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Research article

Study on combustion characteristics of glass fiber/phenolic resin composites

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ABSTRACT

In order to study the combustion characteristics of glass fiber/phenolic resin composites, a conical calorimeter was used to explore the combustion characteristics of glass fiber/phenolic resin composites in an aircraft frame under different thermal radiation intensities, and the fire hazard of the materials was evaluated by evaluation index, and the limiting oxygen index at different temperatures was explored by combining the high temperature oxygen index meter. The test results show that when the ambient temperature increases from 20 °C to 220 °C, the limiting oxygen index first increases from 86.6 % to 93.7 %, and then decreases to 84.4 %. The oxygen consumption and CO_2 release increase with the increase of thermal radiation intensity during combustion, and the release of CO decreases with the increase of thermal radiation. The heat release rate curve of the test material has only 1 enhancement peak. The heat radiation intensity increased from 50 kW/m^2 to 70 kW/m^2, and the peak heat release rate of the test material combustion increased from 64.7 kW/m^2 to 100.7 kW/m^2. The rate of mass loss of materials accelerates with the increase of thermal radiation intensity; As the intensity of thermal radiation increases, the fire hazard of the material increases.

1. Introduction

Composite materials have the advantages of light weight, good mechanical properties, low cost and high degree of environmental integration. In the aerospace industry, composites are widely used as an alternative to metal elements [1–3]. Phenolic composites account for 80%–90 % of the interior furnishings of modern civil airliners. Mainly used for ceilings, interior wall panels, kitchen structures, floor structures and overhead storage boxes. However, once the resin used in the composite material is exposed to the fire environment, it has relatively high flammability, and a large amount of heat and toxic gases are released during the combustion process, which increases the difficulty of personnel evacuation in the fire environment and poses a serious threat to people's lives. This is a major factor hindering their widespread acceptance in the aerospace industry. Therefore, it is very important to study the combustion characteristics of carbon fiber/phenolic resin composites [4–8].

While several methods are available for measuring the thermal degradation and combustion properties of solids [8], conical

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calorimetry measurements are the most reliable and commonly used technique [9,10]. Therefore, many investigations describe such a technique to measure the thermal degradation and fire behavior of several structural composite materials, and a large database is available pertaining to their time to ignition, heat release rates (HRRs), combustion toxicity and so on [5,11–24]. The decisive factor in the combustion and ablation behavior of glass fiber/phenolic composites is the stability and integrity of the carbonaceous residue formed during combustion. This coke acts as an isolation barrier, protecting most of the material and reducing the overall combustion rate [25].

Rui et al. The ignition and combustion characteristics of fiber-reinforced phenolic composites were studied by cone calorimeter experiments. Various parameters were measured and given, including ignition time, mass loss and mass loss rate (MLR), heat release rate (HRR), and concentration of carbon dioxide and carbon monoxide [26]. Wang et al. The pyrolytic combustion characteristics and reaction kinetics of epoxy resin matrix and epoxy-based glass fiber/epoxy composites were studied by conical calorimetry and thermogravimetry [27]. Chuan et al. The oxidation pyrolysis behavior of epoxy resin in fiber/epoxy composites was studied by thermogravimetric device and fixed-bed reactor, respectively [28]. Chen et al. Thermogravimetric analysis (TGA), in situ Fourier transform infrared (FTIR) and online TGA-FTIR mass spectrometry (MS) analysis methods were used to study the pyrolysis kinetics, volatilization products and reaction mechanism of a typical waste thermosetting phenolic fiber reinforced plastic (phenolic FRP) [29].

