Chapter 5
Advanced Flame Protection of CFRP Through Nanotechnology

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Abstract This chapter refers about the optimization of fire resistance of CFRP. For this optimization the most promising nano scaled additives are used and varied regarding the particle content, size and effect of flame retardancy. One major challenge is to optimize the particle dispersion and to determine the optimal particle concentrations in consideration of the effect of flame retardancy and the resulting material properties. Additionally a fire testing method has to be determined that resolves the potentially small differences in the used variations. Therefore standard fire and mechanical tests are used as well as a simple thermal material method, given with the thermo gravimetric analysis (TGA) including a single differential thermal analysis (SDTA) that also suits for a fast comparison of the materials fire properties. Hereby obtained results are compared and a related behaviour of the fire properties can be shown between standard fire tests and thermal material tests using the TGA-device.

5.1 Protection Against Fire

A major fire is normally defined as an independent spreading fire causing damages and health impairments to objects and people. The causes of a fire can be various. Especially regarding the safety of civil aircrafts the fire prevention is of particular importance. A fire scenario of great relevance is the so called Post Crash Fire.

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A Post Crash Fire is a fire which can occur after a crash caused by leaking kerosene and an ignition source. In this case the mechanical stability has to be guaranteed until survivors and casualties have been evacuated. There is not only the risk of heavily loaded components falling down and injuring people but also the immediate danger through the release of great heat, smoke and toxic gases. Especially during the combustion of fiber composites containing polymer matrices many reaction products are released which can not be characterized as harmless. In addition to the strong emission of smoke and soot which probably block escape routes these are unhealthy gases and toxic fiber particles in the air breathed. While the term fire protection mostly describes concrete actions to extinguish a fire the flame retardancy directly influences the material itself so that a fire ideally can be prevented. One possibility is the usage of hardly or non flaming materials another option is to use additives within or at the component which effectively optimize the fire properties. The importance of flame retardants increases continuously [1, 2].

5.1.1 Flame Retardants for Fiber Composites

Though CFRP laminates are already widespread used and are still prevailing for further applications they show some critical drawbacks that prevent a more extensive use. Especially the low fire resistance of CFRP mainly due to the plastic matrix is a problem to be solved. Generally flame retardants are applied as coatings [3] that disadvantageously increase the components weight. An approach to prevent this disadvantage could be the modification of the polymeric matrices of CFRP by nano particles. This modification bears the opportunity of material integrated flame retardancy for CFRP manufactured with the injection technology. On the one hand the usage of nano particles is compulsory to prevent the particles from being filtered out by the fiber semi finished products with diameters of a few microns during the injection process. On the other hand nano scaled particles have a disproportionately higher surface than the same amount of larger particles. This bears the possibility of an even further enhancement of the effect of flame retardancy where for example a cooling effect is transmitted by the particles surface. In addition to the improvement of the flame properties of CFRP material integrated particles can lead to a structural reinforcement in case of a fire. Another demand for the daily use is that the mechanical properties of the materials like stiffness and strength should not be influenced negatively by the application of these modifications. These effects can not be reached by classical micro particles but due to nano particles as already shown in previous chapters of this book. Subsequently the integrated flame retardants used for the optimization of the flame properties of CFRP have to be nano scaled. For the selection of suitable particles based on nanotechnology the combustion process has to be regarded. A fire to get started and keep going needs the following prerequisites as pictured in Fig. 5.1 (left): heat, oxygen and burnable material. If these prerequisites are present the heat input initiates the pyrolysis. This is followed by an oxidation of the pyrolysis products
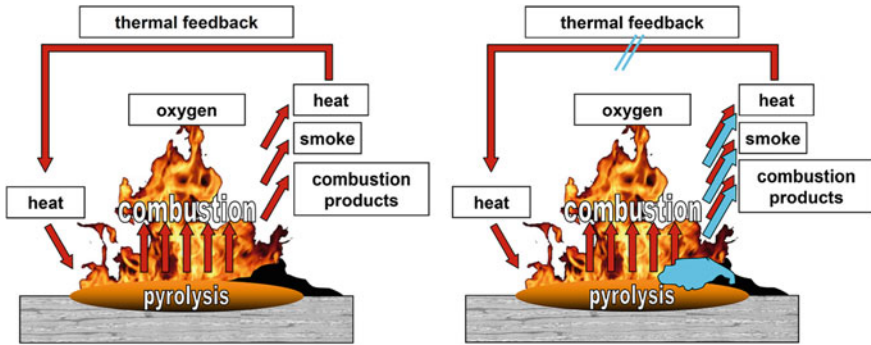
Fig. 5.1 Schematic combustion process (*left*); influence of flame retardants on combustion process (*right*) [1]

