Developing advanced composites for space structures: the effect of carbon nanotubes and fibres on resin flammability

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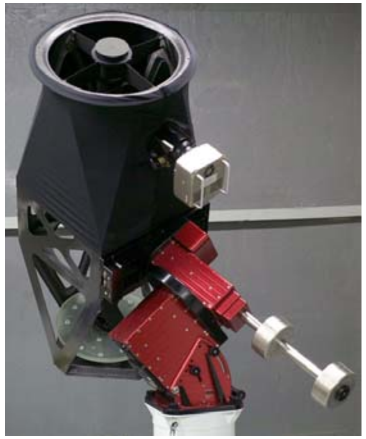
Agenda

- Introduction
- Objectives
- Experimental Procedure
- Results
- Conclusions

INTRODUCTION- epoxy resins

- Epoxy resins have been widely used in many fields:
  - Fibre-reinforced composites
  - Adhesives
  - …

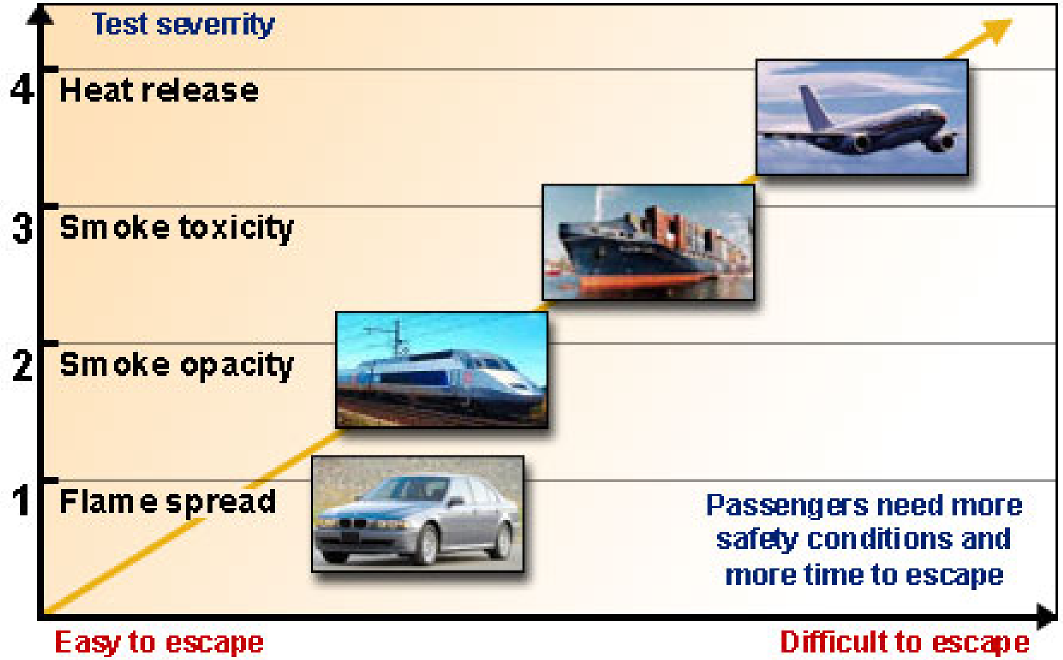


- Major advantages
  - Good mechanical and electrical properties
  - Reasonable chemical resistance

INTRODUCTION- epoxy resins

Cured epoxy resins are very **flammable.**

Stringent fire regulations govern the use of materials in aircraft, ships, buildings, land transport and other applications.



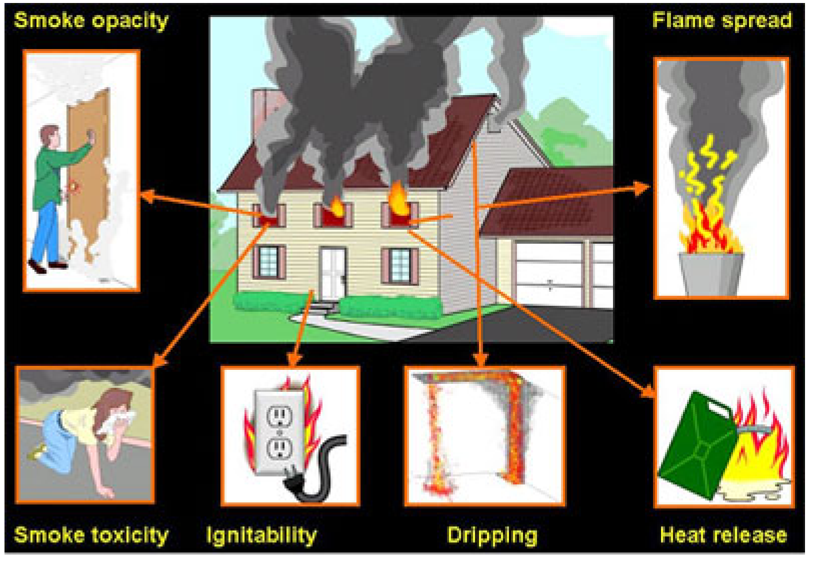
The **severity of regulations** and tests is **linked to the difficulty** to **escape from fire scenario**.

INTRODUCTION- Fire regulations

These **regulations require** that the **fire reaction** properties **meet specified levels**.

Fire reaction properties:

- Time-to-ignition
- Heat release rate (HRR)
- Flame spread rate
- Smoke density
- Yield of toxic gases



Time-to-ignition, **heat release rate** (HRR) and **flame spread rate** are usually used to define the fire hazard and they influence the temperature and spread of fire.

Smoke density and **yield of carbon monoxide** gas determine survivability.

INTRODUCTION- Flame retardants

To accomplish these legal requirements **flame retardants** need to be added in polymer materials.

