

DETERMINATION OF CHARACTERISTIC PARAMETERS FOR THE THERMAL DECOMPOSITION OF EPOXY RESIN/CARBON FIBER COMPOSITES IN CONE CALORIMETER

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ABSTRACT

The thermal degradation of two epoxy resin/carbon fiber composites which differ by their volume fractions in carbon fiber (56 and 59 vol%.) was investigated in cone calorimeter under air atmosphere with a piloted ignition. The external heat flux of cone calorimeter was varied up to 75 kW.m⁻² to study the influence of the carbon fiber amount on the thermal decomposition of those composites. Thus, main parameters of the thermal decomposition of two different composites were determined such as: mass loss, mass loss rate, ignition time, thermal response parameter, ignition temperature, critical heat flux, thermal inertia and heat of gasification. As a result, all the parameters that characterize the thermal resistance of composites are decreased when the carbon fiber volume fraction is increased.

Keywords: epoxy resin, carbon fiber, thermal degradation, cone calorimeter, composite materials, hydrogen storage.

NOMENCLATURE

t_{ig}	ignition delay, s
λ	thermal conductivity, kW.m ⁻¹ .K ⁻¹
ρ	density, kg.m ⁻³
C_p	thermal capacity, kJ.g ⁻¹ .K ⁻¹
T_{ig}, T_{∞}	ignition temperature, ambient temperature, K
T_v	vaporization temperature, K
$\dot{q}''_{e}, \dot{q}''_{fl}$	external heat flux, flame heat flux, kW.m ⁻²
TRP	thermal response parameter, kW.s ^{1/2} .m ⁻²
L	heat of gasification, kJ.g ⁻¹
\dot{m}''	mass loss rate per unit of area, g.s ⁻¹ .m ⁻²
ε	emissivity of material
σ	Stefan-Boltzmann constant (56.7×10 ⁻¹² kW.m ⁻² .K ⁻⁴)
P	thermal inertia (kW ² .s.m ⁻⁴ .K ⁻²)

INTRODUCTION

Among the several existing hydrogen storage methods, the high-pressure fully wrapped composite cylinder is currently the most common option for fuel cell electric vehicle application, because of its light weight and good mechanical properties which allow the storage of a large volume of hydrogen at a very high pressure. The epoxy resin/carbon fiber composite laminate is the load-bearing unit in the hydrogen storage vessel. The use of epoxy resin results in excellent mechanical performance, chemical and electrical resistance and low shrinkage on cure [1]. A few millimeters thick liner is also used in the hydrogen storage vessel for gas tightness. The fire safety strategy of a fully wrapped composite

cylinder consists in preventing the cylinder from the burst by releasing hydrogen through a thermal pressure release device (TPRD), which is activated by a thermo-fusible material. Reviews of the accidents of the CNG (Compressed Natural Gas) and H₂ composite cylinder [2, 3] showed that overpressure and resulting fragments from the cylinder burst could have catastrophic consequences. In addition, the burst accidents are mainly caused by a localized fire or the improper design of the TPRD opening size. In order to define an appropriate TPRD design and to estimate the need of a specific thermal protection cover, a better understanding of the thermal behavior of the epoxy resin/carbon fiber composites in fire is critical.

The literature on the thermal properties (thermal conductivity, thermal capacity and thermal diffusivity) of the epoxy resin/carbon fiber composites is scarce [4 – 6]. In general, some parameters influence the thermal properties of the composites such as: decomposition temperature, carbon fiber fraction [4, 5], and nature of carbon fiber [4, 6]. Pilling et al. [4], Knibbs et al. [5], Shim et al. [6] showed that thermal conductivity (λ) increased significantly by increasing the temperature and the carbon fiber fraction. It can be deduced that the increases of temperature and carbon fiber fraction induce an increase of heat transfer within the composites, favor their decomposition, and so reduce the thermal resistance of materials in fire.

Recently, the thermal degradation of the epoxy resin/carbon fiber composites has drawn the attention of several researchers [1, 7 – 9]. Many parameters characterizing the composite materials thermal behavior have been discussed: mass loss, activation energy (E_a) [7 – 9], heat release rate (HRR), limiting oxygen index (LOI) [1] and released gases from the oxidation [8], etc. However, most of studies were performed at the elementary level with well-controlled conditions by using thermogravimetric analysis (TGA), differential thermal analysis (DTA) or differential scanning calorimetry (DSC). For example, Régnier and Fontaine [7] evaluated the decomposition activation energy of the epoxy resin/carbon fiber composite containing 55wt% of carbon fibers. Three-step mass loss in oxidative atmosphere was observed during dynamic thermogravimetric analysis (TGA): epoxy resin devolatilisation, oxidation of non-volatile residues formed during the first step and carbon fibers degradation. The temperatures corresponding to the three stages were about 215, 500 and 615 °C, respectively. This three-step mass loss decomposition was confirmed by Noël et al. [9] by using differential scanning calorimetry (DSC) with composites reinforced with 58 wt% of carbon fibers.

To our knowledge, there has been no attempt yet to conduct a systematic study of characteristics for the thermal decomposition of epoxy resin/carbon fiber composites using larger scale tests such as cone calorimeter, fire propagation apparatus (FPA), or radiant panels. These test results lead to a better knowledge of composite thermal behavior in realistic cases of fire accident.

