Pyrolysis and combustion characteristics and reaction kinetics of carbon fiber/epoxy composites

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ABSTRACT

The pyrolysis and combustion characteristics and reaction kinetics of epoxy resin matrix and carbon fiber/epoxy composites based on epoxy resin were studied by cone calorimetry and thermogravimetry. The results show that with the increase in thermal radiation intensity (increase from 25 kW m$^{-2}$ to 55 kW m$^{-2}$), the average ignition time of the experimental samples decreases, the peak heat release rate increases, and the peak appears earlier. Carbon fiber can inhibit the pyrolysis and combustion of epoxy resin. It can effectively inhibit the droplet and splash phenomenon during the combustion process. The time of ignition, heat release, and the peak value of the heat release rate are delayed. The ignition temperature of foam core materials in carbon fiber/epoxy foam laminates is low, which makes the average ignition time and peak heat release rate appear earlier. The theoretical critical heat fluxes of four experimental samples (epoxy resin matrix, carbon fiber/epoxy bidirectional woven fabric, carbon fiber/epoxy prepreg, and carbon fiber/epoxy foam laminate) were obtained by calculation. The theoretical critical heat fluxes are 12.12 kW m$^{-2}$, 13.21 kW m$^{-2}$, 11.12 kW m$^{-2}$, and 0.93 kW m$^{-2}$, respectively. The pyrolysis of carbon fiber/epoxy bidirectional woven fabric can be divided into three stages: two stages of epoxy resin matrix decomposition and carbon fiber decomposition. The heating rate has a significant influence on the pyrolysis process. With the increase in heating rate, the maximum weight loss rate temperature moves toward high temperature. The Kissinger method and Flynn-Wall-Ozawa method were used to analyze the pyrolysis kinetics. The apparent activation energy and pre-exponential factors were obtained at different heating rates. The results obtained by the two methods are basically the same. When the pyrolysis temperature of the three composites reached 450 °C, the mass loss was 20%, 17%, and 28%, respectively. This shows that the thermal stability of carbon fiber/epoxy prepreg is the best, the thermal stability of the two-way woven fabric of carbon fiber is better, and the thermal stability of the carbon fiber sandwich board is the weakest. It is consistent with this rule at any temperature.

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I. INTRODUCTION

Carbon fiber/epoxy composites have excellent properties such as corrosion resistance, creep resistance, design ability, high specific strength, and high specific modulus. The carbon fiber/epoxy composite with foam as a sandwich material has better static and dynamic performance, lower cost, and weight. It is widely used in structural components in aerospace and other fields. However, most of the resin matrix used in composites is flammable. Epoxy resin and foam core materials are highly flammable thermosetting materials. This makes the carbon fiber/epoxy composite and foam core composite easy to ignite. Once exposed to high temperature fire, the mechanical properties of composites such as tensile, shear, and modulus of elasticity will decrease. This will seriously threaten the safety of human life. It is necessary to study the thermal and fire-resistant properties of carbon fiber/epoxy composites and foam core sandwich composites in order to protect human life and property. Therefore, it is of great significance to study the pyrolysis and combustion characteristics and reaction kinetics of carbon fiber/epoxy composites.
In recent years, many scholars have studied the pyrolysis and combustion characteristics of carbon fiber/epoxy composites. It mainly concentrates on pyrolysis behavior and fire reaction performance as well as toughening, modification, interfacial adhesion, and other properties. Kim et al. characterized the resistance heating and thermal behavior of discontinuous carbon fiber/epoxy composites. It is found that the heating efficiency of carbon fiber resistance increases with the increase in applied voltage and carbon fiber content. The effect of the carbon fiber content in carbon fiber/epoxy composites on the fire reaction properties was studied by Quang Dao. It is concluded that the heat release rate and total heat release rate decrease with the increase in carbon fiber content. The pyrolysis kinetic parameters of carbon fiber/epoxy composites were determined by Régnier. Apparent activation energies of materials at different decomposition stages in air and nitrogen atmosphere were calculated by two methods. Shimokawa tested the variation of tensile and compressive properties of open and nonporous carbon fibre reinforced plastics laminates at different temperatures. Fiedler analyzed the failure process of the carbon fiber composite matrix by establishing the finite element model. The effect of temperature on the stress-strain curve was studied. The predicted results of the finite element model are compared with the experimental results to verify the feasibility of the finite element model. Lee tested the mechanical properties of carbon fiber composites at different temperatures. The failure mechanism of materials at different temperatures was analyzed. The fracture morphology of the material was observed. It was found that the sample fractured directly in the middle when the temperature was low. When the temperature is high, the experimental samples are separated between layers. Chen et al. studied that the thermal ablation rate of carbon fiber/epoxy composites increases with the increase in peak power density and repetition frequency under the action of repetitive laser. The thermal ablation rate decreases with the increase in irradiation time. Finally, they all tend to be fixed values. Fan and Li studied the thermo-oxidative aging properties of three-dimensional braided carbon fiber/epoxy composites. It was found that oxidative chain breakage and degradation of interfacial bonding force of matrix resin caused by thermal oxidative aging were the reasons for the decrease of mechanical properties of composites.

In conclusion, the research on carbon fiber/epoxy composites mainly focuses on their mechanical properties. The experimental and theoretical studies on their pyrolysis and combustion properties, especially the matrix materials, epoxy resin, and foam sandwich composites, are few. The research on the thermal stability of carbon fiber/epoxy composites is not comprehensive. The effect of epoxy resin on the combustion properties of carbon fiber/epoxy composites is seldom studied. Therefore, the pyrolysis and combustion characteristics of the epoxy resin matrix and carbon fiber/epoxy composites based on epoxy resin were studied by cone calorimetry and thermogravimetric analysis. This provides a theoretical basis for general aviation aircraft fire prevention.

II. EXPERIMENTAL METHOD

A. Experimental sample

The experimental samples used in this paper are typical carbon fiber/epoxy composites and epoxy resin matrix used in an electric light sport aircraft (RX1E). The four experimental materials are epoxy resin matrix, carbon fiber/epoxy bidirectional woven fabric, carbon fiber/epoxy prepreg, and carbon fiber/epoxy foam laminate. The epoxy resin matrix is the matrix material of carbon fiber/epoxy composites. It is made of epoxy resin (liquid) Araldite 1527-SP and hardene ZH3832 curing agent (liquid) according to the mass ratio of 100:34. After preparation, it is a kind of curing substance. Carbon fiber/epoxy bidirectional woven fabric is a carbon fiber/epoxy composite material made by the wet forming process with polyacrylonitrile (PAN) based carbon fiber T300-3000 and epoxy resin. Carbon fiber prepreg is used in the instrument panel of the electric light aircraft operating platform. It consists of 3K carbon cloth and one-way prepreg. Carbon fiber/epoxy foam laminates are made of carbon fiber/epoxy bidirectional woven fabric. The middle is a layer of 4 mm thick Divinycell L70 foam core. Its structure is shown in Fig. 1. The reinforcing materials of carbon fiber/epoxy composites are all 3K carbon fibers of T300 type. The composition of the four experimental samples and their application in aircraft are shown in Table I.

B. Experimental method

1. Cone calorimetry

Four experimental samples, epoxy resin matrix, carbon fiber/epoxy bidirectional woven fabric, carbon fiber/epoxy prepreg, and carbon fiber/epoxy foam laminate, were prepared into square specimens of 100 mm × 100 mm size. The outer edge of the sample is coated with aluminum foil. The combustion characteristics of the experimental samples in different fire environments were studied by
using the FTT-CONE-0242 cone calorimeter produced from FTT Company in Britain. The ignition time, heat release rate, and mass loss rate of the experimental samples were compared and analyzed. Different thermal radiation intensities (25 kW m\(^{-2}\), 35 kW m\(^{-2}\), 40 kW m\(^{-2}\), 45 kW m\(^{-2}\), 50 kW m\(^{-2}\), and 55 kW m\(^{-2}\)) were set to simulate different fire environments. The intensity of thermal radiation and the corresponding ambient temperature are shown in Table II.

### 2. Thermogravimetric analysis

Two kinds of experimental samples, epoxy resin matrix and carbon fiber/epoxy bidirectional woven fabric, were placed in a DMN-230H vacuum drying chamber for drying. Powder materials with 25 mm sieve mesh were taken from 3 to 5 mg, respectively. Temperature control is programmed by a DTG-60 (AH) thermogravimetric-differential thermal synchronous analyzer. The heating rates were set at 5, 10, 20, 30, and 40 °C min\(^{-1}\), respectively. The experimental temperature range of the epoxy resin matrix is set from room temperature to 800 °C. The experimental temperature range of carbon fiber/epoxy composites is set to 1200 °C. The TG and DTG curves of pyrolysis of experimental samples were determined. The thermal stability of the experimental samples was analyzed.