The **role of flame retardants** is to :

-Slow down polymer combustion and degradation (**fire extinction**),

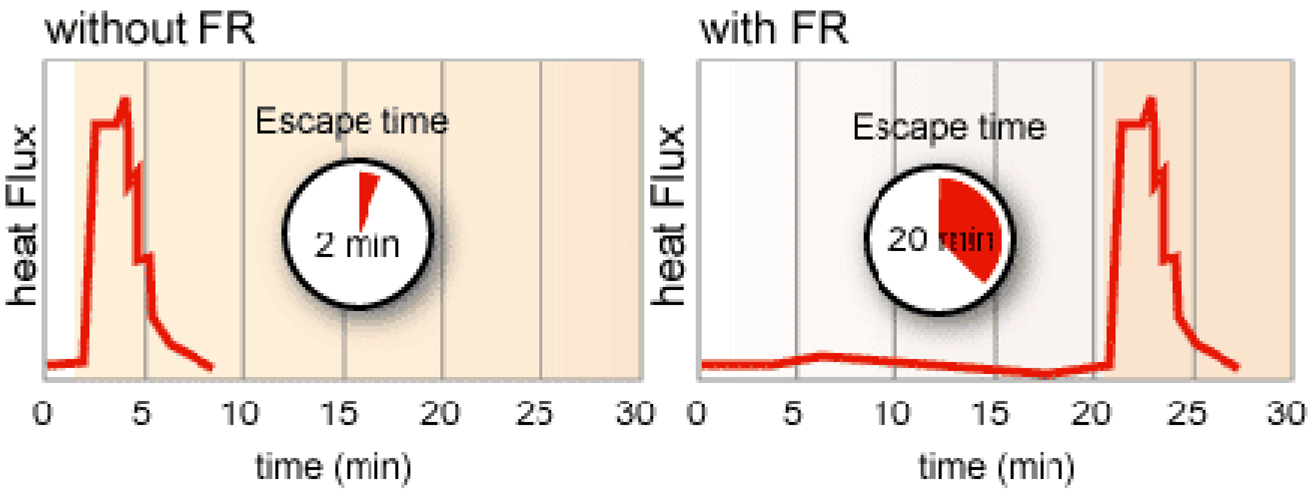
-**Reduce smoke** emission,

-**Avoid dripping**,

in order to increase the escape time of persons.

INTRODUCTION- Flame retardants

Flame retardants contribute directly to the saving of lives. The use of fire retardant **reduces the flame spread** and so the rate at witch the smoke develops. **Less smoke production** gives an increase in the escape time available**.**

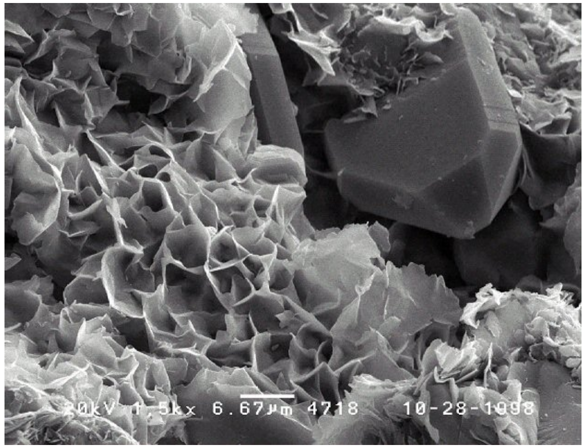


INTRODUCTION- Flame retardants

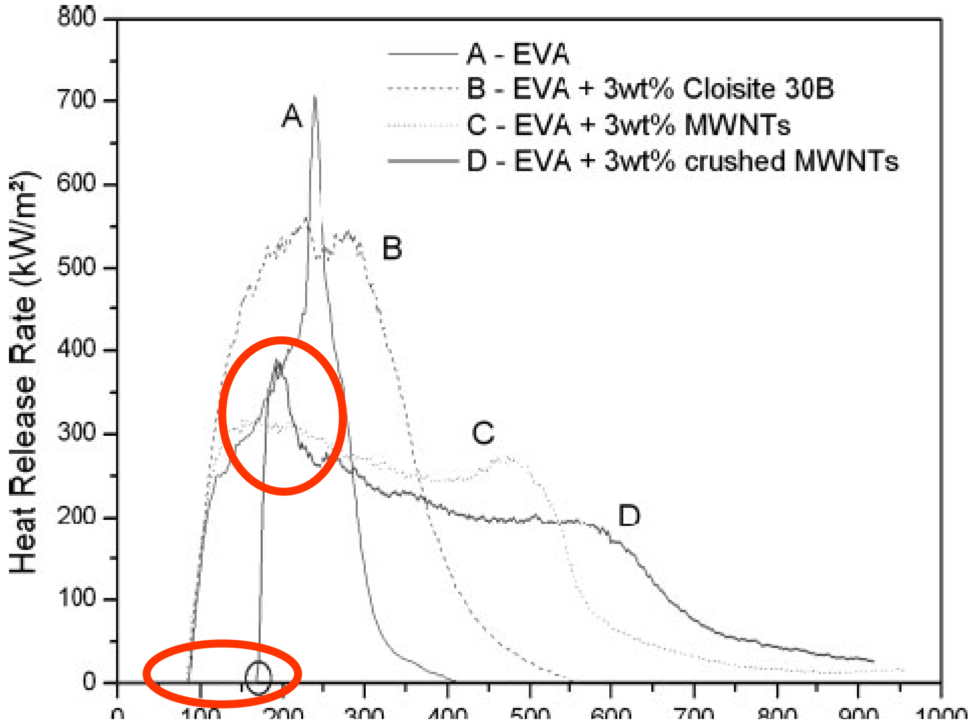
Traditional flame retardant solutions require **high portion of the filler** within the polymer matrix, leach out, etc.

Clear disadvantages exist in the end products due to the **non-durable** effect, the **high density**, the **lack of flexibility**, **the low mechanical properties** observed.

Recently, it appears interesting to use CNT at a low loading content to obtain materials with reduced flammability.



INTRODUCTION- Carbon nanotubes as polymers flame retardant



These researchers observed that MWNTs have a significant effect on the flammability properties of EVA-based composites.

Two important parameters have been influenced by adding a small amount of crushed MWNTs in EVA: TTI which is largely increased and HRR, which is significantly decreased.

This phenomenon can be attributed to a chemical effect through the chemical reactivity of the radical species existing at the surface of crushed MWNTs during combustion.