The aim of this paper is to investigate the influence of carbon fibers fraction on thermal decomposition of epoxy resin/carbon fiber composites in cone calorimeter apparatus. Several parameters that characterize the composites thermal decomposition are determined such as: mass loss, mass loss rate, piloted ignition time, thermal response parameter, ignition temperature, thermal inertia and heat of gasification.

1 - MATERIALS

The commercial composites were provided by EADS Composites Aquitaine in a pre-preg form (carbon fiber pre-impregnated with epoxy resin). The composite consists of an epoxy resin with a hardener, and no flame retardant and reinforced by different volume fractions of carbon fibers (56 and 59 vol%). This composite is representative of the major part of this kind of composite commercialized. An elementary analysis of the epoxy resin and the composite epoxy resin reinforced with 56 and 59 vol% of carbon fibers was performed by coupling catharometry and ND-IR detection. Table 1 presents the composition in mass fraction along with the analysis methods. The elementary analysis was repeated three times and the maximal deviation for each element was of ± 0.4 wt%. The analysis showed that the materials contained essentially four main elements C, O, H and N representing 100

wt%, 98.4 wt% and 98.6 wt% of the total mass for the epoxy resin and the composite with 56 and 59 vol% carbon fibers, respectively. The difference of 1.6 and 1.4 wt% in composition for the two composites may be due to the presence of the other minor compounds such as ash. The presence of N-element in the epoxy resin results from the use of a hardener. Moreover, the addition of carbon fibers in the composites led to an increase of C and N atom amounts which may be due to the presence of the (–CN) chemical functions in the carbon fiber precursors during the fabrication of these epoxy resin/carbon fiber composites.

Table 1: Elementary mass fraction of the epoxy resin and the epoxy resin/carbon fiber composites

Element	Epoxy resin	Composite 56 vol% CF	Composite 59 vol% CF	Method of measurement
C	70.1%	81.6%	84.6%	Catharometry by transformation in CO ₂
O	17.0%	6.6%	5.4%	ND-IR by transformation in CO
H	8.7%	4.6%	2.9%	Catharometry by transformation in H ₂ O
N	3.1%	5.1%	5.4%	Catharometry by reduction in N ₂
Water	1.1%	0.5%	0.3%	Karl-Fischer
Residue	<0.1%	<0.1%	<0.1%	
Cl	0.1%	410 ppm	390 ppm	ND-IR detection
S	<10 ppm	<10 ppm	<10 ppm	

Some preliminary tests were performed to determine the main properties of the epoxy resin/carbon fiber composites such as: density, heat capacity, thermal conductivity and diffusivity at the ambient conditions (293 K and 1 atm.). All these tests were conducted with the composite containing 59 vol% of carbon fibers. The density (ρ) was calculated by measuring the mass and the volume of each composite sample. The specific heat capacity (C_p) was determined by differential scanning calorimetry (DSC). The thermal diffusivity (α) was measured by using a laser source and an infrared camera. Finally, the thermal conductivity (λ) was calculated from the heat capacity and the diffusivity.

As a result, the composite density (ρ) was $1472 \pm 20 \text{ kg.m}^{-3}$. The specific heat capacity (C_p) was $0.9 \text{ kJ.kg}^{-1}.\text{K}^{-1}$. The diffusivity (α) was measured in the parallel and the transverse direction of the carbon fibers, 2.75 ± 0.10 and $0.40 \pm 0.04 \text{ mm}^2.\text{s}^{-1}$, respectively. In the same way, the conductivity (λ) was found to be $3.30 \pm 0.30 \text{ W.m}^{-1}.\text{K}^{-1}$ in the parallel direction and $0.48 \pm 0.05 \text{ W.m}^{-1}.\text{K}^{-1}$ in the transverse direction of the carbon fibers.

2 - EXPERIMENTAL SETUP

The thermal degradation of epoxy resin reinforced by carbon fibers was studied in a cone calorimeter developed by Fire Testing Technology Limited (ISO 5660 standard [10]) under well-ventilated conditions. The plate samples were $100 \pm 0.5 \text{ mm}$ long \times $100 \pm 0.5 \text{ mm}$ wide \times $10.1 \pm 1.5 \text{ mm}$ thick and were exposed to external heat fluxes in the range $14\text{-}75 \text{ kW.m}^{-2}$. The objective was to increase the heat flux in order to reach a heat radiation representative of a fire, around 150 kW.m^{-2} . Because of the heater capacity, the external heat flux was limited at about 75 kW.m^{-2} . The sample initial mass was equal to $171.2 \pm 2.8 \text{ g}$ and $148.7 \pm 1.8 \text{ g}$ for the composites with 56 vol% and 59 vol% carbon fibers, respectively. Tests were carried out with a piloted ignition (spark ignition plug) positioned above the sample surface contained in the cone metal holder under air atmosphere and were repeated at least three times for each condition to confirm experimental result reproducibility. Mass loss, mass loss rate (MLR), piloted ignition time were recorded simultaneously. The apparatus, the instrumentation and the standard test procedure for the cone calorimeter were presented in detail in reference [10].