At present, many scholars have studied the combustion characteristics and pyrolysis characteristics and laws of different types of composite materials, and there are few studies on the combustion characteristics of carbon fiber/phenolic resin composites. In this paper, the combustion characteristics of carbon fiber/phenolic resin composites in different fire environments were tested by cone calorimetry and high temperature oxygen index meter, and the changes of flue gas release, heat release rate, mass loss rate, limiting oxygen index and other parameters were explored, and the fire hazard was calculated and evaluated by these parameters. The materials on civil airliners need to pass strict fireproof airworthiness verification before they can be used, the international fireproof airworthiness requirements are becoming increasingly stringent, the fire performance of carbon fiber phenolic composite materials lacks systematic testing, and its combustion characteristics and mechanism research are not perfect. Its combustion characteristics are studied, and the data and theoretical support for the fireproof and airworthiness of composite materials of civil passenger aircraft are provided.

2. Experiment

2.1. Materials

The glass fiber/phenolic resin composite material for an aircraft frame is selected, the grade is ML6038/300 T, and the material layer method is shown in Table 1. According to the requirements of the test content, the samples required for the conical calorimetry test and the high temperature oxygen index test were prepared respectively.

2.2. Experimental instruments

Guangzhou European and American land instruments and equipment are limited firm Cone calorimeter,FTT-0242; High temperature oxygen index meter,FTT-OL-1402072.

2.3. Characterization

High temperature oxygen index test: tested according to ISO 4589–2:2017 and ISO 4589–3:2017 [30,31], using temperature increase from 20 °C to 50 °C, 100 °C, 150 °C and 220 °C, respectively, to simulate the real fire temperature; Flue gas release and combustion test: according to BS ISO 5660–1:2015 standard test, electric spark ignition, thermal radiation intensity selected 50, 60, 70kW/m_2 [32]. Before the test, the test specimens were pretreated for 24 h at a temperature of (21 °C ± 2 °C) and a relative humidity of (55 ± 10) %.

3. Results and discussion

3.1. LOI analysis

The limiting oxygen index is the minimum oxygen concentration that just maintains the combustion of the material when oxygen and nitrogen mixtures are introduced, and is expressed as a percentage by volume. It is often used to quantify the flammability of organic polymers and composites to characterize the fire performance of materials, and the higher the limiting oxygen index, the less

Table 1
Laying method of glass fiber/phenolic resin composite.

Specimen grade	Ply method	Fiber volume fraction (%)	Thickness (mm)	Molding process
ML6038/301 F	[0]	62	2	Autoclave

Table 2
LOI of glass fiber/phenolic resin.

Temperature (°C)	LOI (%)
20	86.6
50	89.1
100	93.7
150	87.2
220	84.4

flammable the material is. The limiting oxygen index is generally expressed as LOI (Limit Oxygen Index). After the test, the ambient and high temperature limiting oxygen indices of the glass fiber/phenolic resin composites were calculated as shown in Table 2.

Table 2 shows the limiting oxygen index of glass fiber/phenolic resin composites is inconsistent with temperature changes, first reaching a maximum of 93.7 % at room temperature with temperature increase to 100 °C, and after exceeding 100 °C, due to the reduction of heat required to maintain decomposition and combustion, the limiting oxygen index begins to decrease to 84.4 % of 220 °C, which is 90 % of the room temperature limiting oxygen index value. This is due to the fact that the oxygen index of resin matrix composites increases with their ability to produce carbon in fire, and the formation of carbon consumes combustible volatiles, which in turn increases the concentration of oxygen required to maintain flame combustion.

3.2. Flue gas analysis

Smoke and toxic gases in fire are the main reasons affecting personnel evacuation and life safety, so the smoke production performance of composite materials during burning is another important parameter to measure the fire safety of materials. Fig. 1 shows the change of O_2, CO and CO_2 emissions of glass fiber/phenolic composites when burned under different thermal radiation intensities.