INTRODUCTION- Carbon nanotubes as polymers flame retardant

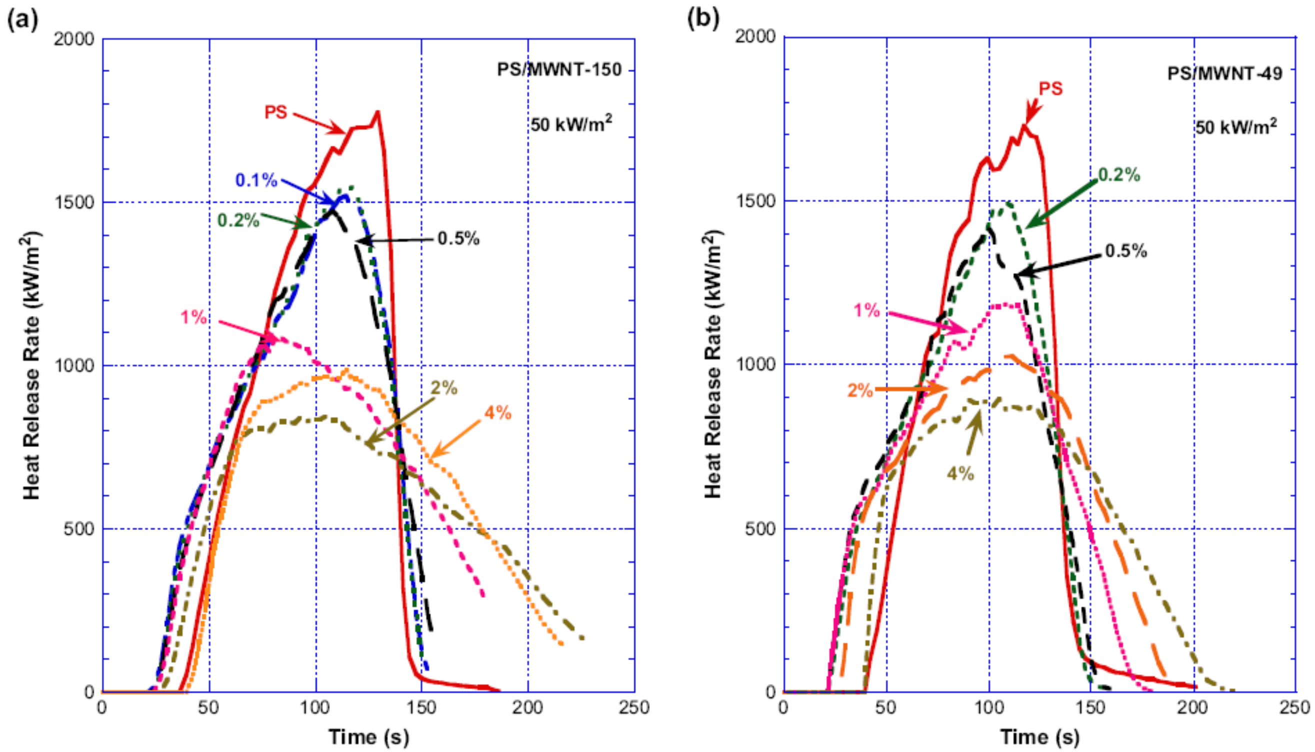
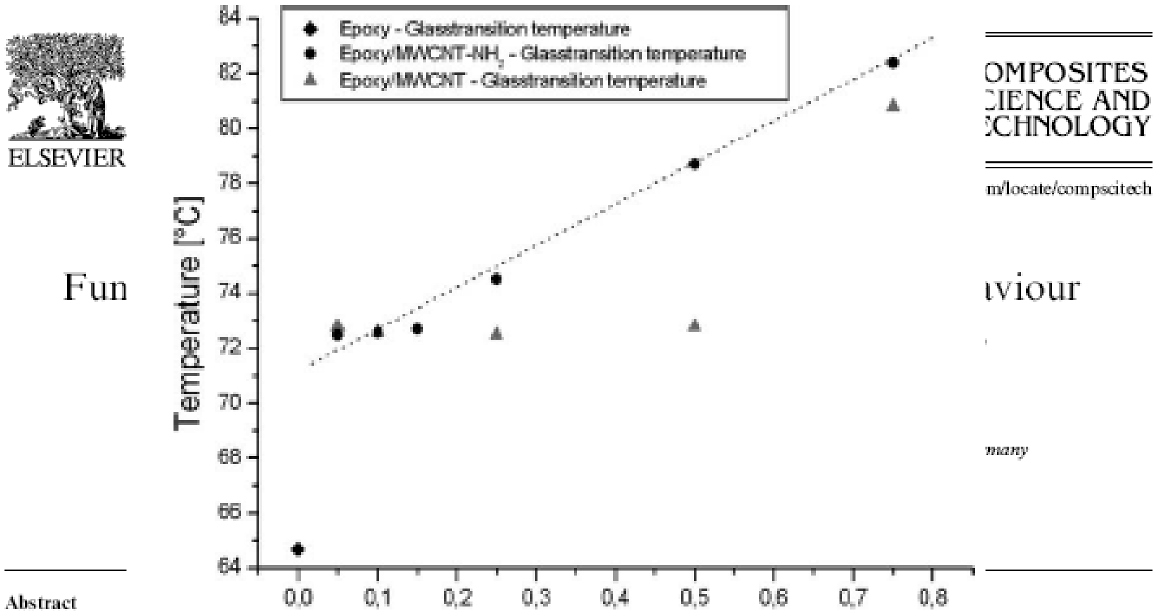


Fig. 12. Heat release rate curves of PS/MWNT nanocomposites at various mass concentrations of MWNT at 50 kW/m^2: (a) with MWNT-150 and (b) with MWNT-49.

The results show that the addition of MWNT with large aspect ratios significantly reduces the flammability of polymers.

INTRODUCTION- Carbon nanotubes in epoxy resin



These authors observed and concluded:

- a general increase in thermal stability through the addition of nanotubes;
- the increase of the glass transition temperature of the nanocomposites containing functionalised carbon nanotubes is linearly dependent on the nanotube content;
- evidence for an influence of a chemical functionalisation of the nanotubes surface on the interfacial adhesion between the nanotubes and the epoxy resin.