The temperature profile measurement during the thermal decomposition of each type of composite was also performed during this work. The results obtained allowed determining the ignition temperature (T_{ig}), and so calculating the material thermal inertia. This calculation details calculus will be presented in the following part. Two 1 mm diameter wire type K thermocouples were mounted

from the bottom to the top surface and to the middle-thickness surface of the composite sample to measure the temperature profiles (Fig. 1).

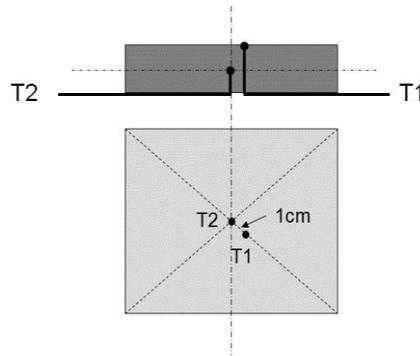


Figure 1. Thermocouple set-up

As can be seen in Fig. 1, the two thermocouples were located at the center or near the center of the sample, and the distance between the two thermocouple locations was set at 1 cm. The temperature measurement was repeated three times for each composite and the maximum range of the observed deviation was $\pm 20^\circ\text{C}$.

3 - RESULTS AND DISCUSSIONS

3.1 - Ignition time and temperature

The ignition time (t_{ig}) is one of critical parameters for the materials thermal resistance. The higher the ignition time value, the longer it takes for the material to heat up, ignite, and initiate a fire. The ignition time (t_{ig}) of the epoxy/resin composites was experimentally determined as the delay from the test start ($t = 0$) until the appearance of a supported flame on the material surface ($t = t_{ig}$). Theoretically, for the thermally thick materials and for the high external radiation levels, the ignition time is calculated by Eq. (1) [11]:

$$t_{ig} = \frac{\pi}{4} (\lambda \rho C_p) \left(\frac{T_{ig} - T_\infty}{\dot{q}''_e} \right)^2 \quad (1)$$

Fig. 2 presents the evolution of ignition time (t_{ig}) as a function of heat flux, for the latter increasing up to 75 kW.m^{-2} , for the composite epoxy resin reinforced with 56 and 59 vol% carbon fibers(CF).

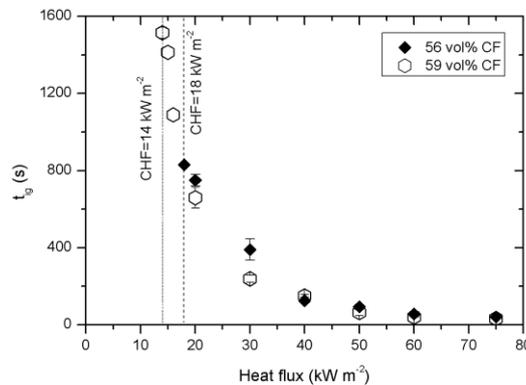


Figure 2. Evolution of ignition time as a function of heat flux up to 75 kW.m^{-2} for two epoxy resin/carbon fiber composites (56 and 59 vol% CF)

As can be seen on Fig. 2, the heat flux increase induced a rapid ignition time decrease. For example, ignition time (t_{ig}) of the composite with 56 vol% CF decreases from about 830 to 40 s when the heat flux increases from 18 to 75 $\text{kW}\cdot\text{m}^{-2}$. Similarly, for the composite with 59 vol% CF, t_{ig} decreases from about 1500 to 30 s when the radiation level increases from 14 to 75 $\text{kW}\cdot\text{m}^{-2}$. For both composites, the ignition time curves approach the vertical asymptotes which intercept the x-axis at a value corresponding to the critical heat fluxes (CHF) for each composite. The critical heat flux (CHF) is defined as the minimum value of heat flux for which the composite inflammation is observed (i.e. 14 $\text{kW}\cdot\text{m}^{-2}$ and 18 $\text{kW}\cdot\text{m}^{-2}$ for composite with 59 and 56 vol% of carbon fibers, respectively). Thus, CHF decreases from 18 to 14 $\text{kW}\cdot\text{m}^{-2}$ when the carbon fiber amount increases from 56 and 59 vol%, respectively. For the heat flux below these critical values, no inflammation was detected although a very slight mass loss is observed corresponding to a light devolatilisation of the material.

From the ignition time data, other critical parameters such as thermal response parameter (TRP) can be calculated. Theoretically, the relation between the square root of the inverse of the ignition time [$(1/t_{ig})^{1/2}$] and the heat flux allows calculating the thermal response parameter (TRP).

Fig. 3 displays $(1/t_{ig})$ (Fig 3-a) and $[(1/t_{ig})^{1/2}]$ (Fig 3-b) versus external heat flux for both composites with 56 and 59 vol% CF.