resulting in further heat, smoke and several combustion products. The heat thereby produced in turn results in a thermal feedback keeping the combustion going. Due to the oxidation of pyrolysis products a char is formed acting as a flame barrier.

The combustion process can be influenced by flame retardants as pictured in Fig. 5.1 (right) either by building an additional intumescing barrier or char preventing the oxygen from feeding the base of fire or by diluting the combustion products through inert gas or by actively cooling through for example the release of water and therefore preventing thermal feedback. Nanotechnology offers several particle systems which are already well examined in literature for the use as flame retardants. Suitable particle systems are carbon nano tubes (CNT) which function due to thermal conduction cooling down the base of fire, organoclays building an intumescing barrier layer and aluminium trihydroxide (ATH) and magnesium dihydroxide (MDH) known for splitting up water at definite temperatures and therefore cooling down and diluting the combustion products. All particle systems integrated into the matrix additionally reduce the burnable material by their embedded content. It depends on the dispersion quality if there is a further use due to the nano particles small size. Nano particles tend to agglomerate as described in the sections before so the use of dispersion devices is necessary to separate the agglomerates ideally up to the particles primary size. If possible several predefined agglomerate sizes can be produced to examine the influence of this value on the resulting effect of flame retardancy [1–5].

5.1.2 Fire Tests and Supplemental Characterizations

To evaluate the optimizations achieved by the modifications used in this research small scale fire tests as well as thermal tests were made. Due to these tests it is possible to determine whether the use of flame retardants is necessary or basically suitable. However, these coupon tests do not represent the real properties of a structural component exposed to fire. Therefore original scale components have to

Fig. 5.2 Schematic picture
of the heat release rate of a
polymer [1]
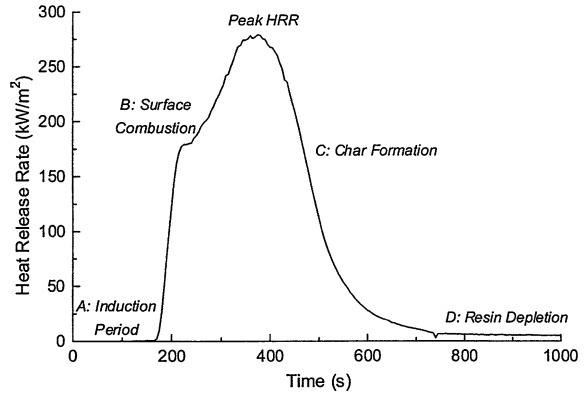
be tested in a suitable experimental set-up with authentic loads in a realistic fire
scenario. The major drawback of small scale coupon tests is that normally stan-
dardized burners are used and the experimental set-up does not meet the conditions
of a real fire. The same applies to the release of the evaluated smoke and toxic
gases giving no directly usable prediction about a realistic toxicity as for example
the carbon monoxide concentration of a lab fire may significantly differ from the
concentration resulting from a real fire. Though the deliverables of lab scale tests
differ from these of a realistic fire scenario the results are of great importance for
the estimation of the fire behaviour and toxicity of materials.

While the standard fire-smoke-toxicity (FST) tests qualitatively picture the
behaviour of a fire especially in the case of fiber reinforced polymer composites,
the most important quantitative value to be measured in a fire is the rate of the heat
released representing the released energy which is schematically shown in the
Fig. 5.2. Hereby each material has a specific character which can be measured
using a cone calorimeter or an Ohio-State-University (OSU) calorimeter as
widespread used and accepted standard methods.

Also important is the progression of the mass decomposition which also can be
recorded by the cone calorimeter or using small scale tests performed with the
thermo gravimetric analysis.