Objectives

Evaluate the effect of carbon nanotubes (CNT) on epoxy resin flammability and on thermo-mechanical properties.

Comparing with the effect of carbon fibers (CF) and one traditional flame retardant.

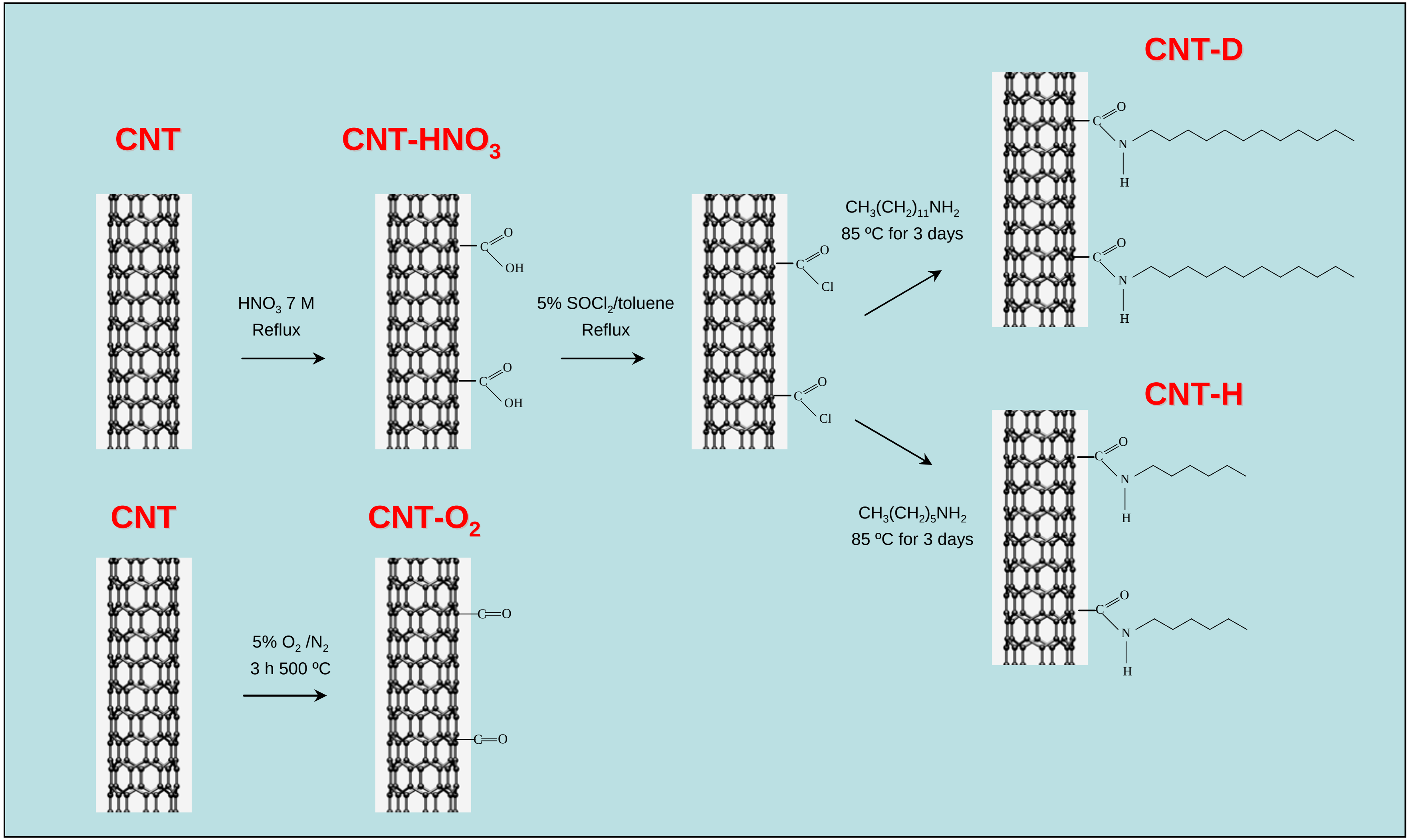
Epoxy resins are very flammable and it is difficult to reduce their heat release rates with environmentally friendly flame retardants.

Experimental Procedure

- ***Materials***
  - Epoxy resin: REAPOX 550LV
  - Carbon nanotubes (0.1wt% and 1.0 wt%)
  - Hardener: REAPOX 558
  - Flame retardant: APP
  - Carbon fibres (CF): tissue 1:1