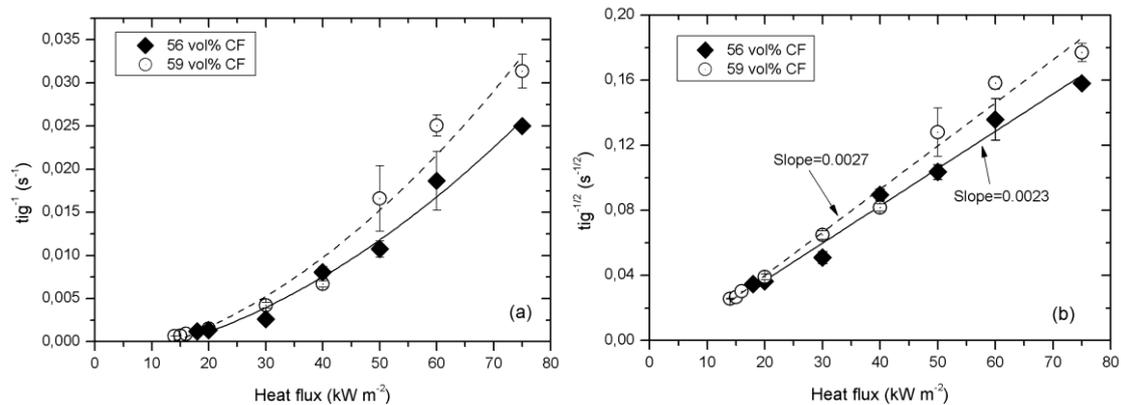


Figure 3. Ignition data for both epoxy resin/carbon fiber composites exposed to different heat fluxes up to 75 $\text{kW}\cdot\text{m}^{-2}$: (a) inverse of the ignition time; (b) square root of the inverse of the ignition time

For both types of epoxy resin/carbon fiber composites studied in this work, the plots of $(1/t_{ig})$ as a function of the external heat flux are not linear (Fig. 3-a). On the contrary, $[(1/t_{ig})^{1/2}]$ plots versus external heat flux are linear (Fig. 3-b). These observations allow concluding that the epoxy resin/carbon fiber composites are thermally thick materials. Indeed, while a thermally thick solid material is heated up, a temperature gradient is observed inside the sample. On the other hand, the temperature inside the sample is uniform in a thermally thin material.

In order to verify the thermally thick property of the epoxy/carbon composites, some experiments were conducted to measure the temperature profiles at the surface exposed to the cone calorimeter heat flux and at the middle-thickness of the sample, by using two thermocouples (as previously shown in Fig. 1). Thus, the thermocouple placed at the exposed surface allows also measuring the ignition temperature (T_{ig}) that is defined as the onset of the sudden rise in temperature [11]. Fig. 4 shows a typical profile of temperatures measured at the top surface (T1) and at the middle-thickness (T2) of the composites epoxy resin reinforced with 56 vol% carbon fibers exposed to 40 $\text{kW}\cdot\text{m}^{-2}$ external heat radiation level.

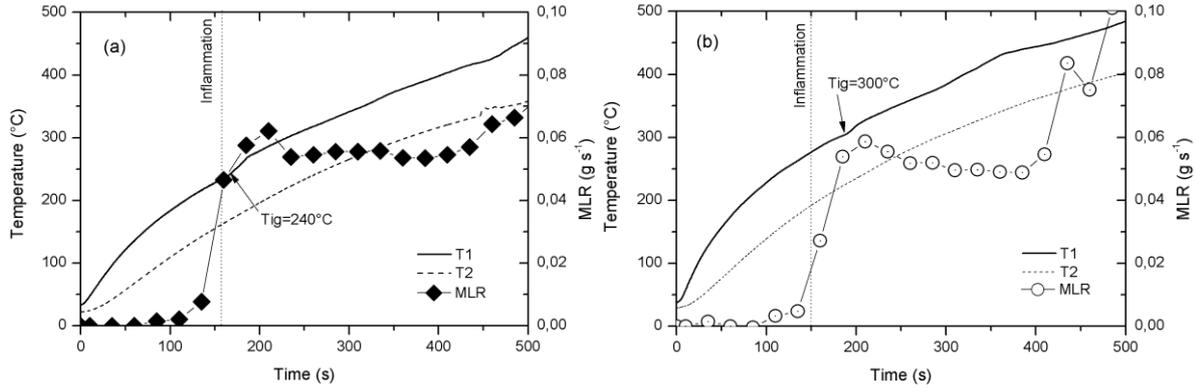


Fig. 4. Temperature profiles at the exposed surface (T1) and at the middle-thickness (T2) of the composites with: (a) 56 vol% CF (the ignition time was at 152 ± 10 s) and (b) 59 vol% CF (the ignition time was 150 ± 8 s), for an external heat flux of $40 \text{ kW}\cdot\text{m}^{-2}$

A maximum difference of about $100 \text{ }^\circ\text{C}$ between both temperatures inside a given sample is observed in Fig. 4. This gradient of temperature inside the material permits to confirm the thermally thick property of the epoxy resin/carbon fiber composites. Moreover, the sudden rise point of the top surface temperature profile (T1) corresponds to the first peak observed in the MLR profile. Taking into account the top surface temperature (T1) in Figs. 4-a and 4-b, the ignition temperatures (T_{ig}) were evaluated at 240 and $300 \text{ }^\circ\text{C}$ for the composites reinforced with 56 and 59 vol% carbon fibers, respectively (see Table 2).