### 3. Scanning electron microscope analysis

In the cone calorimeter experiment, the microstructure of carbon fiber/epoxy bidirectional woven before and after combustion was observed by Hitachi TM3000 scanning electron microscopy (SEM). The effect of carbon fibers on the pyrolysis and combustion of carbon fiber/epoxy composites was analyzed. The surface of the residue of the burned sample was observed. The formation law of the carbon layer was studied.

## III. RESULTS AND ANALYSIS

### A. Ignition time of experimental samples

The ignition time (TTI) refers to the duration of flame ignition on the whole surface of the experimental sample. The epoxy resin matrix used in carbon fiber/epoxy composites can be ignited in very short time when exposed to fire. Composite materials will spread and burn rapidly with high temperature flame. Therefore, ignition time is an important index to describe the combustion characteristics of composite materials. Figure 2 and Table III show the ignition time of epoxy resin matrix, carbon fiber/epoxy bidirectional woven fabric, carbon fiber/epoxy prepreg, and carbon fiber/epoxy foam laminate in six different heat radiation conditions (25 kW m\(^{-2}\), 35 kW m\(^{-2}\), 40 kW m\(^{-2}\), 45 kW m\(^{-2}\), 50 kW m\(^{-2}\), and 55 kW m\(^{-2}\).

### TABLE I. Composition of four experimental samples and their applications in aircraft.

| Number | Test sample                     | Applied to electric small aircraft parts | Composition                                                                 |
|--------|---------------------------------|-----------------------------------------|----------------------------------------------------------------------------|
| 1      | Epoxy resin matrix              | Matrix material of the composite material | Epoxy resin (Araldite LY1564SP):curing agents (HardenerXB3487) = 100:34 (mass ratio) |
| 2      | Carbon fiber/epoxy bidirectional woven fabric | Fuselage frame position                 | Carbon fiber/epoxy resin = 34:100 (mass ratio)                             |
| 3      | Carbon fiber/epoxy prepreg      | Instrument panel                        | Composition of 3K carbon cloth and unidirectional prepreg                   |
| 4      | Carbon fiber/epoxy foam laminate | Instrument box                          | Epoxy resin/carbon fiber composite and 4 mm thick H60 Divinycell foam      |

### TABLE II. Environmental temperature corresponding to different thermal radiation intensities in experiments.

| Thermal radiation intensity (kW m\(^{-2}\)) | Ambient temperature (°C) |
|--------------------------------------------|---------------------------|
| 25                                         | 635                       |
| 35                                         | 712                       |
| 40                                         | 737                       |
| 45                                         | 765                       |
| 50                                         | 796                       |
| 55                                         | 813                       |

FIG. 2. The relationship between TTI and heat radiation flux of four experimental samples.
55 kW m\(^{-2}\)) in a cone calorimeter experiment. With the increase in thermal radiation intensity, the average ignition time of the four experimental samples was significantly shortened. Because the heat radiation flux increases, the heat exposure is strengthened. The rate of volatile matter release increased rapidly.

Under the same heat flux, the ignition time of the carbon fiber/epoxy foam laminate is the shortest. Carbon fiber/epoxy bidirectional woven fabric has the longest ignition time. This is due to the intrinsic low thermal decomposition temperature of foam core materials. The foam core material has a great influence on the ignition time of the carbon fiber/epoxy foam laminate. Therefore, the carbon fiber/epoxy foam laminate was first ignited. The ignited substance in carbon fiber/epoxy foam laminate is the carbon fiber/epoxy composite in the fire field. Figure 3 shows the relationship between thermal radiation flux \(q_{\text{net}}\) and thermal decomposition temperature of foam core materials. The foam core material has the longest ignition time. This is due to the intrinsic low thermal decomposition temperature of foam core materials. The foam core material has the longest ignition time. This is due to the intrinsic low thermal decomposition temperature of foam core materials.

Their ignition time (TTI) has their own models for different types of combustible materials.\(^{21}\) The types of combustible materials are represented by the corresponding coefficients. A combustible material with a coefficient less than 0.1 is a thin thermal material. For combustible materials with a coefficient greater than 1, it is a thick thermal material. For a combustible material having a coefficient of 0.1 or more and less than or equal to 1, between a thin heat material and a thick heat material, referred to herein as a balance heat material.\(^{22,23}\) The \(t_{ig}\) models of these three materials can be described by the following formulas:

\[
t_{ig} = \frac{\rho c L_0}{q_{\text{net}}} (T_i - T_0),
\]

\[
t_{ig} = \frac{\rho c k}{4} \left[ \frac{1}{q_{\text{net}}} \right]^{\frac{2}{3}},
\]

\[
t_{ig} \sim \rho c \sqrt{k L_0} \left[ \frac{1}{q_{\text{net}}} \right]^{\frac{1}{3}}.
\]

In these formulas, \(\rho\) denotes the density of combustible materials; \(c\) denotes the specific heat capacity; \(k\) denotes the thermal conductivity; \(L_0\) denotes the thickness of materials; \(T_i\) denotes the surface temperature of experimental samples at ignition; \(T_0\) denotes the ambient temperature; and \(q_{\text{net}}\) denotes the heat radiation flux.

The following three new models (1')–(3') can be obtained by changing formula (1)–(3):

\[
\frac{1}{t_{ig}} = \frac{1}{\rho c L_0 (T_i - T_0)} q_{\text{net}},
\]

\[
\left( \frac{1}{t_{ig}} \right)^{\frac{2}{3}} = \frac{1}{\sqrt{\rho c k L_0} (T_i - T_0)} q_{\text{net}},
\]

\[
\left( \frac{1}{t_{ig}} \right)^{\frac{1}{3}} \sim \frac{1}{\sqrt{\rho c} (k L_0)^{\frac{1}{3}} (T_i - T_0)} q_{\text{net}}.
\]

According to formula (1')–(3'), the functions of ignition time \(\left( \frac{1}{t_{ig}} \right)^{n}\) and heat radiation flux \(q_{\text{net}}\) are obtained. The ignition time measured by the four experimental samples and the corresponding heat radiation flux were substituted into (1')–(3'), respectively. Then on the left side of the formula (1')–(3'), \(\left( \frac{1}{t_{ig}} \right)^{n}\) corresponds to 1, 1/2, and 2/3, respectively, to determine the type of thermal behavior of the carbon fiber/epoxy composite in the fire field. Figure 3 shows the relationship between thermal radiation flux \(q_{\text{net}}\) and epoxy resin matrix, carbon fiber/epoxy bidirectional woven fabric, carbon fiber/epoxy prepreg, and carbon fiber/epoxy foam laminate, when \(n = 1, 1/2, 2/3\).

When \(n = 1\), \(n = 1/2\), and \(n = 2/3\), the fitting formulas of \(\left( \frac{1}{t_{ig}} \right)^{n}\) and \(q_{\text{net}}\) for each experimental sample are as follows:

**Epoxy resin matrix:**

\[
\frac{1}{t_{ig}} = 0.00146 q_{\text{net}} - 0.0177, R^2 = 0.9750,
\]

\[
\left( \frac{1}{t_{ig}} \right)^{\frac{1}{2}} = 0.00371 q_{\text{net}} + 0.0504, R^2 = 0.9739,
\]

\[
\left( \frac{1}{t_{ig}} \right)^{\frac{1}{3}} = 0.00287 q_{\text{net}} + 0.00208, R^2 = 0.9743.
\]

**Carbon fiber/epoxy bidirectional woven fabric:**

\[
\frac{1}{t_{ig}} = 0.0007845 q_{\text{net}} - 0.01037, R^2 = 0.9795,
\]
FIG. 3. Linear correlations between \((1/t_{ig})\) and the \(q_{net}\) of four experimental samples. (a) Epoxy resin matrix, (b) carbon fiber/epoxy bidirectional woven fabric, (c) carbon fiber/epoxy prepreg, and (d) carbon fiber/epoxy foam laminate.

\[
\left( \frac{1}{t_{ig}} \right)^{1/2} = 0.00276q_{net} + 0.03204, \quad R^2 = 0.9933, \quad (8)
\]