Experimental Procedure

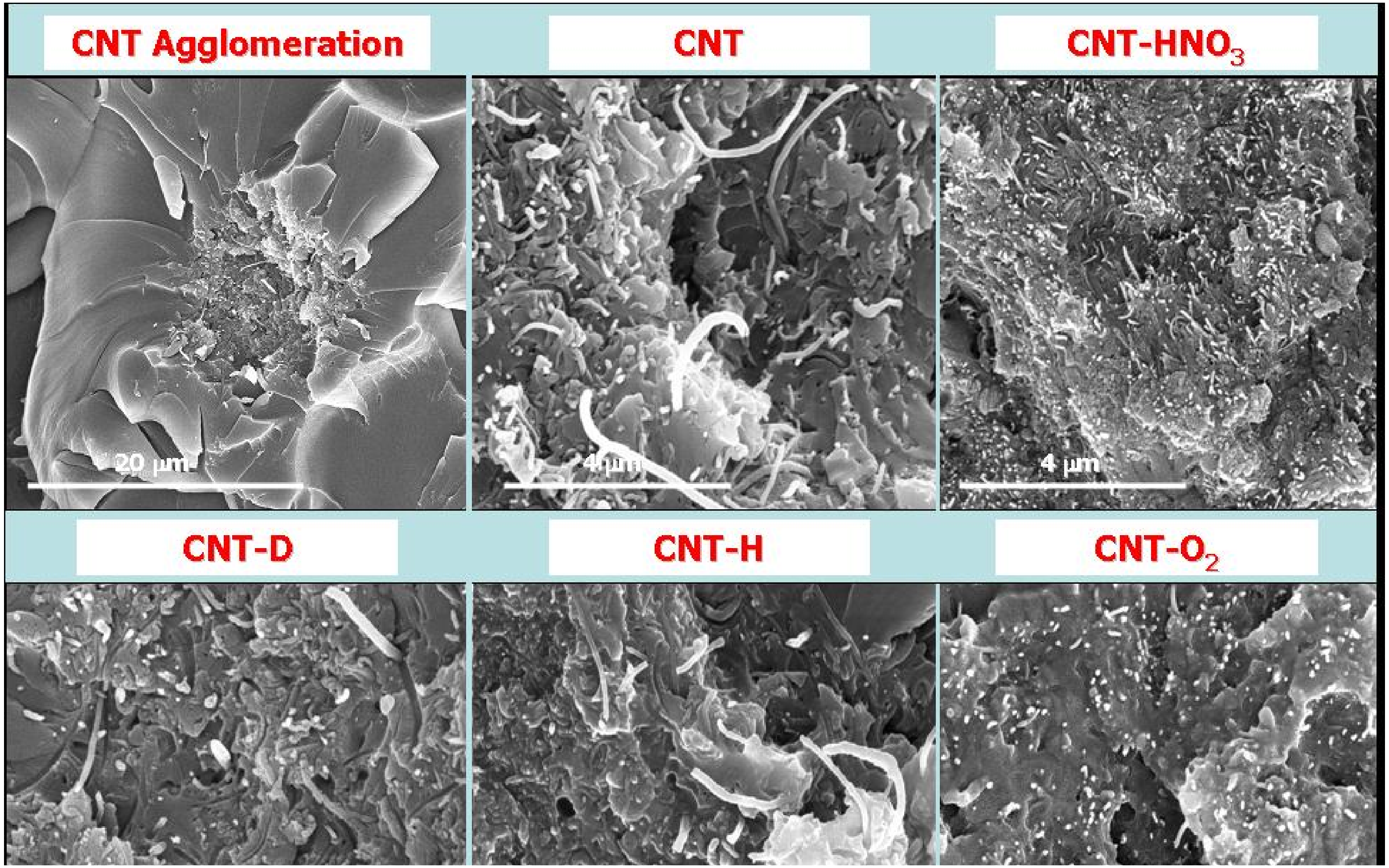
Functionalization of Carbon Nanotubes



Experimental Procedure

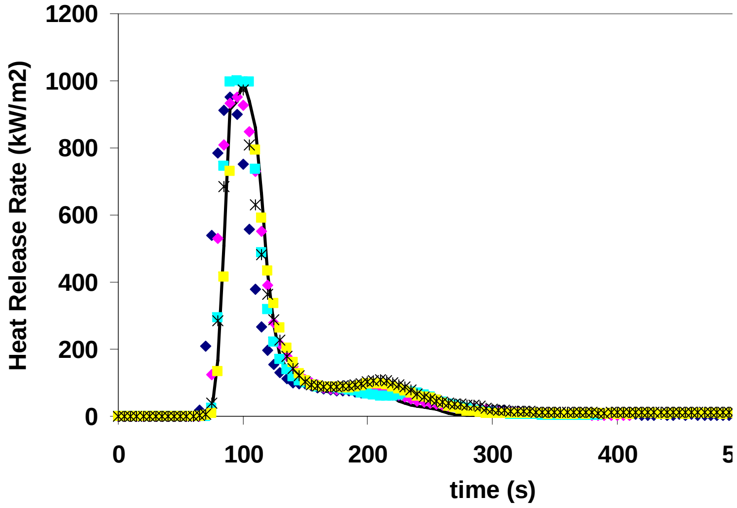
- ***Preparation of the CNT/epoxy samples***
  1. Disperse CNT into the liquid viscous resin
  2. Mixing: manual and mechanical stirrer
  3. Hardener addition
  4. Pre-cast, cure and pos-cure
- ***Characterization***
  1. Scanning Electron Microscopy
  2. Fire reaction: **Cone Calorimeter** (25 kW/m2)
  3. Thermo-mechanical: **DMTA** (f=1Hz, 25-150ºC, heating rate of 1.5ºC/min)

