



Thermal degradation behaviors and reaction mechanism of carbon fibre-epoxy composite from hydrogen tank by TG-FTIR

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ABSTRACT

Thermal degradation behaviors and reaction mechanism of Carbon fibre-epoxy composite, obtained from Chinese widely applied hydrogen storage tank, were studied by thermogravimetry combined with Fourier transform infrared spectrometry at varying heating rates. The pyrolysis of carbon fibre-epoxy composite mainly occurs at 550–750 K. The average value of final residue is 72.42%. The calculated activation energies increase exponentially from 206.27 KJ/mol to 412.98 KJ/mol with the average value of 276.6 KJ/mol. The fourth reaction order model is responsible for the pyrolysis of carbon fibre-epoxy composite. The absorption spectra of the evolved gases provided the information that the main evolved products are H₂O, CO₂, C=O (acid anhydride, ketone or aldehyde), ε-caprolactam, alcohols and phenol. Moreover, C=O group > alcohols > phenol > ε-caprolactam > CO₂ > H₂O. Epoxy is the main pyrolysis crude material in carbon fibre-epoxy composite.

1. Introduction

With the depletion of fossil fuels and the promotion of people's awareness of environmental protection, hydrogen has emerged as an attractive alternative fuel. Except nuclear fuel, hydrogen combustion heat is the highest in all fossil fuels, chemical fuels and biofuels. Hydrogen can be stored onboard the vehicles as compressed gas, cryo-compressed liquid, or in advanced storage materials, such as chemical hydrides, metal hydrides, or sorbents. Nowadays, Type 3 (metal-lined) and Type 4 (polymer-lined) high pressure hydrogen storage tanks or bottles, both made by carbon fibre-epoxy composite, are widely used [1]. Type 3 tanks or bottles, which can also stand 70 MPa hydrogen, have been manufactured and widely used in China. The 70 MPa Type 4 hydrogen tank in the United States, Europe, Japan etc. has passed quality verification and put into commercialization. Moreover, in General Motors, Ford, Bavarian, Toyota and other large motor companies, hydrogen fuel-powered vehicles have been manufactured. However, the promotion of hydrogen fuel-powered vehicles is still being confronted with great difficulties, since safety storage of hydrogen is a huge challenge for the use of hydrogen as an energy carrier [2]. Tanks or bottles have the flammable composite (carbon fibre-epoxy) laminates and high-pressure hydrogen is stored inside, which brings a high risk of the tank failure under external flame. Furthermore, hydrogen has flammability and wide explosion limit. In the case of leakage, it possibly brings a more serious fire or explosion [3].

Pyrolysis, the first step in the all combustion process, is the most significant in the thermal chemical conversion [4]. Thermogravimetric (TG) and Fourier transform infrared (FTIR) analysis are two main methods for pyrolysis analysis. The former can output mass loss rates and chemical kinetic parameters while the latter is an impactful method to analyze substances and functional groups in produced gases. So TG analysis combined with FTIR can effectively study thermal decomposition characteristics, reaction mechanisms and evolved products during pyrolysis process [5].

For the pyrolysis characteristic of carbon fibre-epoxy, Ulrike Braun et al. [6] studied flame retardation effect on phosphoric carbon fibre-epoxy material using TG-FTIR and cone calorimeter, and analyzed the flame retardancy mechanisms. They found that the flame inhibition decreased with increasing oxidation state of the phosphorus. Tranchard et al. [7] carried out kinetic analysis of the pyrolysis of carbon fibre-epoxy composite from Airbus by TG-FTIR. A kinetic decomposition model was developed and the released gas products were analyzed. Two obvious thermal degradation processes were observed. Dao et al. [8] and Hidalgo et al. [9,10] employed epoxy resin/carbon fibre composites from hydrogen storage tank to carry out cone calorimeter test, and the latter also carried out the FTIR analysis of the produced gas. Dao et al. studied two carbon fibre/epoxy composites with carbon fibre contents of 56 and 59 vol%. Several characteristic parameters of the thermal decomposition were systematically measured. It was found that the increase of the carbon fibre fraction in the composites leads to a

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Nomenclature

	conversion rate
$f(\alpha)$	reaction mechanism function
$g(\alpha)$	integral function of the conversion rate
t	time, s
T	the absolute temperature, K
T_0	the initial temperature, K
$k(T)$	reaction rate constant
m_0	the initial mass, g

m_t	the mass at any time t , g
m_∞	the final mass, g
E_α	reaction activation energy, kJ/mol
R	the universal gas constant (8.314 J/(K mol))
A	the pre-exponential factor
β	the heating rate, K/min
DTG_{peak}	the peak value of mass loss rate, K ⁻¹
T_{peak}	temperature corresponding to the peak of mass loss rate, K
R_0^2	correlation coefficient

worse thermal resistance of the material.