Carbon fiber/epoxy prepreg:

\[
\left( \frac{1}{t_{ig}} \right)^{1/2} = 0.00191q_{net} - 0.00161, \quad R^2 = 0.9956. \quad (9)
\]

\[
\left( \frac{1}{t_{ig}} \right)^{1/2} = 2q_{net} - 0.00734, \quad R^2 = 0.9954, \quad (10)
\]

\[
\left( \frac{1}{t_{ig}} \right)^{1/2} = 0.00245q_{net} + 0.0383, \quad R^2 = 0.9885, \quad (11)
\]

\[
\left( \frac{1}{t_{ig}} \right)^{1/2} = 0.00167q_{net} + 0.00375, \quad R^2 = 0.9902. \quad (12)
\]

Carbon fiber/epoxy foam laminate:

\[
\left( \frac{1}{t_{ig}} \right)^{1/2} = 0.00346q_{net} - 0.06938, \quad R^2 = 0.8527, \quad (13)
\]

\[
\left( \frac{1}{t_{ig}} \right)^{1/2} = 0.006521q_{net} - 0.00611, \quad R^2 = 0.9358, \quad (14)
\]

\[
\left( \frac{1}{t_{ig}} \right)^{1/2} = 0.00556q_{net} - 0.05856, \quad R^2 = 0.9122. \quad (15)
\]

Table IV shows the linear fit equations for the highest \(R^2\) values for each of the four experimental samples.

The performance of the epoxy resin matrix in the fire field can be characterized by the thin thermal model according to Table IV. The performance of carbon fiber/epoxy bidirectional woven fabric can be characterized by the equilibrium model. The carbon fiber/epoxy foam laminate can be characterized by the thin thermal model, and the carbon fiber/epoxy prepreg can be passed through the thick thermal model.

The ignition time of the materials can be predicted through the linear fitting equation of the above materials under different thermal radiation intensities. The theoretical minimum of the external thermal radiation flux required to ignite the materials can be obtained. The theoretical critical heat radiation fluxes of the four experimental
samples are 12.12 kW m$^{-2}$, 13.21 kW m$^{-2}$, 11.12 kW m$^{-2}$, and 0.93 kW m$^{-2}$, respectively.

From the critical heat flux of the four experimental samples, it can be seen that the critical heat radiation flux of the carbon fiber/epoxy foam laminate is the lowest due to the existence of the foam core material. The foam core material has a negative effect on the ignition performance of carbon fiber/epoxy composites.

**B. Heat release rate of experimental samples**

The heat release rate (HRR) is one of the most important characteristics of fire hazard.\textsuperscript{19,25} The flue gas generation and CO emission in the fire site are all related to the HRR.\textsuperscript{25} The total heat release rate (THR) is also a very important parameter for evaluating the flammability of materials, which can be used to characterize fire intensity and flame propagation rate.\textsuperscript{26}

![FIG. 4. Heat release rate curves of four experimental samples under different thermal radiation intensities. (a) Epoxy resin matrix, (b) carbon fiber/epoxy bidirectional woven fabric, (c) carbon fiber/epoxy prepreg, and (d) carbon fiber/epoxy foam laminate.](https://sample.com/figure4.png)
| Thermal radiation intensity (kW m\(^{-2}\)) | Epoxy resin matrix | Carbon fiber/epoxy bidirectional woven fabric | Carbon fiber/epoxy prepreg | Carbon fiber/epoxy foam laminate |
|---------------------------------------------|-------------------|---------------------------------------------|---------------------------|--------------------------------|
| Peak Heat release rate (kW m\(^{-2}\)) | Average value (300 s) | Peak Heat release rate (kW m\(^{-2}\)) | Average value (300 s) | Peak Heat release rate (kW m\(^{-2}\)) | Average value (300 s) | Peak Heat release rate (kW m\(^{-2}\)) | Average value (300 s) | Peak Heat release rate (kW m\(^{-2}\)) | Average value (300 s) |
| 25 | 605.9 | 83.7 | 83 | 386.8 | 59.3 | 113 | 382.9 | 59.9 | 113 | 405.7 | 42.3 | 39 |
| 30 | 643.7 | 86.1 | 67 | 427.5 | 63.3 | 97 | 429.3 | 65.5 | 98 | 445.6 | 45.9 | 47 |
| 35 | 699.6 | 88.4 | 53 | 460.7 | 68.4 | 78 | 463.1 | 70.2 | 79 | 499.2 | 48.4 | 23 |
| 40 | 745.9 | 91.3 | 42 | 482.3 | 71.2 | 63 | 485.6 | 73.1 | 64 | 551.7 | 52.3 | 18 |
| 50 | 890.2 | 96.6 | 37 | 537.8 | 74.6 | 55 | 541.9 | 76.6 | 57 | 634.3 | 55.8 | 14 |
| 55 | 960.1 | 105.2 | 30 | 579.6 | 80.9 | 49 | 581.9 | 82.1 | 52 | 669.3 | 60.1 | 10 |

Table V shows the peak value of heat release rate, the peak time, and the internal heat release rate of the epoxy resin matrix, carbon fiber/epoxy bidirectional woven fabric, carbon fiber/epoxy prepreg, and carbon fiber/epoxy foam laminates under different thermal radiation intensities. It is shown in Fig. 4 and Table V that with the increase in the heat radiation intensity, the peak value of the heat release rate of the four experimental samples and the average heat release rate increased within 300 s and the peak appearance time was significantly advanced. The peak heat release rate (Peak-HRR) increases as the radiant heat flux increases.

The peak heat release rate reached 634.3 kW m\(^{-2}\). As the combustion progresses, the epoxy resin therein is ignited. The heat release rate increased sharply and a second peak (334.9 kW m\(^{-2}\)) appeared, which is lower than the first peak. The peak of the heat release rate of the carbon fiber/epoxy bidirectional woven fabric is significantly delayed compared with the epoxy resin matrix, which is mainly due to the carbon fiber’s inhibition of the pyrolysis and combustion of the epoxy resin.

Figure 5 shows the total heat release rate curves of four experimental samples. The total heat release rate of epoxy resin is the largest of the four materials (28.53 MJ m\(^{-2}\)). This is mainly because epoxy resin is the burning substance in composite materials. Its quality is much higher than that of epoxy resin in the other three composites. Since the carbon fiber/epoxy bidirectional woven fabric and the carbon fiber/epoxy prepreg have greater mass than the carbon fiber/epoxy foam laminate, the total heat release rate of the carbon fiber/epoxy bidirectional woven fabric (21.87 MJ m\(^{-2}\)) and the total heat release rate (22.37 MJ m\(^{-2}\)) of the carbon fiber/epoxy prepreg is higher than that of the carbon fiber/epoxy foam laminate.
The total heat release rate of the carbon fiber/epoxy foam laminate is higher than that of the carbon fiber/epoxy bidirectional woven fabric and the carbon fiber/epoxy prepreg by comparing the total release rate per unit mass of each composite experimental sample. This shows that carbon fiber/epoxy foam laminates release more heat per unit mass in the combustion reaction. This is because the foam core material in the carbon fiber/epoxy foam laminate releases a lot of heat.

**C. Mass loss rate**

The Mass Loss Rate (MLR) denotes the change rate of mass with time during combustion. It reflects the degree of pyrolysis, volatilization, and combustion of materials at a certain fire intensity. In the process of combustion, combustibles will inevitably cause mass loss. Mass loss is a very important parameter in measuring material fire risk. The decomposition rate in composites can be determined by measuring the weight change of the experimental sample.

Table VI shows the residual percentage of the experimental samples after combustion under different thermal radiation intensities. With the increase in thermal radiation intensity, the residual percentage of experimental samples after combustion decreases. This shows that the greater the thermal radiation intensity, the more thorough the pyrolysis and combustion of the experimental samples. Among them, the epoxy resin matrix has the greatest reduction. When the thermal radiation intensity is 50 kW m$^{-2}$, the residual percentage is only 1%. This shows that the epoxy resin matrix burns most fully. The decrease of carbon fiber/epoxy bidirectional woven fabric is small. When the radiation intensity is 50 kW m$^{-2}$, the residual percentage is 63.29%. It also shows that carbon fibers have obvious inhibitory effects on the pyrolysis and combustion of epoxy resin.

When the thermal radiation intensity is 50 kW m$^{-2}$, the residual percentages of the three composites are 63.29%, 62.98%, and 32.00%, respectively. It can be seen that carbon fiber/epoxy foam laminates irradiated by a thermal radiation cone can consume more combustibles. Carbon fiber/two-way braided cloth and carbon fiber/epoxy prepreg, compared with the carbon fiber/epoxy foam laminate, consume less combustible materials.