For this research flammability tests performed by a Bunsen burner according to
AITM 2.0002B were chosen to visualize the optimization due to the modification
of the polymer. The flammability test samples were 75×305 mm in size with a
thickness of 2 mm and they were exposed to the Bunsen burner flame for 12 s.
Afterwards the after burn duration was recorded and the burning notch length was
measured.

For a comprehensive material characterization the quantity of heat produced at
combustion was measured by a thermo gravimetric analysis TGA/SDTA 851
(Mettler Toledo, Germany) containing a single differential thermal analysis real-
ized by the usage of a temperature sensor placed near the probe. The temperature
of the combustion- or oven chamber is predetermined by the chosen temperature
program. Knowing the probes temperature as well as the oven temperature the heat

flow can be determined and consequently the quantity of heat. The weighing cell of the device records the probes weight during the whole measurement procedure. Therefore two important measured variables concerning the combustion process could be determined using the TGA. These measurements were conducted using a mixture of oxygen and nitrogen at a mixture ratio of 2:1 as a purge gas and a gas flow rate of 60 ml/min. The intension was to use a gas mixture with higher nitrogen content for a more realistic measurement environment. Unfortunately a mixture of both gases could not contain more than 20 ml/min of nitrogen. This is a limitation given by the device. Therefore a mixture of both gases could not simulate the conditions of air without further equipment. The temperature programme for this measurement was set to run from 200–600°C and the heating rate was 4 K/min to accelerate the measurement procedure. Samples with an initial weight of 25 mg were used.

The pyrolysis combustion flow calorimetric (PCFC) measurements were conducted using samples of 2 mg in size. The temperature programme for this measurement was set to run from 75–750°C and the heating rate was 60 K/minute. These measurements were conducted using a mixture of oxygen and nitrogen at a mixture ratio of 1:4 as in air and a gas flow rate of 100 ml/min.

The research was conducted with a Cone Calorimeter (Fire Test Technology, East Grinstead, UK) according to ISO 5660. The samples of the Cone Calorimeter were 100×100 mm in size with a sample thickness of 2 mm and were conditioned for at least 48 h at 23°C and 50% relative humidity before the measurement. The measurement was conducted with an irradiance of 50 kW/m^2 at a distance of 25 mm between the radiation source and the samples surface [6–12].

5.2 Materials and Methods

For the optimization of fire properties different types of nanoparticles are available as presented in the previous section. Some of these particles are commonly available as micron particles and are already widespread used. There are already several studies focussing on the effect of flame retardancy of CNTs and organoclays respectively nanoclays which can be found in literature [13–17]. The examinations of the fire properties of CFRP herein focus on the use of ATH-nanoparticles provided by the company Sasol [18].

5.2.1 Nanoparticles and Resins

The ATH particles by the company Sasol were delivered in several versions differing in particles size, surface modification and modification amount realized through the modification during different manufacturing process steps of the particles.

The resin used in this study is an epoxy resin which is partly well approved in aircraft industry. It is a three-component diglycidyl ether of bisphenol A (DGEBA) based epoxy resin with a T_G of 120°C (Araldite LY556 from Huntsman), the anhydride curing agent HY917 and the amine accelerator DY070. This resin system is cured for 4 h at 80°C and postcured for 4 h at 120°C.

### 5.2.2 Dispersion Process and Material Characterisation

Several dispersion devices were available for the examination as for example a dissolver, a torus mill, a ball mill and later during the last period of the examination a calender also usable for highly vicious systems containing high particle contents. During this process the particles provided by the company Sasol could be optimized themselves in respect of the surface modification with the aim of a better dispersion quality. As the result a modification of the particles surface with taurine showed the best dispersion quality. This optimization was accomplished by the company Sasol taking into account the results of the dispersion examination. To produce a particle-resin-masterbatch during the dispersion process only the resin component is used to avoid curing during this process step. For further processing the particle-resin-batch is mixed with the hardener and accelerator component. The dispersion quality is verified by the SEM. The ATH particle system by the company SASOL was used for a comprehensive material characterisation giving a detailed correlation between the particle content and the resulting reduction of the exothermal combustion heat. These tests were performed by the TGA as explained in the previous section [19].