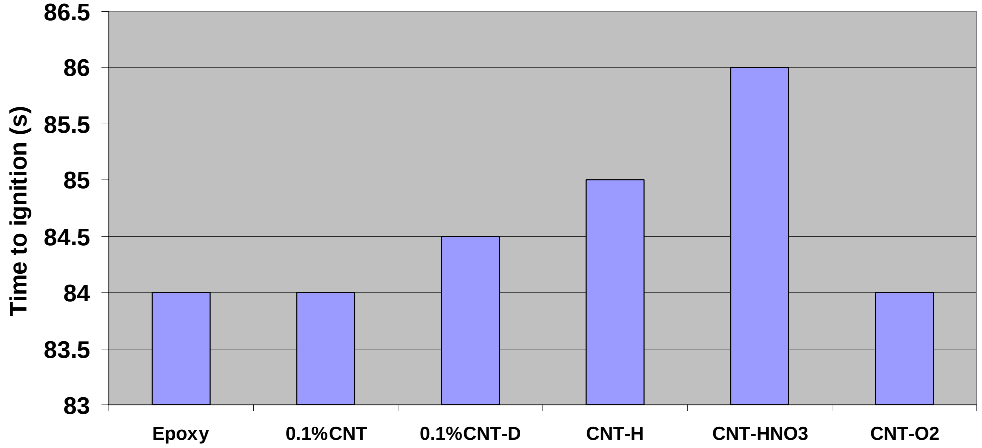
Results- SEM observations

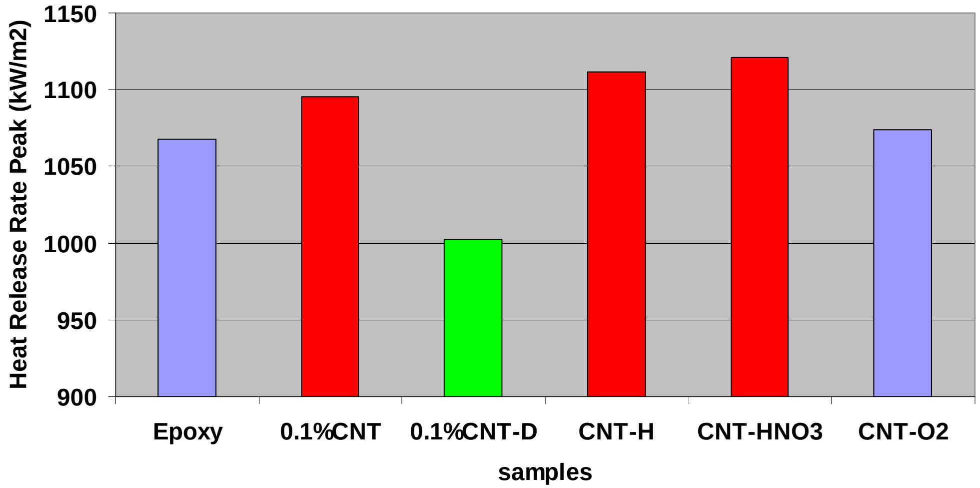


The most homogeneous dispersion in the matrix was achieved with amine functionalized CNT. (few agglomerates remaining). The amino groups seems to stabilise the CNT-dispersion by stronger interactions with the epoxy matrix.

Results- Effect of CNT functionalization on epoxy flammability: heat release rate

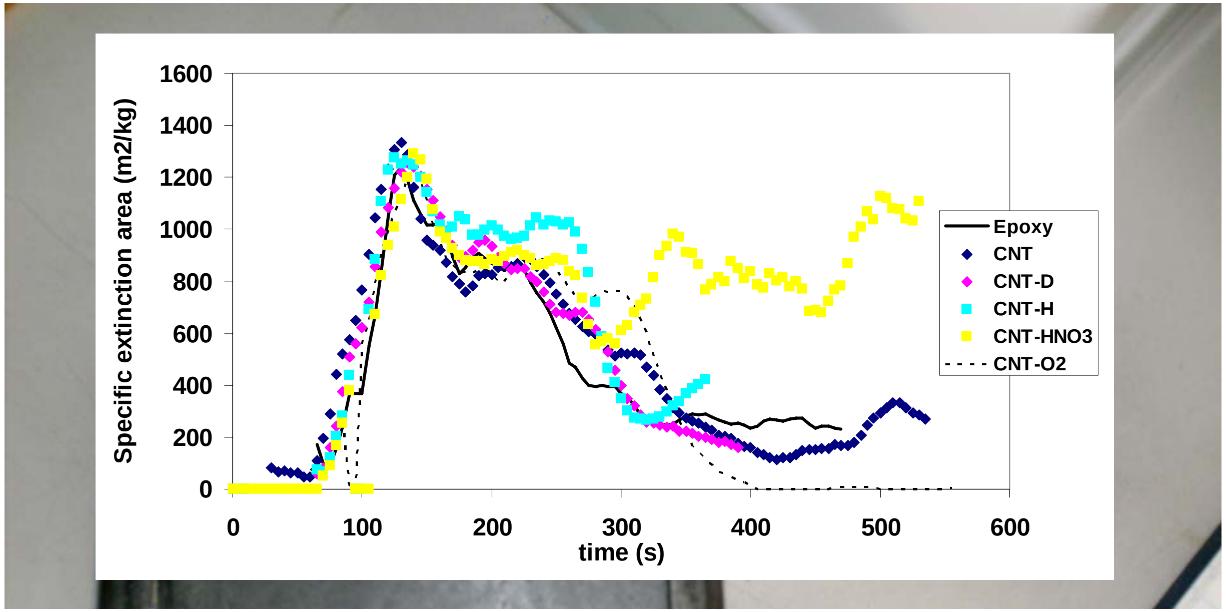






Compared to neat epoxy, Cone Calorimeter results show no significant changes in flammability by the use of 0.1wt% of CNT (functionalized and no-functionalized).
Time-to-ignition increases with HNO3 treated and amine functionalized CNT.
Heat release rate peak is 15% reduced for D treated samples.

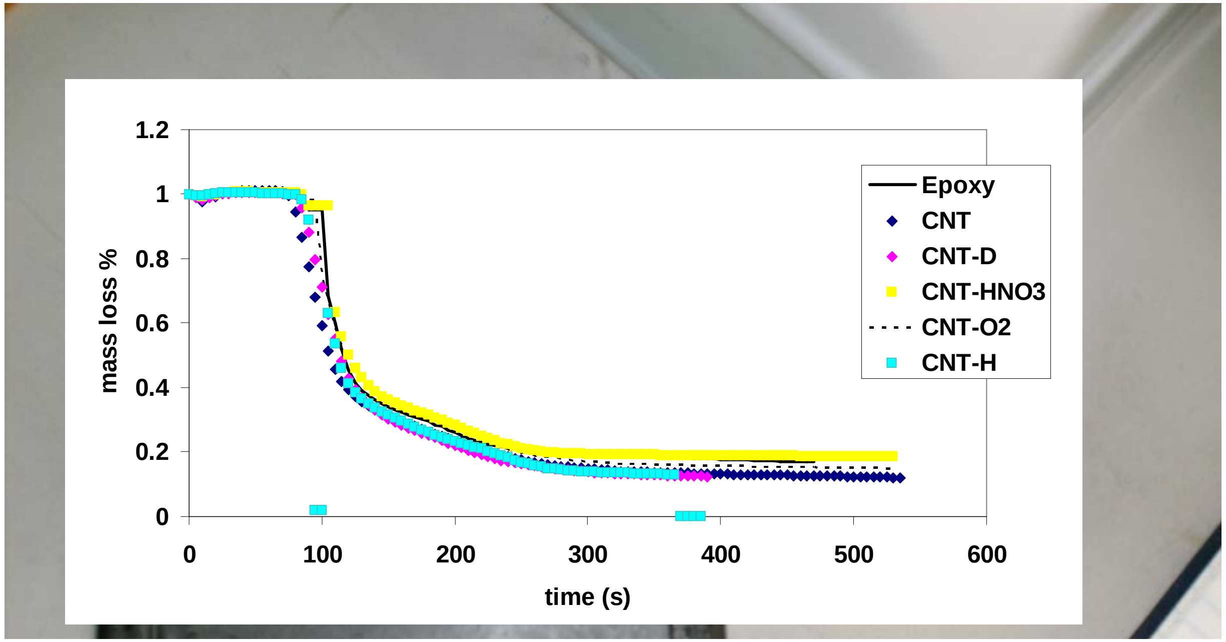
Results- Effect of CNT functionalization on epoxy flammability: smoke release



Almost all the 0.1% CNT/epoxy samples release the same quantity of smoke from volatiles as pure resin.