The time corresponding to the onset of the sudden rise in top surface temperature occurs slightly later than the ignition time. This observation can be explained by the definition of the ignition time (t_{ig}) which is the moment when the flame is supported anywhere onto the sample surface and not only at a specific point (e.g. particular points of T1 and T2 thermocouples) of the material. This delay time may be due also to the response time of the thermocouple.

By considering the temperature at the same sample surface, the surface temperature increases when the carbon fiber fraction in the composite increases (thus, the sample thermal conductivity increases).

3.2 - TRP

The thermal response parameter (TRP) is another critical parameter characteristic of the material thermal behavior. It allows obtaining an estimate of the material resistance to generate a combustible mixture. The higher the TRP value, the longer it takes for the material to heat up, ignite, and initiate a fire. The material thermal response parameter (TRP) depends on ignition temperature (T_{ig}), ambient temperature (T_∞), material thermal conductivity (λ), material specific heat (C_p) and material density (ρ) as defined in the Eq. (2) [12 – 14]:

$$TRP = (T_{ig} - T_\infty) \sqrt{\frac{\lambda \rho C_p \pi}{4}} \quad (2)$$

On the other hand, Eq. (1) can be rewritten as:

$$t_{ig}^{-1/2} = \frac{1}{\sqrt{\frac{\pi}{4} \lambda \rho C_p}} \frac{\dot{q}''_e}{T_{ig} - T_\infty} \quad (3)$$

From Eq. (2) and Eq. (3), $[(1/t_{ig})^{1/2}]$ can be presented as a function of the external heat flux and the inverse of TRP (Eq. 4):

$$t_{ig}^{-1/2} = \frac{1}{TRP} \dot{q}''_e \quad (4)$$

The plot of the square root of the ignition time inverse versus external heat flux for both composites studied in this work is displayed in Fig. 3-b. The slopes of the curves in Fig 3-b allow calculating the thermal response parameter (TRP) by (Eq. 5):

$$TRP = \frac{1}{Slope} \quad (5)$$

TRP values of the composites constituted by epoxy resin reinforced with 56 and 59 vol% carbon fibers are presented in Table 2.

Table 2. Comparison of the characteristic parameters for the thermal decomposition of two epoxy resin/carbon fiber composites with the other materials

Material	CHF, (kW.m ⁻²)	T _{ig} , (°C)	TRP, (kW.s ^{1/2} .m ⁻²)	P, (kW ² .s.m ⁻⁴ .K ⁻²)	L, (kJ.g ⁻¹)	Reference
56 vol% CF	18	240	435	5.07	48	This work
59 vol% CF	14	300	370	2.25	44	This work
Nylon	14	380	275	0.87	3.80	[11]
Polyethylene (PE)	9	200	310	1.80	3.60	[11]
Polypropylene (PP)	5	210	227	2.20	3.10	[11]
PMMA	4	180	198	2.10	2.80	[11]
Epoxy resin	-	-	457	-	-	[15]

It was found that TRP value (Table 3) decreased from 435 to 370 kW.s^{1/2}.m⁻² when volume fraction of carbon fibers increased from 56 to 59%, respectively. This observation is due to the decrease of the thermal capacity and of the density when the carbon fiber fraction increases, and so the material resistance to generate a combustible mixture decrease. In comparison with the other materials, it was found that composite TRP values were slightly smaller than the epoxy resin one [15]. This comparison allows confirming the influence of the carbon fibers that lead to an increase of thermal conductivity and a decrease of the composites thermal resistance. On the other hand, the epoxy resin/carbon fiber composites show TRP values higher than the ones of other thermoplastics such as Nylon, PE, PP, etc. [11].

3.3 - Thermal inertia

Ignition temperature (section 3.1) permits to calculate the material thermal inertia. Thermal inertia (P) is a measurement of a material ability to resist to a temperature variation. Thermal inertia is linked to the material density (ρ), specific heat capacity (C_p) and thermal conductivity (λ) according to Eq. 6:

$$P = \lambda \rho C_p \quad (6)$$

Thermal inertia (P) can be calculated from TRP (Eq. 2), ignition and ambient temperatures as below (Eq. 7):

$$P = \lambda \rho C_p = \frac{4}{\pi} \left(\frac{TRP}{T_{ig} - T_{\infty}} \right)^2 \quad (7)$$

The results calculated for both epoxy resin/carbon fiber composites are presented in Table 2. An increase of the carbon fiber fraction from 56 to 59 vol% induces a decrease of the thermal inertia from 5.07 to 2.25 kW².s.m⁻⁴.K⁻², respectively. This result shows that the material resistance to the temperature change or the material thermal resistance decrease when the carbon fiber fraction in the composite increases. In comparison with other thermoplastics (Nylon, PE, PP, PPMA), the epoxy resin/carbon fiber composites show a higher thermal inertia value, or better thermal resistance properties.

