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Determination of characteristic parameters for the thermal decomposition of epoxy resin/carbon fibre composites in cone calorimeter

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ABSTRACT

Present study concerns to the thermal degradation of two carbon fibre/epoxy composites, which differ by their volume fractions in carbon fibre (56 and 59 vol%), investigated in cone calorimeter (under atmospheric condition with a piloted ignition). In order to study the influence of the carbon fibre amount on the composite thermal decomposition, the cone calorimeter external heat flux was varied up to 75 kW m^{-2}. Thus, main parameters of the thermal decomposition of two different composites determined were: mass loss, mass loss rate, ignition time, thermal response parameter, ignition temperature, critical heat flux, thermal inertia and heat of gasification. As a result, when carbon fibre fraction decreases from 59 to 56 vol%, an increase of the thermal parameters was observed: 14–18 kW m^{-2} for critical heat flux, 370–435 kW $s^{1/2}$ m^{-2} for thermal response parameter, 2.25–5.07 kW^2 s m^{-4} K^{-2} for thermal inertia and 16–18 kJ g^{-1} for gasification heat. By analysing the mass loss rate evolutions, a four phases thermal decomposition mechanism is proposed. In the first phase, epoxy resin is cracked to form low molecular weight gaseous species and epoxy-derived compounds. For two next phases, the combustion of epoxy resin and liquor monomer solvent is observed that induces the formation of carbon char. In the last phase, char oxidation and carbon fibre decomposition are identified. Further, during the composite decomposition process, thermal behaviour of solid matrix is changed from a thermally thick material to a thermally thin one when sample is exposed at high external heat flux above 20 kW m^{-2}.

1. 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 gaseous hydrogen at a very high pressure. The carbon fibre/epoxy composite laminate acts as a load-bearing unit in the hydrogen storage cylinder, results in excellent mechanical performance, chemical and electrical resistance and low shrinkage on cure [1]. Mechanical behaviour of the composite is due to interaction between fibres and resin. This is a reason why two important parameters govern the mechanical

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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
h_c	convective heat transfer coefficient, W m^{-2} K^{-1}
$\dot{q}''_e$, $\dot{q}''_{fl}$	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}
$\dot{m}''$	steady-state mass loss rate, 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}

behaviour of such composites: extraction of water during cure (reticulation) and surface treatment of carbon fibres to increase their wettability. A few millimetres 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 H_2 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 behaviour of the carbon fibre/epoxy composites in fire is critical.

The literature on the thermal properties (thermal conductivity, thermal capacity and thermal diffusivity) of the carbon fibre/epoxy composites is scarce [4–6]. In general, some parameters influence the thermal properties of the composites such as: decomposition temperature, carbon fibre fraction [4,5], and nature of carbon fibre [4,6], etc. Pilling et al. [4], Knibbs et al. [5], Shim et al. [6] showed that thermal conductivity (λ) of virgin composites increased significantly by increasing the temperature and the carbon fibre fraction. It can be deduced that the increases of temperature and carbon fibre fraction induce an increase of heat dissipation within the composites, favour their decomposition, and so reduce the thermal resistance of materials in fire. Moreover, the composite thermal conductivity values measured in the transverse and parallel directions with carbon fibre are totally different because of the thermal expansion/thermal contraction behaviour. In fact, the carbon fibre dilatation is observed when the composites are heated: expansion in fibre diameter, reduction in fibre length. On the other hand, the thermal properties of composite are changed during the thermal decomposition. They are assumed to be dependent on the relative mass fractions of the virgin composite and fully decomposed materials (char) [7,8]. The thermal properties are those of the virgin composite material prior to decomposition, but those of the fully decomposed (char) material after the decomposition.

Recently, the thermal degradation of the carbon fibre/epoxy composites has drawn the attention of several researchers [1,9–12]. Many parameters characterizing the composite materials thermal degradation have been discussed: mass loss, kinetic mechanism [9–11], heat release rate (HRR) and released gases from the oxidation [8], etc. However, most of studies were performed at the elementary level with well-controlled conditions by using thermo-gravimetric analysis (TGA), differential thermal analysis (DTA) or differential scanning calorimetry (DSC). For example, Régnier and Fontaine [9] performed a kinetic study on the thermal degradation of carbon fibre-reinforced epoxy resin contained 55 wt % of carbon fibres in inert and air atmospheres. Three-step mass loss in oxidative atmosphere was observed during dynamic thermo-gravimetric analysis (TGA): thermal cracking of epoxy resin and char forming, oxidation of non-volatile residues (carbon char) formed during the first step and carbon fibres degradation at high temperatures. The temperatures corresponding to the three stages were about 215, 500 and 615 °C, respectively. This three-step mass loss decomposition mechanism of epoxy composites was also confirmed by Noël et al. [11] and Branca et al. [12] by using DSC and TGA.

The extensive studies on the thermal behaviour of epoxy reinforced composites used for different applications (naval vessels, shipboard, submarine, etc.) have been investigated since decades in larger test scale of cone calorimeter [1,13–19]. For example, Hshieh and Beeson (1997) investigated a study of the influence of O_2 mole fraction in controlled atmosphere of cone calorimeter on ignition time, peak of heat release and CO yield of epoxy composites [13]. Sorathia et al. (1997, 2001) proposed also a lot of ignition delay time, and peak of heat release rate (PHR) as function of heat fluxes for epoxy composites [14,15]. Mouritz et al. (2006) studied the relationship between heat release rate (HRR) and other fire reaction properties (smoke specific extinction area, ignition time, total mass loss, averaged and peak mass loss rates, averaged CO and CO_2 emission yields) of fibre-reinforced polymer composite materials [16]. Nevertheless, several studies still remain confidential, and so the literature on epoxy/carbon composites is still limited, especially works investigating at 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 behaviour in realistic cases of fire accident.

The objective of the present study is to contribute to the understanding of the influence of carbon fibre fraction on thermal decomposition of carbon fibre/epoxy composites in cone calorimeter apparatus. This work is a part of longer and broader research programme studying the fire behaviours of different materials (composite laminate, thermoplastic liners and fire protective materials) used in high pressure hydrogen composite cylinders. Several parameters that characterize the epoxy/carbon 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. Furthermore, the material thermal decomposition mechanism is also identified.