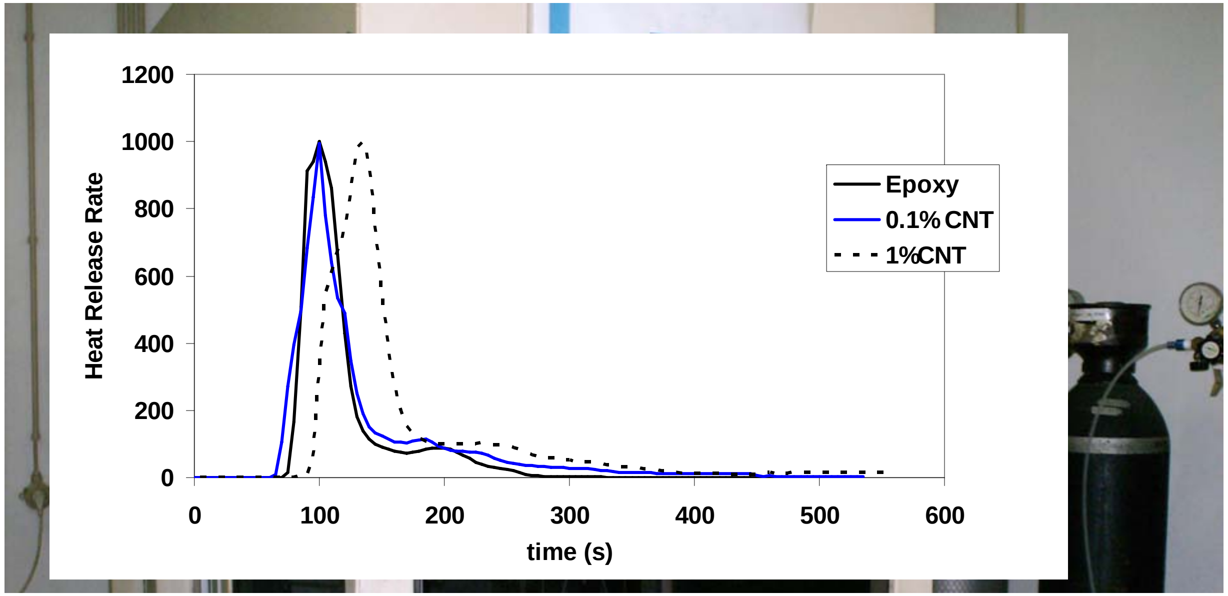
It is just noted a longer release of smoke for the HNO3 treated CNT sample.

Results- Effect of CNT functionalization on epoxy flammability: mass loss



Mass loss curves **do not show significant changes** with the different CNT treatments.
It is just marked an improvement in thermal stability with the introduction of HNO3 treated CNT in resin.

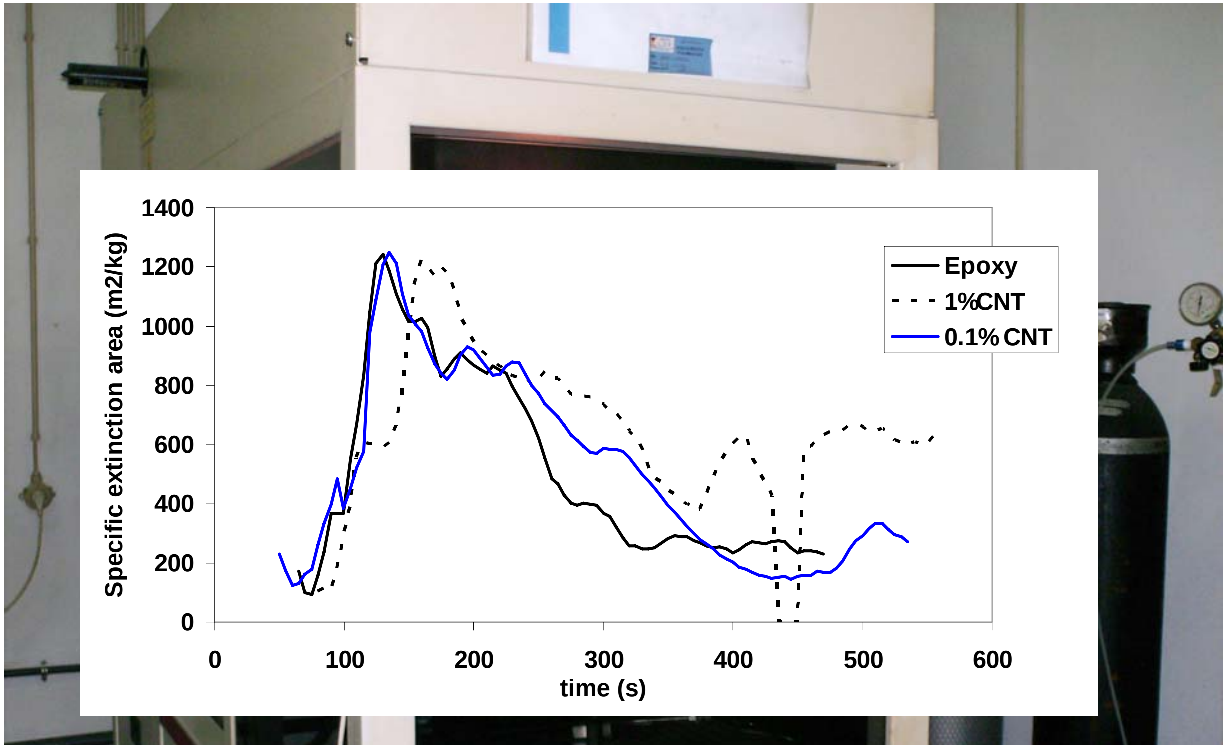
Results- Effect of CNT amount on epoxy flammability: heat release rate