3.4 - Mass loss and MLR

In Figs 5-a and 5-b, mass loss of the epoxy resin reinforced with different volume fractions of carbon fibers (56 and 59 vol%) was measured under air atmosphere at different external heat flux up to 75 kW.m⁻². As shown on Fig. 5, for a given composite, mass loss at a given time increases when heat flux increases. For example, the composite with 56 vol% carbon fibers loses from 20 to 35% of its initial mass by increasing the heat flux from 18 to 75 kW.m⁻², respectively (Fig. 5-a). In addition, the increase of the irradiance levels accelerates the sample mass loss. Indeed, as can be seen in Fig. 5-a, after a test time of 1250 s, the samples loose 30% of their initial mass for 75 kW.m⁻² and only 5% for 18 kW.m⁻². Similar phenomena are observed for the composite with 59 vol% carbon fibers (Fig. 5-b).

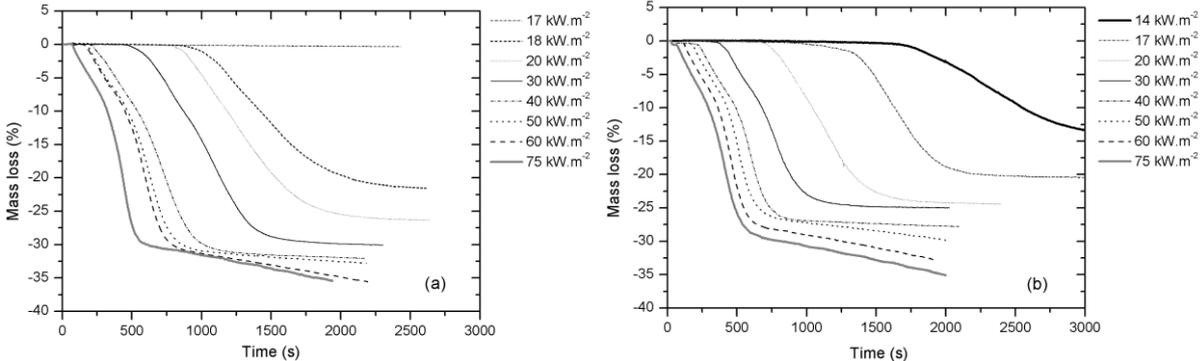


Fig. 5. Mass loss evolution as a function of time for eight heat fluxes, for the composites constituted of epoxy resin reinforced with (a) 56 vol% CF; (b) 59 vol% CF

Figs 6-a and 6-b present the transient evolutions of mass loss rate (MLR) for different external heat fluxes up to 75 kW.m⁻², for the epoxy resin reinforced with 56 and 59 vol% carbon fibers composites.

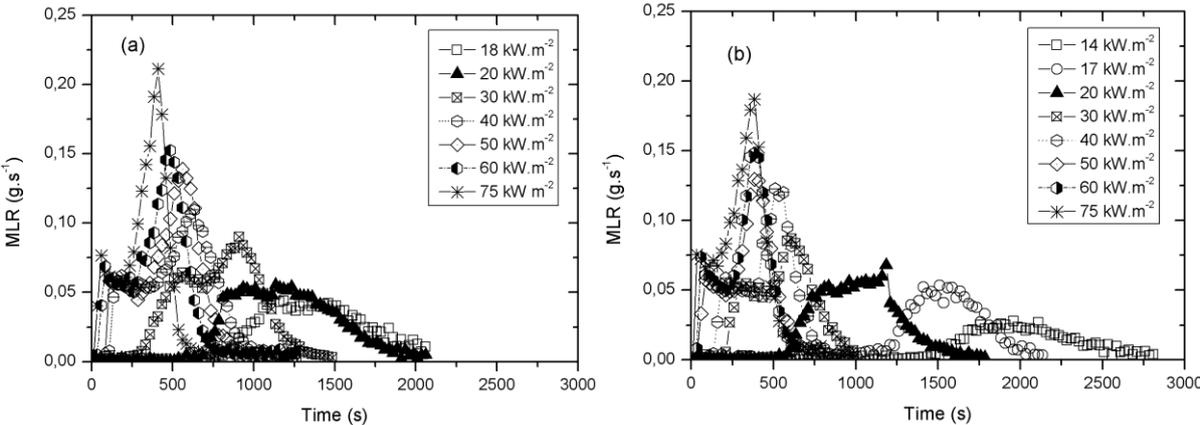


Figure 6. Evolution of mass loss rate (MLR) as a function of time, for different external heat fluxes for the composites constituted of epoxy resin reinforced with: (a) 56 vol% CF; (b) 59 vol% CF

It is observed that MLR peak amplitude increases and MLR peak width decreases strongly with an increase of the irradiance level (Fig 6). For example, the MLR peak amplitude for the composite with

56 vol% CF increases from about 0.05 to 0.22 g.s⁻¹ when heat flux increases from 18 to 75 kW.m⁻², respectively (Fig. 6-a). Moreover, at 18 kW.m⁻², the composite thermal decomposition occurs during a period of about 1300 s (from about 700 to 2000 s) while at 75 kW.m⁻², the thermal decomposition occurs in about 700 s (from about 50 to 750 s). Similar phenomena are observed for the second composite constituted of 59 vol% CF (Fig. 6-b). These observations show that the heat flux increase accelerates the decomposition of composites and decreases their thermal resistance.