Figure 7 shows the combustion morphology of four experimental samples at 50 kW m$^{-2}$ thermal radiation intensity. It can be seen that almost all of the epoxy resin matrix is burnt out from Fig. 7(a). The residual percentage was 1.00%. It can be seen that there are obvious delamination phenomena after combustion of carbon fiber/epoxy bidirectional woven fabric, carbon fiber/epoxy prepreg, and carbon fiber/epoxy foam laminate from Figs. 7(b) and 7(c). Almost all the epoxy resins in the three typical carbon fiber/epoxy composites were burnt out. The foam core materials of the carbon fiber laminate burn out, the mechanical properties are lost, and the overall structure is destroyed. The mass loss of carbon fibers is not obvious. This is mainly because the selected heat radiation flux is 50 kW m$^{-2}$ and the corresponding radiation temperature is 796 °C. The oxidation reaction of carbon fibers will be limited when the temperature is lower than about 1000 °C. The foam core material is completely burned under this condition. Therefore, the residual quality of the carbon fiber/epoxy foam laminate is less than that of carbon fiber/epoxy bidirectional woven fabric and carbon fiber/epoxy prepreg.

The mass loss of carbon fiber/epoxy bidirectional woven fabrics is mainly due to the pyrolysis of the epoxy resin matrix. The main pyrolysis components of the carbon fiber/epoxy foam laminate include foam core material and epoxy resin matrix.

The flammable gases and volatiles of the experimental samples produced more in unit time. Its quality loss is getting faster and faster. The mass loss rate increases with the increase in thermal radiation intensity.

### TABLE VI. Residual percentages of four experimental samples after combustion under different thermal radiation intensities.

| Heat release rate (kW m$^{-2}$) | Epoxy resin matrix (%) | Carbon fiber/epoxy bidirectional woven fabric (%) | Carbon fiber/epoxy prepreg (%) | Carbon fiber/epoxy foam laminate (%) |
|-------------------------------|------------------------|-----------------------------------------------|-------------------------------|-----------------------------------|
| 25                            | 10.00                  | 69.45                                         | 69.32                         | 57.46                             |
| 30                            | 5.00                   | 68.90                                         | 68.76                         | 53.71                             |
| 35                            | 2.00                   | 68.71                                         | 68.10                         | 46.69                             |
| 40                            | 1.60                   | 66.51                                         | 65.39                         | 39.26                             |
| 50                            | 1.00                   | 63.29                                         | 62.98                         | 32.00                             |
| 55                            | 0.70                   | 60.02                                         | 59.31                         | 28.31                             |
radiation intensity. In the actual fire field, the greater the mass loss rate is, the faster the flame propagation speed is, and the greater the fire risk is.\textsuperscript{32–34} With the increase in heat radiation flux, the mass residual rate of the experimental sample decreases gradually. The residual mass fraction of the carbon fiber/epoxy foam laminate under all thermal radiation fluxes is lower than that of carbon fiber/epoxy bidirectional woven fabric and carbon fiber/epoxy prepreg. Due to the existence of foam core material, the carbon fiber/epoxy foam laminate has a faster burning rate than carbon fiber/epoxy bidirectional woven fabric and carbon fiber/epoxy prepreg.

D. Combustion inhibition of carbon fiber

Figures 8(a) and 8(b) show the surface micromorphology of carbon fiber/epoxy bidirectional woven fabric enlarged 500 times before and after combustion, respectively. As shown in Figs. 8(a) and 8(b), before combustion, carbon fiber bundles are crosslinked with epoxy resin. After combustion, the epoxy resin almost completely burns up. Carbon fiber bundles are arranged tightly. Some epoxy resin is burned to form a carbon layer covering the surface of the fiber tow. The thermal decomposition of epoxy resin was inhibited. The contact between epoxy resin and oxygen is hindered, because of limited heat transfer. Combustion was suppressed. Expansion and melting of the epoxy resin matrix samples occurred during heating, and the flammable liquid vapor was continuously released. It burns boiling after ignition. In the combustion process, there are droplets dropping and splashing. There was no drooping phenomenon in the experimental samples of three typical carbon fiber/epoxy composites. This is mainly because the dense structure formed by carbon fiber bundles can effectively inhibit the melting droplets and splashing during combustion.

Figures 8(c) and 8(d) are the microscopic morphologies of the carbon layer formed by combustion of epoxy resin matrix and carbon fiber/epoxy bidirectional woven fabric, which enlarges 3000 times. From Figs. 8(c) and 8(d), it can be seen that the carbon layer formed after combustion is a dense and uniform spongy structure. The structure is a carbon layer formed by breaking of chemical bonds on the main chain of the epoxy resin matrix and retained in the form of carbon. The breakage of chemical bonds on the main chain of the epoxy resin matrix is due to the continuous heat absorption and internal conduction of the epoxy resin matrix after being

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{The morphology of the four experimental samples after combustion at 50 kW m\textsuperscript{-2} thermal radiation intensity. (a) Epoxy resin matrix, (b) carbon fiber/epoxy bidirectional woven fabric, (c) carbon fiber/epoxy prepreg, and (d) carbon fiber/epoxy foam laminate.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Morphology image of carbon fiber/epoxy bidirectional woven fabric before combustion. (b) Morphology image of carbon fiber/epoxy bidirectional woven fabric after combustion. (c) The carbon layer morphology image of the epoxy resin matrix after combustion. (d) The carbon layer morphology image of carbon fiber/epoxy bidirectional woven fabric after combustion.}
\end{figure}
It shows that the epoxy resin matrix participates in the charring process during combustion. This kind of spongy structure has more complete microcell and contains a large number of complete closed honeycomb structures. This structure can effectively prevent oxygen from diffusing to the surface of the epoxy resin matrix and also prevent the pyrolysis of flammable gases and liquid vapor from diffusing to the combustion zone, thus limiting the heat transfer from the combustion zone to the epoxy resin matrix. It is also shown in Figs. 8(c) and 8(d) that only a dense and uniform spongy carbon layer is formed at the cross section of the epoxy resin matrix after combustion. Carbon fiber/epoxy bidirectional woven fabrics formed a dense and uniform spongy carbon layer on the whole surface after combustion. This indicates that the carbon layer formed by the combustion of carbon fiber/epoxy bidirectional woven fabric has a stronger inhibition on combustion than the carbon layer formed by the combustion of the former itself.

E. Pyrolysis analysis

1. Effect of different heating rates on pyrolysis of experimental samples

Figures 9 and 10 show the TG and DTG curves of the epoxy resin matrix at heating rates of 5, 10, 20, 30, and 40 °C min⁻¹ in air. Table VII shows the main thermogravimetric parameters of the epoxy resin matrix.

There are two obvious inflection points in the TG curve of the epoxy resin matrix, as shown in Figs. 9 and 10. These two inflection points correspond to the two peaks of the DTG curve, respectively. The pyrolysis of the epoxy resin matrix can be divided into two stages. In an oxygen atmosphere, the radicals in the initial reaction rapidly combine with oxygen to form new peroxide radicals. The degradation of peroxide radicals is the first stage of the decomposition reaction. The second stage of decomposition is caused by the breakdown of the polymer network in the first stage. According to Table VII, the initial decomposition temperature \( T_i \) of the epoxy resin matrix did not change much (240 °C–260 °C) with the increase in heating rate but increased slightly. The termination temperature \( T_f \) moves toward high temperature. The pyrolysis temperature range of the two stages is widened. The temperature range of the second stage is larger than that of the first stage. The maximum mass loss rate temperature of the two pyrolysis stages also moves toward high temperature. A higher pyrolysis temperature is required to achieve the same weight loss rate.

Figures 11 and 12 show the TG and DTG curves of carbon fiber/epoxy bidirectional woven fabrics with heating rates of 5, 10, 20, 30, and 40 °C min⁻¹ in air. Table VIII shows the main thermogravimetric parameters of carbon fiber/epoxy bidirectional woven fabrics.