The thermal degradation of the carbon fibre/epoxy changes from one system to another and generalization of its parameters and theories is difficult [11,12]. The carbon fibre-epoxy composite produced from carbon fibre and epoxy with different volume fraction can result in different thermal degradation and corresponding parameters. According to authors' best knowledge, there are not many studies on the thermal degradation of carbon fibre-epoxy composite from the hydrogen tank, especially the carbon fibre-epoxy composite used in China. Moreover, their activation energy, reaction mechanism and evolved products are really important for tank material improvement, risk assessment and numerical simulation of tank pyrolysis in the case of fire.

In this paper, we carried out the thermogravimetric and FTIR analysis of carbon fibre-epoxy composite widely used in China at different heating rates (10–40 K/min). The activation energy was evaluated by both model-free and model-fitting methods, and the latter can be also employed to obtain the suitable mechanism function and pre-exponential factor. Gas product analysis was performed by the absorbance spectra as function of wavenumber and temperature from FTIR tests. Especially, the obtained kinetic parameters and pyrolysis behaviors can provide the guide in tank material improvement and the important pyrolysis model for simulating hydrogen tank pyrolysis and risk assessment in the case of fire.

2. Kinetic method analysis

Thermogravimetric analysis relies on the relationship of the mass loss as a function of temperature [13]. Kinetics of the pyrolysis reactions can be expressed as follows:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \quad (1)$$

where t , T , $k(T)$ and $f(\alpha)$ denote the conversion rate in thermal decomposition period, time, the absolute temperature, reaction rate constant, and the reaction mechanism function, respectively. and $k(T)$ can be described by Eqs. (2) and (3)

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (2)$$

$$k(T) = A \exp\left(\frac{-E_\alpha}{RT}\right) \quad (3)$$

where m_0 , m_t and m_∞ are the initial mass, the mass at any time t and the final mass of the sample. E_α denotes reaction activation energy (kJ/mol). R is the universal gas constant (8.314 J/(K mol)) and A is the pre-exponential factor.

Combining Eqs. (1) and (3), the formula can be rewritten as:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_\alpha}{RT}\right) f(\alpha) \quad (4)$$

The heating rate β is a constant, then $\beta = dT/dt$, and Eq. (4) can be rewritten as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E_\alpha}{RT}\right) f(\alpha) \quad (5)$$

Through the integration and transformation, Eq. (6) can be obtained as:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E_\alpha}{RT}\right) dT \quad (6)$$

where $g(\alpha)$ is an integral function of the conversion. T_0 is the initial temperature in the reaction and T can be expressed as $T_0 + \beta t$.

2.1. Flynn-Wall-Ozawa (FWO) method

The FWO method was proposed by Doyle's approximation [14], and developed by Flynn and Wall [15], as well as Ozawa [16]. The reaction rate can be expressed as:

$$\ln\beta = \ln\left(\frac{AE_\alpha}{Rg(\alpha)}\right) - 1.052\left(\frac{E_\alpha}{RT}\right) - 5.331 \quad (7)$$

2.2. Kissinger Akahira and Sunose (KAS) method

Kissinger [17], Akahira and Sunose [18] developed the KAS method, which is expressed as follows:

$$\ln\frac{\beta}{T^2} = \ln\left(\frac{AE_\alpha}{Rg(\alpha)}\right) - \frac{E_\alpha}{RT} \quad (8)$$

2.3. Coats-Redfern (CR) method

Based on $2RT/E_\alpha \rightarrow 0$, the logarithmic equation of the CR method is expressed as:

$$\ln\frac{g(\alpha)}{T^2} = \ln\left(\frac{AR}{\beta E_\alpha}\right) - \frac{E_\alpha}{RT} \quad (9)$$

$g(\alpha)$ can be evaluated when the reaction mechanism is assumed. Thus the activation energy can be calculated by the slope of the straight line of $\ln(g(\alpha)/T^2)$ versus $1/T$. The common reaction mechanisms in solid state reactions are listed in Table 1 [19].

3. Experimental setup

The carbon fibre-epoxy composite in current study was the outer material of 70 MPa hydrogen tank, which is widely being used in China. The fibre content in specimen is 64%. Carbon fibre and epoxy are T700 and 0164 obtained from the manufacturer, respectively. Table 2 illustrates the elemental analysis results of carbon fibre-epoxy composite on weight percent. Crude samples were crushed firstly and sieved to size range of 0–0.2 mm [20]. Before the test, the samples had been dried at a temperature of 100 °C for 24 h.

The thermogravimetric experiment was conducted on a TG thermal analyzer (PerkinElmer TGA 8000). The sample temperature was increased from 300 K to 1300 K at different heating rates of 10, 20, 30 and

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