In addition, the increase of carbon fiber fraction leads to the MLR peak amplitude decrease at a given external heat flux. Fig. 7 presents the comparison of the transient mass loss rate evolution for both composites at 20, 30, 50 and 75 kW.m⁻².

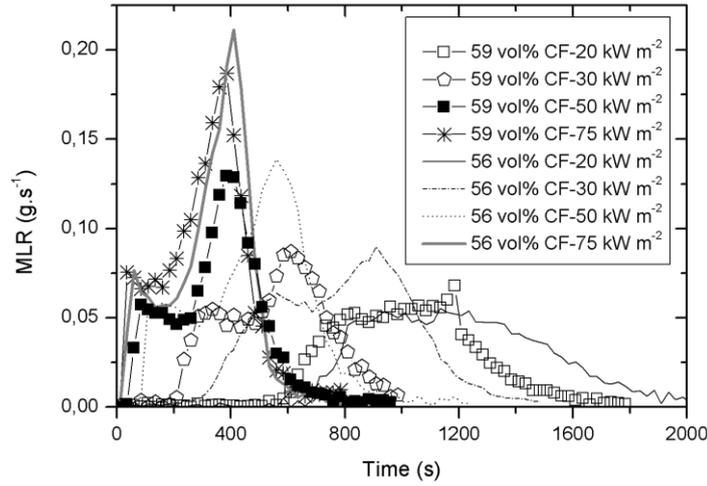


Figure 7. Transient mass loss rates for the epoxy/carbon composites (56 and 59 vol% CF) exposed to 20, 30, 50 and 75 kW.m⁻²

For 75 kW.m⁻², MLR peak amplitude decreases from about 0.22 to 0.18 g.s⁻¹ when the carbon fiber fraction increases from 56 to 59 vol%, respectively. The same observation can be made for other heat fluxes (i.e. 20, 30 and 50 kW.m⁻²). The MLR higher values for the composite with 56 vol% CF are mainly due to a higher epoxy resin volume in this composite, as compared to the other one. Furthermore, for any heat flux considered, MLR peaks shift to the right side of the graph for low carbon fiber amount, which corresponds to a composite thermal decomposition occurring later. Thus, when the carbon fiber fraction in composite increases, the mass loss rate is lower but the material thermal resistance is worse.

3.5 - Heat of gasification

The heat of gasification (L), parameter used to evaluate the fire resistance of a material, can be calculated from Eq. 8 where specific mass loss rate (or mass loss rate per unit of area) is a function of external heat flux (\dot{q}''_e), flame heat flux transferred to the surface (\dot{q}_{fl}), emissivity (ϵ) and vaporization temperature (T_v) [11].

$$\dot{m}'' = \left(\frac{1}{L}\right) \dot{q}''_e + \frac{(\dot{q}_{fl} - \epsilon\sigma T_v^4)}{L} \quad (8)$$

Subsequently, specific mass loss rate is plotted as a function of external flux, which allows determining the heat of gasification (L) by using Eq. 9:

$$L = \frac{1}{Slope} \quad (9)$$

Fig. 8 shows the plots of averaged specific mass loss rate (SMLR) of both composites as a function of the external heat flux.

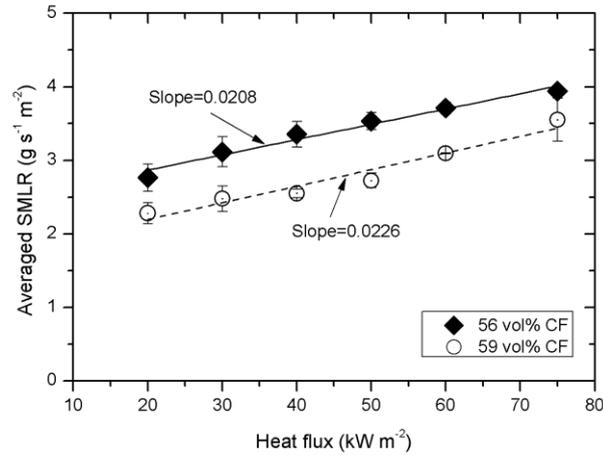


Figure 8. Averaged SMLR of two epoxy/carbon composites at different heat fluxes

The gasification heat results for the epoxy resin reinforced with 56 and 59 vol% carbon fibers composites are summarized in Table 2. As shown in Table 2, an increase of the carbon fiber volume fraction in the composites from 56 to 59 vol% leads to a decrease of the heat of gasification (L) from 48 to 44 (kJ.g^{-1}), respectively. These results show that a carbon fiber fraction increase favors the transfer and the distribution of heat within the composite material (*i.e.* an inflammability decrease and a combustibility increase of the composite material). Then, the energy necessary for gasification becomes lower and the composite resistance to produce gaseous combustible mixture decreases. In addition, Table 2 shows that the heat of gasification (L) values for the composites are about 15 times higher than the ones of other materials such as nylon, PE, PP or PPMA. This means that the epoxy resin/carbon fiber composite presents a better thermal resistance.

3.6 - Thermal decomposition phases

Fig. 9 shows, as an example, the plots of mass loss and mass loss rate (MLR) obtained from the thermal decomposition of the composite with 59 vol% carbon fibers exposed to a heat flux of 30 kW.m^{-2} . This graph allows analyzing the decomposition process of the composite in the cone calorimeter. The thermal degradation occurs continuously in four steps.