From Figs. 11 and 12, it can be seen that there are three obvious inflection points in the TG curve of carbon fiber/epoxy bidirectional woven fabric. The three inflection points correspond to the three peaks of the DTG curve, respectively. This indicates that the pyrolysis of carbon fiber/epoxy bidirectional woven fabric can be divided into three stages. It is shown in Table VIII that the initial decomposition temperature of carbon fiber/epoxy bidirectional woven fabrics at different heating rates is basically the same as that of the epoxy resin matrix. The temperature ranges from 241 °C to 258 °C. Compared with the two decomposition stages of the epoxy resin matrix, the temperature range of the first and second stages of carbon fiber/epoxy bidirectional woven fabric is similar. Its reaction is basically the same. This shows that the decomposition of the epoxy resin matrix is the main decomposition of the first two stages and the decomposition of carbon fibers is the third stage. With the increase in heating rate, the termination temperature \( T_f \) moves toward high temperature. The temperature ranges from 704 °C to 917 °C. The pyrolysis temperature range of the three stages is gradually broadened. The temperature range of each stage is higher than that of the previous pyrolysis stage. The maximum weight loss rate temperature also moves toward high temperature. Weightlessness increased significantly. This is the same as that of the epoxy resin matrix. The second stage reacts continuously before the thermal decomposition of carbon fibers. However, the reaction was mild and occasionally peaked.
TABLE VII. Pyrolysis temperature parameters of the epoxy resin matrix.

| Heating rates (°C min⁻¹) | The temperature scope of material loss (°C) | Initial decomposition temperature $T_i$ (°C) | Final temperature $T_f$ (°C) | The temperature of maximum weight loss rates $T_p$ (°C) |
|--------------------------|--------------------------------------------|---------------------------------------------|-----------------------------|---------------------------------------------|
|                          | First stage                                | Second stage                                |                             | First stage                                | Second stage                                |
| 5                        | 240–385                                    | 385–581                                     | 240                         | 581                                        | 279                                        | 513                                        |
| 10                       | 245–393                                    | 393–622                                     | 245                         | 622                                        | 294                                        | 542                                        |
| 20                       | 249–399                                    | 480–678                                     | 249                         | 678                                        | 314                                        | 570                                        |
| 30                       | 254–435                                    | 481–705                                     | 254                         | 705                                        | 328                                        | 591                                        |
| 40                       | 258–446                                    | 502–768                                     | 258                         | 768                                        | 341                                        | 613                                        |

Figures 13 and 14 are the TG and DTG curves of carbon fiber/epoxy prepreg with heating rates of 5, 10, 20, 30, and 40 °C min⁻¹ in air. Table IX shows the main thermogravimetric parameters of carbon fiber/epoxy prepreg.

There are three inflection points in the TG curve of carbon fiber/epoxy prepreg. The three inflection points correspond to the three peaks of the DTG curve, respectively. The pyrolysis reaction of carbon fibre/epoxy prepreg can be divided into three stages at different heating rates. Combined with Table IX, it can be found that with the increase in heating rate, the starting and ending temperatures of each stage move toward high temperature. The initial decomposition temperature of $T_i$ at different heating rates ranges from 287 °C to 337 °C. The starting temperature of the second stage of the reaction is between 360 °C and 425 °C. The end point is between 527 °C and 620 °C. The final end temperature of the reaction is between 657 °C and 810 °C. The pyrolysis temperature range of the three stages gradually widened. The temperature range of each stage is higher than that of the previous pyrolysis stage. In the second stage, the reaction continued before the thermal decomposition of carbon fibers and the peak weight loss rate was more obvious when the heating rate was 5, 10, 20 °C min⁻¹. It shows that the reaction is slightly stagnated. The reaction weightlessness rate increased gradually when the heating rate was 30 °C min⁻¹ and 40 °C min⁻¹. Stagnation time becomes shorter. The maximum weight loss rate temperature also moves toward high temperature. The rate of weightlessness increased obviously.

2. Thermal stability analysis

Figure 17 is the TG curve of three kinds of carbon fiber composites obtained by thermogravimetric experiments at an atmospheric...
TABLE VIII. Pyrolysis temperature parameters of carbon fiber/epoxy bidirectional woven fabric. “—” without peak value.

| Heating rates (°C min⁻¹) | The temperature scope of material loss (°C) | Initial decomposition temperature $T_i$ (°C) | Final temperature $T_f$ (°C) | The temperature of maximum weight loss rates $T_P$ (°C) |
|--------------------------|--------------------------------------------|---------------------------------------------|--------------------------|---------------------------------------------|
|                          | First stage 241–357  | Second stage 459–537  | Third stage 573–704   | 444                                        | 241                                            | 704                                            | First stage 260                                     | Second stage 492                                    | Third stage 637                                  |
|                          | 10            | 244–389  | 393–570  | 570–751                                           | 244                                        | 751                                            | 279                                            | 518                                            | 679                                    |
|                          | 20            | 244–397  | 422–573  | 573–794                                           | 244                                        | 794                                            | 297                                            | —                                             | 692                                    |
|                          | 30            | 245–416  | 416–597  | 597–887                                           | 245                                        | 887                                            | 308                                            | 538                                            | 722                                    |
|                          | 40            | 258–428  | 428–617  | 617–917                                           | 258                                        | 917                                            | 318                                            | 566                                            | 765                                    |

flow rate of 50 ml/min, a heating rate of 20 °C/min⁻¹, and a temperature range of 25–1000 °C. It is shown in Fig. 17 that the mass loss rate of carbon fiber/epoxy bidirectional woven fabrics reaches 20% in air when pyrolysis reaches a certain temperature (450 °C). The mass loss rate of carbon fiber/epoxy prepreg reached 17%. The mass loss rate of the carbon fiber/epoxy foam laminate is 28%. This indicates that at the same temperature, the mass loss of carbon fiber/epoxy prepreg is the least and the weight loss of the carbon fiber/epoxy foam laminate is the most. The lower the mass loss rate is when the temperature reaches a certain value, the better the thermal stability is. At any temperature, the law is in accord with this law. This indicates that the thermal stability of carbon fiber/epoxy prepreg is the strongest. Next is carbon fiber/epoxy bidirectional woven fabric. The thermal stability of the carbon fiber/epoxy foam laminate is weak.

Figure 18 is the DTG curve corresponding to Fig. 17. It is clearly shown in Fig. 18 that the maximum weight loss rate temperatures of carbon fiber/epoxy prepreg at each stage are 361 °C, 551 °C, and 785 °C, respectively. The maximum weightlessness rate temperatures of carbon fiber/epoxy bidirectional woven fabrics at each stage are 297 °C, 546 °C, and 692 °C, respectively. The maximum weight loss rate of the carbon fiber/epoxy foam laminate at each stage is 274 °C, 538 °C, and 658 °C, respectively. The maximum weight loss rate temperature of carbon fiber/epoxy prepreg is lagging behind the other two composites at each reaction stage. This further shows that the thermal stability of carbon fiber/epoxy prepreg is stronger than that of the other two composites. The pyrolysis of the carbon fiber/epoxy foam laminate is earlier than that of the other two composites. Therefore, the thermal stability of carbon fiber/epoxy bidirectional woven fabric is stronger than that of the carbon fiber/epoxy foam laminate.

F. Kinetic analysis of pyrolysis

The Kissinger method and Flynn-Wall-Ozawa method were used for dynamic analysis in order to avoid the calculation error caused by different hypotheses of the mechanism function when calculating the apparent activation energy and apparent pre-exponential factor of epoxy resin matrix, carbon fiber/epoxy bidirectional woven cloth, carbon fiber/epoxy prepreg, and carbon fiber/foam laminate. The thermal stability of the composites was analyzed from the mathematical and physical point of view by the apparent activation energy.