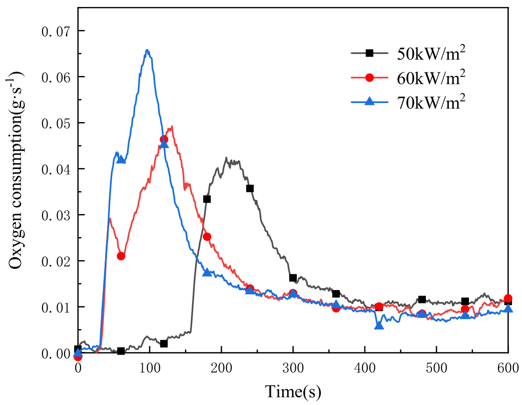
Fig. 1(a) shows that the fiberglass/phenolic resin siding plate burns violently to produce a single peak. The reaction process has been accompanied by the consumption of O_2, and with the increasing intensity of thermal radiation, the consumption of O_2 begins to increase and the consumption rate accelerates. Fig. 1(b) and (c) shows that as the intensity of thermal radiation increases, the rate of CO_2 generation begins to accelerate and the peak time advances. It has been accompanied by a small amount of CO and a large amount of CO_2 production, due to the phenolic resin heat release combustible gas to reach the combustible concentration, the main products at this time are CO and CO_2, with the accumulation of CO content and heat in the environment, CO combustion to generate CO_2, the two different ways of producing CO_2 work together to make the CO_2 release quickly peak. When the heat radiation intensity was 60 kW/m^2 and 70 kW/m^2, the consumption of O_2, CO release and CO_2 emission were consistent. When the heat radiation intensity is 50 kW/m^2, the consumption of O_2 and CO_2 release time are significantly lagged, and the CO release increases significantly at 300s, because the thermal radiation intensity is not enough to pyrolyze the phenolic resin in the first time, the heat accumulation makes the combustible gas reach the combustible concentration, after the flame is extinguished, the carbon components in the composite material and the oxygen molecules in the air are incompletely combusted, and CO is continuously generated, so that the CO release continues to increase until the end of the test.

3.3. CONE analysis

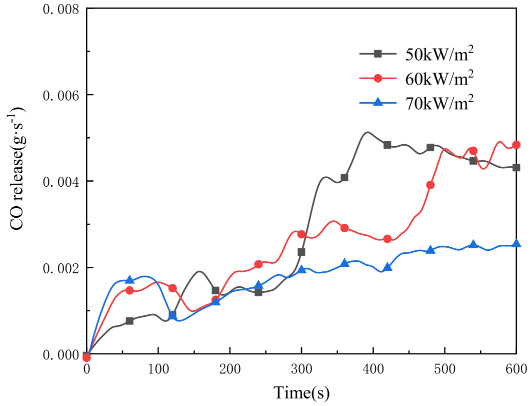
3.3.1. Heat release rate (HRR)

The heat release rate (HRR) is one of the most important parameters in fire behavior and plays a crucial role in the occurrence and development of the flame propagation process [33]. Fig. 2 shows the HRR curve of a fiberglass/phenolic composite.