1. The first step consists in the devolatilisation of epoxy resin which releases the combustible mixture ignited by spark ignition with the oxygen contained in ambient air.
2. The second step is attributed to the thermal decomposition accompanied with phase transitions of epoxy resin. Then, the epoxy resin is decomposed progressively with a sharp increase of the mass loss rate (MLR) (Fig. 9). In this second step, the epoxy resin is transformed into a liquid phase. Experimentally, the liquid resin drops were observed to fall down from the sample holder. The phase transitions from solid to liquid, and then from liquid to vapor for the epoxy resin were endothermic processes. The energy consumption of these processes slowed down the mass loss rate as seen in Fig. 9. Thus, the flame corresponding to the resin combustion was observed to decrease on the sample surface.

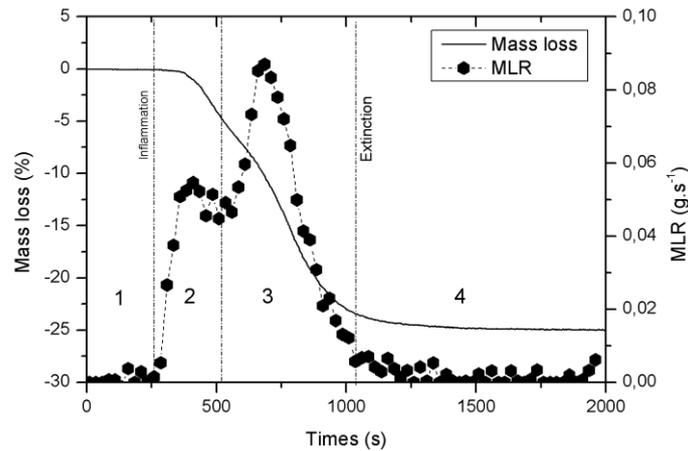


Figure 9. Evolutions of mass loss (%) and mass loss rate (MLR) ($\text{g}\cdot\text{s}^{-1}$) obtained from the thermal decomposition of the 59 vol% CF composite, with an external heat flux of $30 \text{ kW}\cdot\text{m}^{-2}$

3. The third step consists in an acceleration of the thermal decomposition and the combustion of the molten epoxy resin. In this step, since the solid resin was completely changed into liquid phase, a sharp re-increase of the mass loss rate was observed (Fig. 9). The molten epoxy resin flowed to the four edges of sample holder, burnt and dropped down. The resin flame was strongly rekindled. At the end of the step, a rapid decrease of the mass loss rate was observed. This phase corresponds to the flame extinction.
4. The fourth step corresponded to a pyrolysis and an oxidation of the char formed from the epoxy resin combustion. The remaining char after the thermal decomposition of the epoxy resin decomposed slowly. In our experimental conditions, the external heat flux was not high enough to degrade the carbon fibers. Then, at the end of the tests, the carbon fibers still remained.

The epoxy resin/carbon fiber composites thermal decomposition was different depending on the conditions of heat flux. Indeed, for the heat flux below $20 \text{ kW}\cdot\text{m}^{-2}$, the main decomposition of the epoxy resin seems to occur in one step with one MLR peak (Figs. 6-a and 6-b). But for higher heat fluxes, two steps were observed with two different peaks. It can be explained by the fact that the energy absorbed was not enough to re-increase the thermal decomposition of epoxy resin in the conditions of low heat flux. Since an important part of energy absorbed was used to melt the solid resin, it resulted in the flame extinction.

CONCLUSION

The thermal behaviors of two composites constituted by epoxy resin reinforced with different volume fractions of carbon fibers (56 and 59 vol%) have been studied in a cone calorimeter under atmosphere air with a piloted ignition. Several parameters characteristic of the thermal decomposition process such as mass loss data, ignition time, critical heat flux, thermal response parameter, ignition temperature, thermal inertia and heat of gasification were systematically measured and/or calculated. The influence of the carbon fiber volume fraction on the composite thermal properties was discussed. The decomposition step analysis shows that the thermal decomposition of epoxy resin/carbon fiber composite occurs in four phases: the devolatilisation of volatile compounds in the epoxy resin, the decomposition jointly with the solid-liquid phase transition of the epoxy resin, the acceleration of the thermal degradation and the combustion of the molten resin, and the pyrolysis and the oxidation of the char.

The increase of the carbon fiber fraction in the composites leads to a worse thermal resistance of the material. It is found that all the parameters that characterize the material thermal resistance such as

piloted ignition time, thermal response parameter, heat of gasification, thermal inertia and critical heat flux for ignition, decrease when the carbon fiber volume fraction increases from 56 to 59 vol%, respectively. Then, the choice of an optimal carbon fiber fraction is critical to maintain simultaneously good mechanical and thermal resistance properties for epoxy resin/carbon fiber composites.

ACKNOWLEDGEMENTS

The results presented in this paper have been obtained within the frame of the Horizon Hydrogène Energie (H2E) program. The authors acknowledge the French agency for innovation support OSEO and the Air Liquide Group for their financial support of this research.

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