1. Kissinger method

From equation $\frac{d\alpha}{dt} = k f(\alpha)$, $k = A \exp(-E/RT)$, and $f(\alpha) = (1 - \alpha)^n$, we can get that $\frac{d\alpha}{dt} = A e^{-E/RT} (1 - \alpha)^n$. (16)
TABLE IX. Pyrolysis temperature parameters of carbon fiber/epoxy prepreg.

| Heating rates (°C min⁻¹) | The temperature scope of material loss (°C) | Initial decomposition temperature \(T_i\) (°C) | Final temperature \(T_f\) (°C) | The temperature of maximum weight loss rates \(T_p\) (°C) |
|--------------------------|-------------------------------------------|-----------------------------------------------|-------------------------------|------------------------------------------|
|                          | First stage | Second stage | Third stage | First stage | Second stage | Third stage | First stage | Second stage | Third stage |
| 5                        | 287–360    | 360–527     | 627–796     | 287         | 796         | 326         | 505         | 725         |            |
| 10                       | 295–374    | 374–568     | 659–852     | 295         | 852         | 343         | 530         | 758         |            |
| 20                       | 319–384    | 384–588     | 681–906     | 319         | 906         | 361         | 550         | 784         |            |
| 30                       | 328–406    | 417–605     | 709–961     | 328         | 961         | 370         | 569         | 806         |            |
| 40                       | 337–413    | 425–620     | 729–988     | 337         | 988         | 380         | 580         | 825         |            |

Differentiation on both sides of the equation, when \(T = T_p\), from equation \(\frac{d}{dt} \left( \frac{\alpha}{RT} \right) = 0\), we can get that

\[
\frac{E}{RT^2_p} = An(1 - \alpha_p)^{n-1}e^{-E/RT_p},
\]

or

\[
\frac{E\beta}{RT^2_p} = Ae^{-E/RT_p}.
\]

By taking logarithms on both sides of Eq. (18), the following equation or Kissinger equation, is obtained:

\[
\ln \left( \frac{\beta_i}{T^2_{pi}} \right) = \ln A_k R \frac{E_k}{1 - \frac{1}{T_{pi}}}, \quad i = 1, 2, 3, 4 (\text{or} 5 \text{ and } 6).
\]

Fit the data \(\ln \left( \frac{\beta_i}{T^2_{pi}} \right)\) and \(\frac{1}{T_{pi}}\) of four experimental samples with straight lines, as shown in Fig. 19. According to the fitting curve, the slope \(k\) is obtained, and then \(E_k\) and \(\ln A_k\) are obtained. Thermodynamic parameters of four experimental samples were obtained (see Table XI). Table XI shows that the reaction of the epoxy resin matrix in the two stages of pyrolysis has little change. The pyrolysis is stable.

In the three stages of pyrolysis of carbon fiber/epoxy bidirectional woven fabrics, the reaction rate of the first stage is faster than that of the second and third stages. The pyrolysis of the epoxy resin matrix was compared. There is no difference in the first stage. In the second stage, the apparent activation energy of carbon fiber/epoxy bidirectional woven fabric is slightly higher than that of the epoxy resin matrix. This indicates that the thermal stability of the composites is strong when pyrolysis occurs in the second stage of the reaction. Compared with the pyrolysis of the epoxy resin matrix, the pyrolysis of carbon fiber/epoxy bidirectional woven fabrics showed strong thermal stability from the initial reaction.

The reaction of carbon fiber/epoxy prepreg is gradually stable in three stages of pyrolysis. The apparent activation energies of the first and second stages did not change much. This indicates that the pyrolysis reaction has been stable until the third stage. In the third stage of carbon fiber decomposition, the apparent activation energy...
TABLE X. Pyrolysis temperature parameters of the carbon fiber/epoxy foam laminate.

| Heating rates (°C min⁻¹) | The temperature scope of material loss (°C) | Initial decomposition temperature \( T_i \) (°C) | Final temperature \( T_f \) (°C) | The temperature of maximum weight loss rates \( T_p \) (°C) |
|--------------------------|------------------------------------------|---------------------------------|-----------------|---------------------|
|                          | First stage  | Second stage | Third stage  | First stage  | Second stage | Third stage  |
| 5                        | 230–291     | 348–540     | 540–637     | 230          | 637          | 245          |
| 10                       | 245–315     | 375–568     | 568–695     | 245          | 695          | 257          |
| 20                       | 250–350     | 380–595     | 595–758     | 250          | 758          | 274          |
| 30                       | 262–385     | 411–586     | 586–778     | 262          | 778          | 289          |
| 40                       | 273–395     | 415–591     | 591–810     | 273          | 810          | 302          |

Energy was significantly higher than that in the first two stages. The overall apparent activation energy is higher than that of epoxy resin matrix and carbon fiber/epoxy bidirectional woven fabric. This indicates that carbon fiber/epoxy prepreg is not easy to pyrolyze and has strong thermal stability.

Step 1, step 2, and step 3 of the Carbon fiber/epoxy foam laminate represent the first, second, and third stages of pyrolysis of the carbon fiber/epoxy foam laminate, respectively. The apparent activation energy analysis shows that the \( E \) value of the carbon fiber/epoxy foam laminate pyrolysis phase is obviously smaller than that of the second and third stages. The fluctuation is large. This indicates that the initial reaction stage is easy to carry out. It is not easy to decompose in two stages after reaction. Its stability is strong. Compared with carbon fiber/epoxy bidirectional woven fabric, the \( E \) value of the carbon fiber/epoxy foam laminate is similar in the first two stages. The difference of material stability is small. The \( E \) values of the third stage are quite different. It shows relatively strong stability. Compared with carbon fiber/epoxy prepreg, the overall reaction process of the carbon fiber/epoxy foam laminate fluctuates greatly. \( E \) values of the second stage are similar. The carbon fiber/epoxy foam laminate is more easily pyrolyzed and relatively stable than other two kinds of materials.

2. Flynn-Wall-Ozawa method

From equation Flynn-Wall-Ozawa,

\[
\lg \beta = \lg \left( \frac{AE}{RG(a)} \right) - 2.315 - 0.4567 \frac{E}{RT},
\]

\( G(a) \) is a mechanism function in integral form. \( G(a) \) is a constant value when the same \( a \) is chosen, and the \( \beta_i \) is different. Hence, \( \lg \beta \) has a linear relationship with \( 1/T \). The \( E \) value can be calculated by the slope.

The corresponding conversion rate was found at the same temperature according to the experimental data. When the conversion of epoxy resin matrix and carbon fiber/epoxy bidirectional woven fabrics is 5%, 10%, 15%, 25%, 35%, 50%, 75%, and 90%, the relationship curve between \( \lg \beta \) and \( 1/T \) is drawn. Thus, eight parallel lines with different conversion rates were obtained for each experimental sample. The apparent activation energy \( E \) of material pyrolysis at different conversion rates was obtained by the formula. The results are given in Figs. 20 and 21.

It is shown in Fig. 20 that the epoxy resin matrix is in the fast reaction stage in the early stage of the reaction. The reaction
FIG. 19. Relation curves of the pyrolysis process $\ln \left( \frac{\beta}{T_\beta^2} \right)$ and $\frac{1}{T_\beta}$ of four experimental samples. (a) Epoxy resin matrix, (b) carbon fiber/epoxy bidirectional woven fabric, (c) carbon fiber/epoxy prepreg, and (d) carbon fiber/epoxy foam laminate.

| Materials                          | Heating rates ($^\circ$C min$^{-1}$) | Slope $k = -E/R$ | $E_k$ (kJ mol$^{-1}$) | $\ln A_k$ |
|------------------------------------|-------------------------------------|-----------------|----------------------|------------|
| Epoxy resin matrix                 |                                     | −10.318         | 86                   | 10.1       |
|                                    |                                     | −14.293         | 119                  | 9.1        |
| Carbon fiber/epoxy                 |                                     | −10.104         | 84                   | 10.3       |
| bidirectional woven fabric         | 5                                   | −16.861         | 140                  | 13.3       |
|                                    | 10                                  | −13.603         | 113                  | 5.7        |
|                                    | 20                                  | −14.023         | 117                  | 14.9       |
| Carbon fiber/epoxy prepreg         | 30                                  | −16.942         | 141                  | 12.9       |
|                                    | 40                                  | −21.304         | 177                  | 12.2       |
|                                    |                                     | −9.67           | 80                   | 11         |
| Epoxy resin/carbon fiber composite foam laminate | | −17.738 | 147 | 14.4 |
sloows down when the strong energy bond breaks. The activation energy is larger. Then, the reaction rate was the same as the initial reaction. As shown in Fig. 21, the reaction of carbon fiber/epoxy bidirectional woven fabric is always in equilibrium. There was no significant change. Table XII shows the activation energies of epoxy resin matrix and carbon fiber/epoxy bidirectional woven fabric at different conversion rates. The change of pyrolysis reaction is given clearly.

The activation energy of the epoxy matrix pyrolysis reaction is close when the conversion is 5%–35%. This shows that the pyrolysis rate of materials is equal at this stage. The pyrolysis is more uniform. The pyrolysis reaction of the epoxy resin matrix increases abruptly when the conversion is 40%–65%. At this point some of the stronger chemical bonds begin to break. However, the activation energy does not increase significantly. This indicates that the material is still cracked at a relatively uniform rate. The later activation energy is kept within a certain range. The pyrolysis rate is stable. When mass loss reaches 25% and 80%, the maximum weight loss rate temperature corresponds to the two stages, respectively. Compared with the epoxy resin matrix, the thermal activation energies of carbon fiber/epoxy bidirectional woven fabric differ little. This shows that the reaction rate is almost the same and there is no big fluctuation. The pyrolysis is more uniform.