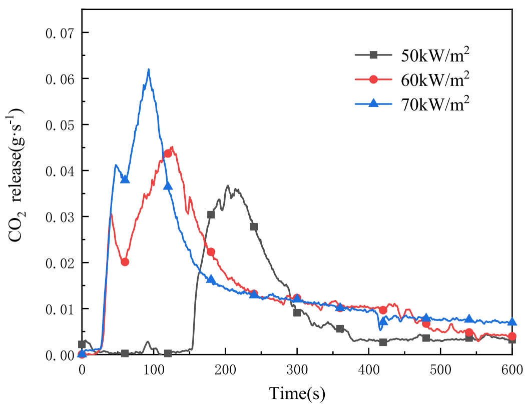
Fig. 2 shows that with the continuous improvement of heat radiation intensity, its HRR is on the rise, and when the thermal radiation intensity is 50 kW/m^2, 60 kW/m^2 and 70 kW/m^2, the pHRR is 64.7 kW/m^2, 70.0 kW/m^2, 100.7 kW/m^2, and the pHRR occurrence time is 207s, 131s, 97s, respectively, as shown in Table 3. The wall plate material is subjected to the continuous action of thermal radiation, and the accumulated heat makes the weak bond of the upper side group of the phenolic backbone in the glass fiber/phenolic resin wall plate begin to break, and the breaking rate of the weak side group bond on the partial phenolic main chain exceeds the cracking reaction rate of the main chain, so that a small amount of phenolic main chain is retained in the form of carbon. This carbon layer has a certain flame retardant effect, which can effectively prevent the flame from continuing to spread and burn, so the glass fiber/phenolic resin wall plate material will not burn when the heat radiation intensity is low, and the phenolic resin in the middle layer gradually decomposes to release combustible gas. The combustible gas does not reach the combustion concentration of phenolic resin, releasing only a small amount of heat. With the increase of heat radiation intensity, phenolic resin pyrolysis is violent, forming an extremely thin carbon layer that is not enough to completely block heat, the release of combustible gas reaches a certain value, phenolic resin begins to burn, glass fiber tow and the formed carbon layer weaken the progress of the reaction, HRR drops rapidly until it is extinguished, and obvious pHRR appears. When the heat radiation intensity is 60 kW/m^2 and 70 kW/m^2, the carbon layer cannot be blocked from the release of combustible gas when it is burned, so there is a weak open flame on the surface of the material that continues to burn, and the HRR remains basically unchanged.



(a)



(b)



(c)

Fig. 1. (a) Oxygen consumption, (b) CO release, (c) CO_2 release.

3.3.2. Total heat release (THR)

Fig. 3 shows that THR increases significantly as the intensity of thermal radiation increases. When the thermal radiation intensity was 50 kW/m^2, 60 kW/m^2 and 70 kW/m^2, the THR was 11.6 MJ/m^2, 13.9 MJ/m^2 and 14.6 MJ/m^2, respectively. The reasons for the increase in THR are the same as for HRR.

3.3.3. Rate of mass loss

Mass loss is another important fire characteristic and an important parameter for post-fire safety evaluation and analysis, which gives a quantitative characterization of the amount of material that decomposes in a fire. In general, the trend of mass loss rate with time under different thermal radiation intensities is similar to the trend of heat release rate, that is, the mass loss rate of the material when it is burned is not constant. The rate of mass loss varies when materials ignite, burn, coke form, and burn-through. Therefore, it is very important to study the law of the change of composite mass loss rate with the increase of fire exposure time. Fig. 4 shows the mass loss rate curve of a glass fiber/phenolic composite at different thermal radiation intensities.

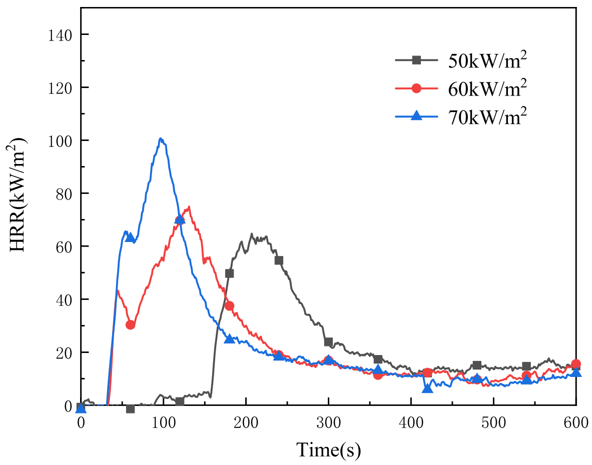


Fig. 2. HRR curve of a fiberglass/phenolic composite.

Table 3
Main measurement parameters of glass fiber/phenolic resin.

