and good effectiveness may be obtained. However, due to large differences occurring between the pyrolysis process of thermosetting plastics and thermoplastics and lack of useful information of pyrolysis of waste phenolic FRP, the applicability of the abovementioned pyrolysis technologies into the pyrolysis recycling of waste phenolic FRP may be questioned. In order to solve this problem, the kinetics, volatile products and reaction mechanisms of pyrolysis of waste phenolic FRP need to be firstly studied.

Thermogravimetric analysis (TGA) is an effective method to study the pyrolysis behaviors of solid materials [31–37]. Using TGA, the mass loss, mass loss rate (MLR) and conversion rate of the solid materials under non-isothermal and isothermal conditions can be obtained. In addition, by combining the thermogravimetric data such as the conversion rate against temperature and conventional kinetic methods

such as Friedman method [8], Kissinger-Akahira-Sunose (KAS) method [9,10,38], Flynn-Wall-Ozawa (FWO) method [11,39,40], and Starink method [41], the kinetic parameters may be well estimated [31]. Meanwhile, in addition to prediction of kinetics by TGA and conventional kinetic methods, FTIR and online TGA-FTIR-mass spectra (MS) can be effectively utilized for detection of volatile products [34,37,42] and analysis of reaction mechanisms [43] in the solid pyrolysis. Therefore, by combining TGA, in situ FTIR and online TGA-FTIR-MS, a comprehensive understanding to the pyrolysis of waste phenolic FRP may be obtained.

In order to provide guidance for reactor design and thermo-chemical process management for waste phenolic FRP pyrolysis recycling, the present study employs TGA coupled with one typical differential model-free method Friedman method and three representative integral model-free methods KAS method [9,38,44], FWO method [11,39,40,45] and Starink method [41] to investigate the pyrolysis kinetics of waste phenolic FRP in nitrogen. The in situ FTIR and online TGA-FTIR-MS are used to characterize the volatile products and reaction mechanisms in the pyrolysis process in inert atmosphere.

2. Experimental and kinetic methods

2.1. Experimental

2.1.1. Material

The waste phenolic FRP used in the present study was provided by Shanghai phenolic FRP Research Institute. On the basis of the technical data about the specimen provided by the supplier, the waste phenolic FRP consists of about 50% fiberglass and 50% phenolic resin (mass fraction). Therein, the phenolic resin was produced by condensation polymerization of phenol and formaldehyde. Proximate and ultimate analyses, as shown in Table 1, were conducted to further determine the composition of the specimen. The chemical structure of the phenolic resin may be expressed as Fig. 1 (*m* denotes the degree of polymerization). The specimen was grinded to powder for all the tests.

2.1.2. Thermogravimetric tests

A SDT Q600 thermal analyzer was employed to perform the thermogravimetric tests in nitrogen atmosphere. The gas flow rate was 100 mL/min. The selected heating rates were 25, 45 and 65 K/min. The program temperature was increased from room temperature (RT) to approximately 1056 K at the end. The selected heating rate and temperature range are consistent with those generally used in the practical reactor for slow solid pyrolysis [5,6,34,35,37,46–51]. The mass of the specimen was approximately 9 mg for all the three cases.

2.1.3. In situ FTIR tests

In situ FTIR tests were performed employing an in situ FTIR spectroscopy (Nicolet 8700 from Thermo Electron Corporation) in nitrogen atmosphere. The pressed-disk technique was utilized with CaF₂ and the monitored spectrum range was 4000–1000 cm⁻¹. Based upon the TGA data at 25 K/min from the thermogravimetric tests, the selected target temperatures for the in situ FTIR tests were RT, 393 K, 483 K, 593 K, 713 K, 793 K and 873 K. Note that target temperature was achieved with the heating rate of 25 K/min, and it was maintained for 30 min for

Table 1
Proximate and ultimate analyses of the specimen.

Proximate analysis (wt%) ^a		Ultimate analysis (wt%) ^a						
Volatile matter	Fixed carbon	Ash	C	H	O	N	S	Other elements ^b
28.26	14.42	57.32	37.52	3.37	10.76	0.05	0.86	47.44

^a Dry basis.

^b By difference.

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