When the conversion of carbon fiber/epoxy prepreg is 5%, 15%, 20%, 30%, 40%, 50%, 95%, and 95%, the relationship curve between \( \log \beta \) and \( 1/T \) is drawn. Thus, eight fitting lines with different conversion rates are obtained, as shown in Fig. 22.

Figure 22 shows that the pyrolysis of carbon fiber/epoxy prepreg continues steadily without obvious fluctuation. According to Table XII, the apparent activation energy of carbon fiber/epoxy prepreg pyrolysis has little change. The apparent activation energy of carbon fiber/epoxy prepreg is higher than that of carbon fiber/epoxy bidirectional woven fabric. This shows that the stability of carbon fiber/epoxy prepreg is stronger than that of carbon fiber/epoxy bidirectional woven fabric. When the mass loss of carbon fiber/epoxy prepreg reaches 10%, 30%, and 60%, the maximum weight loss rate temperature of three stages corresponds, respectively.

When the conversion of the carbon fiber/epoxy foam laminate is 5%, 10%, 20%, 30%, 40%, 50%, 90%, and 95%, the maximum weight loss rate temperature of three stages corresponds, respectively.

The Flynn-Wall-Ozawa method avoids the need to select reaction mechanism function and can directly calculate the E value. In this way, the errors caused by different hypotheses of reaction mechanism functions are avoided. Therefore, the Flynn-Wall-Ozawa method was used to test the activation energy obtained from the hypothetical reaction mechanism function. The apparent activation energy calculated by the Flynn-Wall-Ozawa method can be used to compare the reliability of the Kissinger method. Tables XI and XII show that the apparent activation energies of materials calculated by two methods are within a certain range when the mechanism function is unknown. It can correctly reflect the apparent activation energy of materials. Therefore, the quantitative analysis conclusion is reliable.

Starting from the initial reaction, by comparing the pyrolysis parameters of composite materials obtained by Kissinger
TABLE XII. Flynn-Wall-Ozawa method for calculating apparent activation energies of four experimental samples.

| Conversion (α (%)) | Epoxy resin matrix | Carbon fiber/epoxy bidirectional woven fabric | Carbon fiber/epoxy prepreg | Carbon fiber/epoxy foam laminate |
|-------------------|--------------------|---------------------------------------------|---------------------------|--------------------------------|
| 5                 | 91                 | 78                                          | 104                       | 69                             |
| 10                | 102                | 93                                          | 123                       | 102                            |
| 15                | 99                 | 119                                         | 142                       | 92                             |
| 20                | 102                | 93                                          | 122                       | 101                            |
| 25                | 102                | 92                                          | 127                       | 99                             |
| 30                | 110                | 98                                          | 138                       | 84                             |
| 35                | 121                | 105                                         | 162                       | 85                             |
| 40                | 160                | 107                                         | 148                       | 92                             |
| 45                | 208                | 106                                         | 144                       | 99                             |
| 50                | 269                | 113                                         | 142                       | 102                            |
| 55                | 196                | 113                                         | 141                       | 101                            |
| 60                | 168                | 105                                         | 139                       | 98                             |
| 65                | 130                | 105                                         | 134                       | 100                            |
| 70                | 114                | 97                                          | 129                       | 110                            |
| 75                | 102                | 97                                          | 125                       | 119                            |
| 80                | 102                | 94                                          | 121                       | 123                            |
| 85                | 97                 | 84                                          | 118                       | 120                            |
| 90                | 91                 | 79                                          | 115                       | 113                            |
| 95                | 84                 | 82                                          | 113                       | 103                            |

and Flynn-Wall-Ozawa pyrolysis kinetics, carbon fiber/epoxy bidirectional woven fabrics show strong and stable thermal stability. Compared with carbon fiber/epoxy prepreg, the activation energy of carbon fiber/epoxy prepreg is lower. Carbon fibre/epoxy prepreg exhibits high activation energy, intense intermolecular collision, and difficult reaction. By analyzing the carbon fiber/epoxy foam laminate, it is known that the reaction stability is the worst. The addition of the foam core enhances the cushioning function of the material, but at the same time, it greatly reduces the thermal stability. The carbon fiber/epoxy foam laminate is the most easily pyrolyzed material in the three composites.

FIG. 22. Relation curve of $\lg \beta$ and $1/T$ in the pyrolysis process of carbon fiber/epoxy prepreg.

FIG. 23. Relation curve of $\lg \beta$ and $1/T$ in the pyrolysis process of the carbon fiber/epoxy foam laminate.
IV. CONCLUSION

(1) Carbon fiber/epoxy bidirectional woven fabric and carbon fiber/epoxy prepreg combustion materials are epoxy resin. The combustion material of the carbon fiber/epoxy foam laminate is foam core and epoxy resin. With the increase in thermal radiation intensity, the average ignition time of the experimental samples was shortened, the peak heat release rate and the average heat release rate in 300 s increased, and the peak appeared earlier. The ignition time of the carbon fiber/epoxy foam laminate is the shortest, and the peak of heat release rate is the earliest. Carbon fibers inhibit the pyrolysis and combustion of epoxy resin. The inhibition is manifested in the delay of ignition, heat release, and peak time of the heat release rate.

(2) After combustion of carbon fiber/epoxy bidirectional woven fabric, carbon fiber bundles are arranged tightly. This tight alignment structure hinders the contact between epoxy resin and oxygen. Dense carbon fiber bundles can effectively inhibit the formation of melting droplets and splashing during combustion. The carbon layer formed by combustion of carbon fiber/epoxy bidirectional woven fabric and the dense and uniform spongy structure formed on the whole surface can prevent oxygen diffusion to the epoxy resin surface. This structure also prevents the pyrolysis of flammable gases and liquid vapors from spreading into the combustion zone. Thereby, heat transfer from the combustion zone to epoxy resin is limited. It plays a role in suppressing combustion.

(3) The thermal models of ignition time and heat radiation flux of four experimental samples were obtained. The theoretical critical heat radiation fluxes of the four experimental samples are $12.12\ kW\ m^{-2}$, $13.21\ kW\ m^{-2}$, $11.12\ kW\ m^{-2}$, and $0.93\ kW\ m^{-2}$, respectively.

(4) With the increase in heat radiation flux, the mass residue rate of the experimental sample decreases gradually. The residual mass fraction of the carbon fiber/epoxy foam laminate is lower than that of carbon fiber/epoxy bidirectional woven fabric and carbon fiber/epoxy prepreg under all thermal radiation fluxes. The carbon fiber/epoxy foam laminate has a faster burning rate than carbon fiber/epoxy bidirectional woven fabric and carbon fiber/epoxy prepreg.

(5) The pyrolysis of the epoxy resin matrix can be divided into two stages. The pyrolysis of carbon fiber/epoxy bidirectional woven fabrics can be divided into three stages. Its first and second stages are the two decomposition stages of the epoxy resin matrix. The third stage is the decomposition of carbon fibers. The heating rate has a significant effect on the pyrolysis process. With the increase in heating rate, the maximum weight loss rate temperature moves toward high temperature. The apparent activation energies calculated by the Kissinger method and Flynn-Wall-Ozawa method are basically the same. It shows that the thermal stability of carbon fiber/epoxy composites with this kind of epoxy resin matrix is high. Due to the existence of the foam core material, the cushioning function of the carbon fiber/epoxy foam laminate is enhanced. However, its thermal stability is reduced. The carbon fiber/epoxy foam laminate is the most easily pyrolyzed material. At the same temperature, the weight loss of carbon fiber/epoxy prepreg is the least and the weight loss of the carbon fiber/epoxy foam laminate is the most. This shows that the thermal stability of carbon fiber/epoxy prepreg is the strongest, followed by carbon fiber/epoxy bidirectional woven fabric. The thermal stability of the carbon fiber/epoxy foam laminate is weak.