5.3 Results and Discussion

5.3.1 Thermal Characterization of Very Small Scale Test Specimens

For the purpose of a comprehensive material characterization in addition to the nano particle modified polymer with particle contents ranging from 5 to 40% in steps of 5% the particle powder was measured as well solely in order to achieve the expected reduction of the combustion heat. Due to this knowledge the expected reduction of the combustion heat could be calculated for all measured particle contents. The results are given in Fig. 5.3.

It can be seen that the statistical spread of the measurement is comparatively high for very high particle contents as well as the neat resin specimens. For high particle contents this is presumably caused by a worse dispersion quality compared to lower particle contents. The huge statistical spread of the neat resin samples
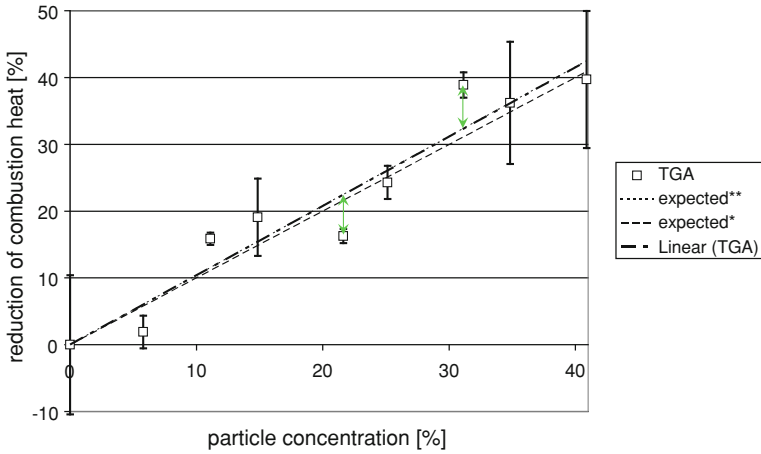
* calculated curve giving the expected reduction of the combustion heat induced
  by the reduction of the burnable material due to the particles

** calculated curve giving the expected reduction of the combustion heat induced
  by the reduction of the burnable material due to the particles and by the cooling
  effect of the particles

Fig. 5.3 Expected and measured reduction of combustion heat depending on the particle content
of ATH1

results from the used gas flow program which obviously was not appropriate for
the high combustion heat release peaks of the neat resin probes showing a very
discontinuously curve character. Two expected curve characteristics are shown in
the diagram. One expected* curve represents the reduction of the combustion heat
induced by the reduction of the burnable material due to the particles, the second
expected** curve also takes into account the cooling effect of the particles. The
trend line of the measured results hereby corresponds well to the expected** curve
characteristics which is not a surprise and certifies the test method. For some
particle contents the deviation from the expected** curve is significantly high as
for example regarding the particle concentrations of 20 and 30%. Where the
measured value is below the expected** curve the particles are not as efficient as
otherwise. This could result through a bad dispersion quality and many micro
scaled agglomerates. The minimum reduction of the combustion heat still
shouldn't be below the expected* curve resulting from the reduction of the
burnable material. For the statistical spread of the particle content was lower than
the deviation in the reduction of the combustion heat some effects of the particles
increasing the combustion heat of the sample have to be taken into account. This
could be an increase of the samples surface due to the particles. Where the
measured results surprisingly show a greater reduction of the combustion heat this
is supposed to be caused by the increased specific surface of the thoroughly
dispersed nano particles for the previously measured particle powder is agglom-
erated and therefore not nano scaled but micro scaled. This nano effect concerning
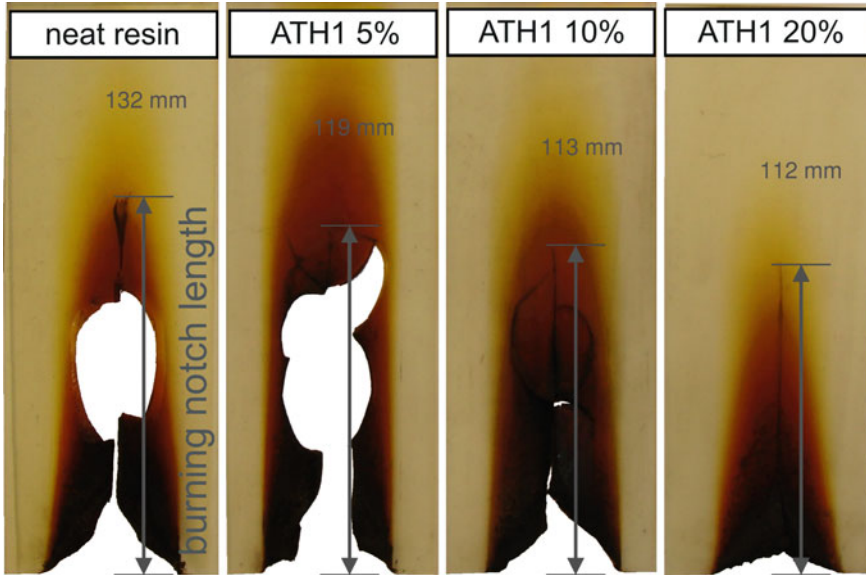
Fig. 5.4 Flammability test specimen with varying particle contents of ATH1