Thermal radiation intensity (kW/m^2)	pHRR (kW/m^2)	Time to pHRR (s)	Ignition time (s)	Burning time (s)
50	64.7	207	172	194
60	70.0	131	33	567
70	100.7	97	31	569

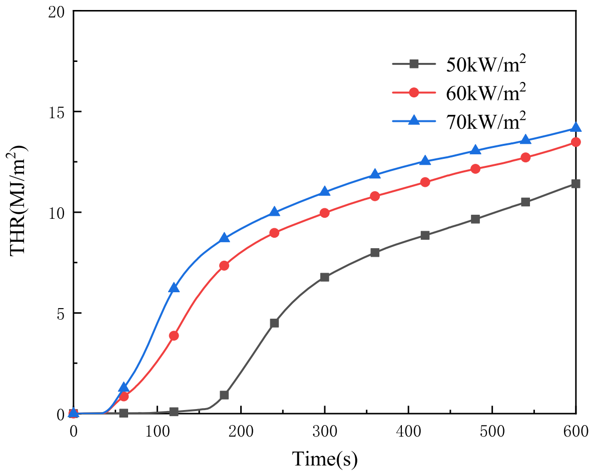


Fig. 3. THR curve of a fiberglass/phenolic composite.

Fig. 4 shows that the higher the intensity of thermal radiation, the earlier and greater the peak of the mass loss rate. The loss of mass is caused by the thermal interpretation of the combustible gas released by phenolic resins. The formation and fracture of the carbon layer are completed at almost the same time, and after the mass loss rate reaches the peak due to the decomposition of the phenolic resin matrix, with the inhibition of the phenolic resin matrix by the glass fiber tow and the carbon layer formed after combustion and the heat resistance of the phenolic resin matrix, the mass loss rate decreases with time until it is stable and unchanged.

3.4. Fire hazard assessment

The fire hazard of fiberglass/phenolic siding was assessed by the Fire Performance Index (FPI) and the Fire Growth Index (FGI), defined as the ratio of ignition time to peak heat release rate, the smaller the FPI value, indicating the faster the sample ignition time and the higher the fire hazard, FGI defined as the ratio of the peak heat release rate to the time to reach the peak. The higher the FGI

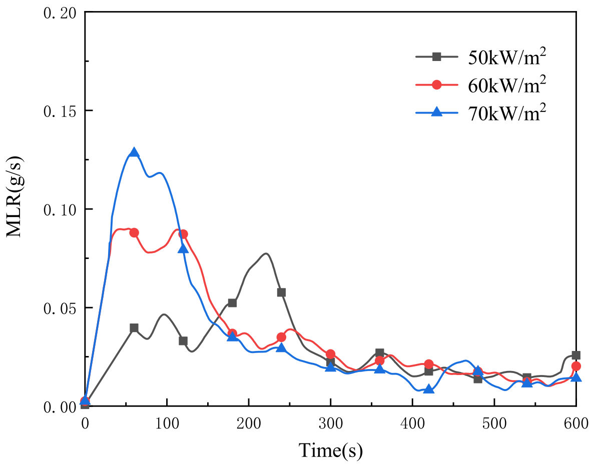


Fig. 4. Mass loss rate curve.

Table 4
Fire performance index and fire growth index of glass fiber/phenolic resin.

Thermal radiation intensity (kW/m2)	FPI	FGI
50	2.658	0.313
60	0.471	0.534
70	0.308	1.038

value and the shorter the time required to reach the peak of the heat release rate, the greater the fire hazard of the material. The calculation formula of FPI and FGI is:

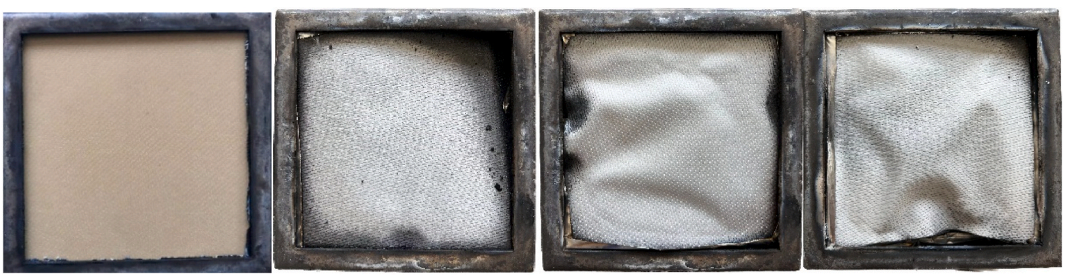
$$FPI = \frac{T_i}{pHRR} \tag{1}$$

$$FGI = \frac{pHRR}{T_x} \tag{2}$$

where *pHRR* is the peak heat release rate, kW/m^2; T_i is the ignition time, s; T_x is the time to pHRR, s.

Table 4 shows that with the increase of thermal radiation intensity, the FPI value decreases and the FGI value tends to increase. The thermal radiation intensity increased from 50 kW/m^2 to 70 kW/m^2, the FPI value of glass fiber/phenolic resin materials decreased from 2.658 to 0.308, and the FGI value increased from 0.313 to 1.038. The calculation results show that after the heat radiation intensity increases, the fire grows faster and is more dangerous. During the test, the test phenomenon of the material under different thermal radiation intensity was observed, and after the thermal radiation intensity increased, the flame height increased and the fire growth accelerated.

Fig. 5 shows that a weak carbon layer forms on the surface of the material at a thermal radiation intensity of 50 kW/m^2, and the carbon layer is completely destroyed at a thermal radiation intensity of 60 kW/m^2 and 70 kW/m^2. Therefore, as the intensity of thermal radiation increases, the degree of damage is greater and the reaction is more violent. The test results are consistent with the settlement results of FPI and FGI, that is, the fire risk is greater after the heat radiation intensity increases.



(a)Before the test (b)50kW/m^2 (c)60kW/m^2 (d)70kW/m^2

Fig. 5. Reaction residues of different thermal radiation intensities.

4. Conclusions

In this paper, the combustion performance of glass fiber/phenolic resin composites tested by conical calorimetry at preset heat fluxes of 50 kW/m^2, 60 kW/m^2, and 70 kW/m^2 is presented, from which the following conclusions can be drawn:

- LOI reaches a maximum of 93.7 % with temperature until it reaches 100 °C, and after 100 °C, LOI begins to decrease to 84.4 % of 220 °C, which is 90 % of the room temperature limiting oxygen index value.
- As the intensity of thermal radiation increases, oxygen consumption begins to increase and the rate of consumption increases. The rate of CO_2 production begins to accelerate and peaks earlier. When the thermal radiation intensity is 50 kW/m^2, the consumption of O_2 and the release time of CO_2 lag significantly, and the amount of CO release increases significantly at 300s.
- With the continuous improvement of heat radiation intensity, its HRR showed an upward trend, the peak heat release rate increased, and the ignition time was advanced. When the heat radiation intensity increases from 50 kW/m^2 to 70 kW/m^2, the peak heat release rate increases from 64.7 kW/m^2 to 100.7 kW/m^2, an increase of 1.6 times.
- The mass loss rate basically corresponds to the higher the intensity of thermal radiation, the earlier the time to peak, and the larger the peak.
- With the increase of thermal radiation intensity, the FPI value decreases, and the FGI value tends to increase. The thermal radiation intensity increased from 50 kW/m^2 to 70 kW/m^2, the FPI value of glass fiber/phenolic resin materials decreased from 2.658 to 0.308, and the FGI value increased from 0.313 to 1.038. After the glass fiber/phenolic resin composite is burned, the carbon layer is obviously burned through. It shows that the intensity of heat radiation increases and the fire risk increases.

CRediT authorship contribution statement

Kaituo Zhang: Data curation, Writing – original draft. **Zhi Wang:** Writing – review & editing. **Jiacheng Nie:** Investigation. **Fang Wen:** Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:Zhi Wang reports financial support was provided by National Natural Science Foundation of China. Zhi Wang reports a relationship with National Natural Science Foundation of China that includes: funding grants.

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