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REFERENCES

1. Z. H. Hua, X. J. Zhou, and J. Z. Liu, “Morphology of pores in carbon fiber reinforced plastics,” Acta Mater. Compositae Sin. 22(6), 103–107 (2005).
2. W. Liu, T. J. Zhang, and J. W. Bao, “Effects of epoxy resin cross-linked structure characteristics on longitudinal compressive performance of carbon fiber reinforced composites,” J. Aeronaut. Mater. 36(1), 75–80 (2016).
3. L. Liu, C. Jia, and J. He, “Interfacial characterization, control and modification of carbon fiber reinforced polymer composites,” Compos. Sci. Technol. 121(1), 56–72 (2015).
4. L. Wu, “The application extent of advanced composite materials: Technology markets of ACM application in aeronautics, astronautics and civil aviation,” New Chem. Mater. 40(1), 4–9 (2012).
5. J. Hu, X. X. Li, and T. M. Zhang, “Design optimization on torsion property of carbon-fiber composite drive shaft,” Acta Mater. Compositae Sin. 26(6), 177–181 (2009).
6. N. Spiccia, M. C. Hawley, and M. Misra, “Characterization of natural fiber surfaces and natural fiber composites,” Composites, Part A 39(10), 1632–1637 (2008).
7. F. I. Palmieri, M. A. Belcher, and C. J. Wohlf, “Laser ablation surface preparation for adhesive bonding of carbon fiber reinforced epoxy composites,” Int. J. Adhes. Adhes. 68, 95–101 (2016).
8. W. Maria, W. Dorota, and G. Weronika, “Functionalization effect on physico-mechanical properties of multi-walled carbon nanotubes/composites,” Polym. Adv. Technol. 22, 48–59 (2011).
9. A. P. Mouritz, “Post-fire flexural properties of fibre-reinforced polyester, epoxy and phenolic composites,” J. Mater. Sci. 37(7), 1377–1386 (2002).
10. H. Yuan, C. G. Wang, and W. B. Lu, “Liquid-phase oxidation modification of pan-based carbon fiber surface,” J. Aeronaut. Mater. 32(2), 65–68 (2012).
11. M. Kim, D. H. Sung, and K. H. Kong, “Characterization of resistive heating and thermoelctric behavior of discontinuous carbon fiber-epoxy composites,” Composites, Part B 90, 37–44 (2016).
12. D. Quang Dao, R. Thomas, and L. Jocelyn, “Thermal degradation of epoxy resin/carbon fiber composites: Influence of carbon fiber fraction on the fire reaction properties and on the gaseous species release,” Fire Mater. 40, 27–47 (2014).
13. N. Régnier and S. Fontaine, “Determination of the thermal degradation kinetic parameters of carbon fibre reinforced epoxy using TG,” J. Therm. Anal. Calorim. 64(2), 789–799 (2001).
14. T. Shimokawa, Y. Kakuta, and Y. Hamaguchi, “Static and fatigue strengths of a G40-800/5260 carbon fiber/bismaleimide composite material at room temperature and 150 C,” J. Compos. Mater. 42(7), 655–679 (2008).
15. B. Fiedler, A. Gagel, and T. Hobbsbrunken, “Modelling of the transverse strength of fibre reinforced epoxy composite at low and high temperature,” Compos. Interfaces 12(3-4), 379–394 (2005).
16. S. Lee, P. Gaudert, and M. Plamondon, “Effect of elevated temperature spikes on the mechanical properties of a carbon fibre epoxy composite,” J. Visualization Soc. Jpn. 28, 28–31 (1993).
19. B. Chen, H. Wan, and J. Y. Mu, “Ablative mechanism of carbon-fiber/epoxy composite irradiated by repetition frequency laser,” High Power Laser Part. Beams 20(4), 547–552 (2008).

20. W. Fan and J. L. Li, “Effects of thermo-oxidative aging on flexural properties of carbon fiber fabric reinforced polymer matrix composites,” Acta Mater. Compositae Sin. 32(5), 1260–1270 (2015).

21. P. Perret, B. Schartel, and K. Stöß, “Novel DOPO-based flame retardants in high-performance carbon fibre epoxy composites for aviation,” Eur. Polym. J. 47(5), 1081–1089 (2011).

22. W. Gu, G. C. Zhang, and S. L. Dong, “Study on the formation of the carbonaceous layer of flame retarding coating and its flame retarding mechanism,” J. Xi’an Shiyou Univ. 21(4), 75–79 (2006).

23. E. Mikola and I. S. Wichman, “On the thermal ignition of combustible materials,” Fire Mater. 14(3), 87–96 (1989).

24. J. Drysdale, An Introduction to Fire Dynamics, 3rd ed. (John Wiley and Sons, Chichester, 2011).

25. R. Huo, X. F. Cheng, and J. S. Xie, “Some discussions on fire behavior in cigarette factories and its proper detect techniques,” China Saf. Sci. J. 5, 155–159 (1995).

26. M. S. Ahmad, M. A. Mehmood, and S. Taqvi, “Pyrolysis, kinetics analysis, thermodynamics parameters and reaction mechanism of Typha latifolia to evaluate its bioenergy potential,” Bioresource Technol. 245, 491 (2017).

27. V. Babrauskas, “Estimating room flashover potential,” Fire Technol. 17(1), 94–103 (1981).

28. B. Szolnoki, K. Bocz, and P. L. Sóti, “Development of natural fibre reinforced flame retarded epoxy resin composites,” Polym. Degrad. Stab. 119, 68–76 (2015).

29. R. Bacaloglu and M. Fisch, “Degradation and stabilization of poly(vinyl chloride). V. Reaction mechanism of poly(vinyl chloride) degradation,” Polym. Degrad. Stab. 47(1), 33–57 (1995).

30. L. S. Tang, Q. M. Liu, Y. Q. Li, and C. Zhang, “Flame retardancy of new phosphorus-nitrogen flame retardant on PA6,” China Plast. Ind. 44(1), 33–57 (2011).

31. N. Yang and K. Song, “Experimental study on effects of burning behaviours of flooring materials caused by external heat radiation,” Fire Sci. Tecnol. 300, 59–86 (2007).

32. Y. Jia, “Comparative research on combustion performance of several wood floor,” Fire Technol. Prod. Info. 11, 44–49 (2007).

33. R. Chen, S. Lu, C. Li, Y. Ding, B. Zhang, and S. Lo, “Correlation analysis of heat flux and cone calorimeter test data of commercial flame-retardant ethylene-propylene-diene monomer (EPDM) rubber,” J. Therm. Anal. Calorim. 123(1), 545–556 (2015).

34. U. A. Khashaba, “Nanoparticle type effects on flexural, interfacial and vibration properties of GFRE composites,” Chin. J. Aeronaut. 29(2), 520–533 (2016).

35. G. Archambault, B. Jodoin, and S. Gaydos, “Metalization of carbon fiber reinforced polymer composite by cold spray and lay-up molding processes,” Surf. Coat. Technol. 300, 78–86 (2016).

36. D. Quang, J. Luche, and F. Richard, “Determination of characteristic parameters for the thermal decomposition of epoxy resin/carbon fibre composites in cone calorimeter,” Int. J. Hydrogen Energy 38, 8167 (2013).

37. M. Miranda, F. Pinto, and I. Gulyurtlu, “Pyrolysis of rubber tyre wastes: A kinetic study,” Fuel 103(1), 542–552 (2013).

38. Z. Q. Chen, H. B. Liu, and Y. D. He, “Thermal characteristics of high char yield phenolic resin,” Eng. Plast. Appl. 34(11), 56 (2006).

39. H. Z. He, Z. Y. Luo, and K. F. Cen, “Study on dynamic reaction parameters of anthracite combustion by using different thermoanalytical methods,” Power Eng. 25, 493 (2005).

40. N. Ren and J. J. Zhang, “Progress in datum treatment methods of thermal analysis kinetics,” Prog. Chem. 18, 410 (2006).

41. K. Kong, R. K. Cheedarala, and M. Kim, “Electrical thermal heating and piezoresistive characteristics of hybrid CuO–woven carbon fiber/vinyl ester composite laminates,” Composites, Part A. 85, 103–112 (2016).

42. M. Miranda, I. Cabrera, and F. Pinto, “Mixtures of rubber tyre and plastic wastes pyrolysis: A kinetic study,” Energy 58(9), 270–282 (2013).

43. A. Prakash and V. R. Rajadurai, “Thermo-mechanical characterization of siliconized E-glass fiber/hematite particles reinforced epoxy resin hybrid composite,” Appl. Surf. Sci. 384, 99–106 (2016).

44. R. Z. Hu, S. L. Gao, and F. Q. Zhao, Thermal Analysis Kinetics, 2nd ed. (Science Press, Beijing, 2008).

45. A. Toldy, A. Szlancsik, and B. Szolnoki, “Reactive flame retardancy of cyanate ester/epoxy resin blends and their carbon fibre reinforced composites,” Polym. Degrad. Stab. 128, 29–38 (2016).

46. C. Huang, H. T. Yang, and X. Y. Li, “Research and development of Kissinger equation,” Chin. J. Explos. Propellants 37(1), 26–30 (2014).