the flame retardancy will be researched and confirmed in further investigations. Obviously there is a linear correlation between the reduction of combustion heat and the particle content.

5.3.2 Comparison to Standard Fire Test Methods

The behaviour showing a linear correlation between the reduction of the fire properties and the particle content seen in the thermal material characterisation corresponds to the results of the flammability test. These tests prove the reduction of the burning notch length of ATH1-modified resin probes according to the increase of the particle content as shown in Fig. 5.4. Probes with an ATH1-Particle content of 20% achieved an improvement of 15% which is a little bit less than expected due to the modification and measured using the TGA.

The results of the examinations using the PCFC and the Cone calorimeter are pictured in Fig. 5.5 next to the results of the examinations presented in the previous section. The very small scale probes of the PCFC show similar results as the TGA test specimens. The trend leads to even higher reductions of the combustion heat. This even exceeds the expectations due to the measured cooling effect of the particles and supports the theory that there is an increased effect using nano particles instead of standard micro scaled particles. On the other hand the results of the examinations using the cone calorimeter show a contrary effect. Comparable to
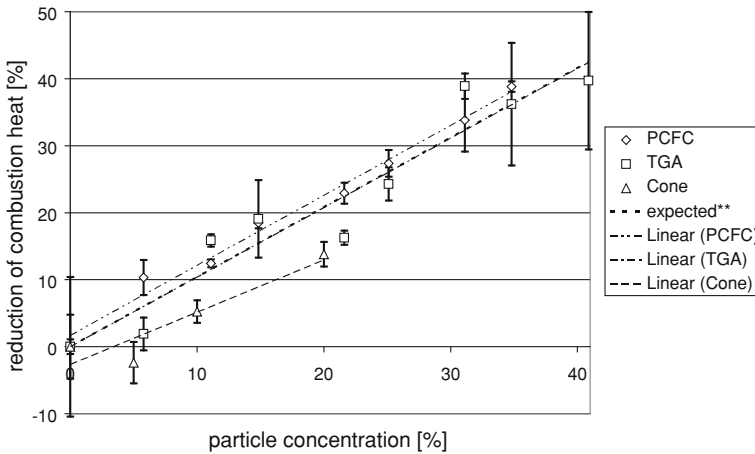
Fig. 5.5 Reduction of combustion heat depending on the particle content of ATH1 measured with PCFC, TGA and cone calorimeter

the trend of the flammability test a reduction of the combustion heat of only about 15% could be reached using a particle content of 20%. For low particle contents of about 5% even an increase of the combustion heat can be detected which supports the consideration of a flammability increasing effect due to the particles.

Very small scale tests seem to profit more from the modification of the polymer with nano scaled ATH than larger scale test configurations though a good trend of the results can be given using very small scale tests which makes them suitable for a comprehensive material characterisation.

Additionally it could be shown, that the nano scaled particles ATH1 by the company SASOL are well suitable as flame retardants for polymers used in CFRP.

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