Cone calorimeter results show some important changes in epoxy flammability, by the use of 1wt% of CNT:

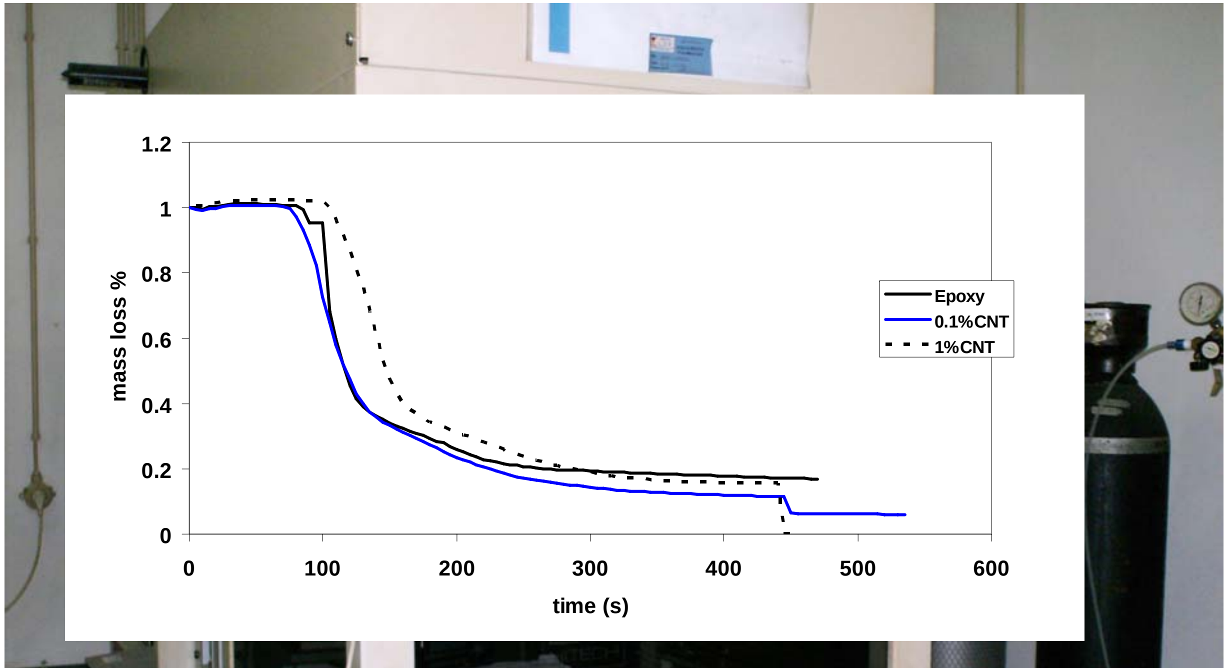
- **20 seconds increase** in time-to-ignition;
- **17% decrease** in heat release rate peak.

Results- Effect of CNT amount on epoxy flammability: smoke release



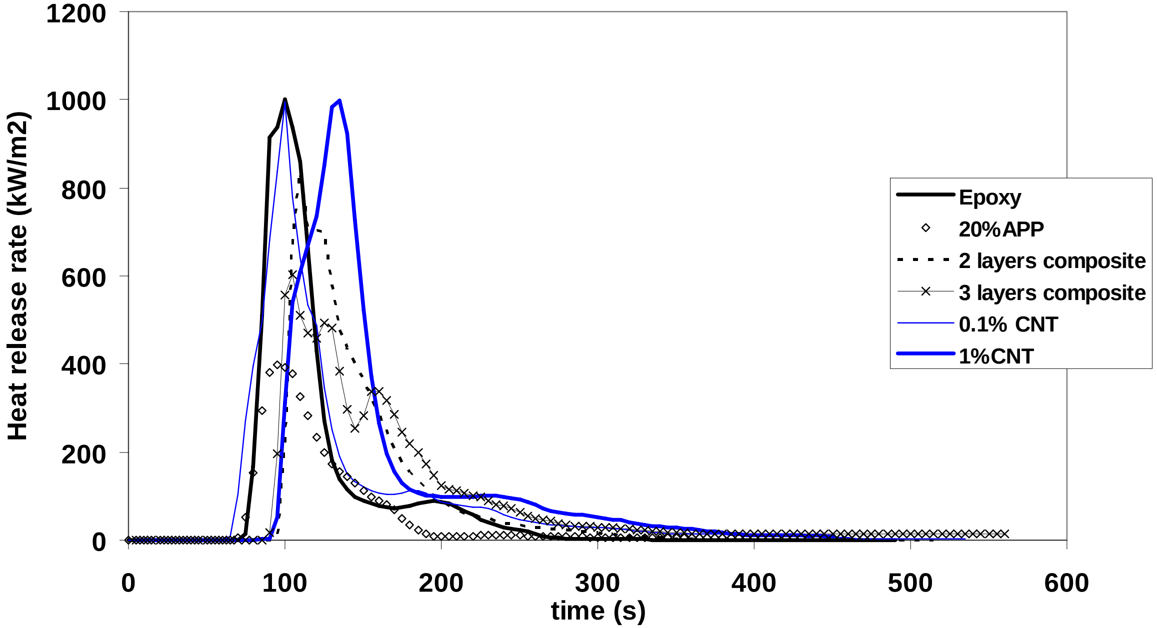
The smoke release is delayed when using 1wt% of CNT.
The fire survivability is increased!

Results- Effect of CNT amount on epoxy flammability: mass loss



Mass loss curves do not show improvements in char formation by the addition of different amounts of CNT.

Results- comparing with the effect of carbon fibers (CF) and APP on epoxy flammability: HRR



When compared to neat epoxy, Heat Release Rate curves show:

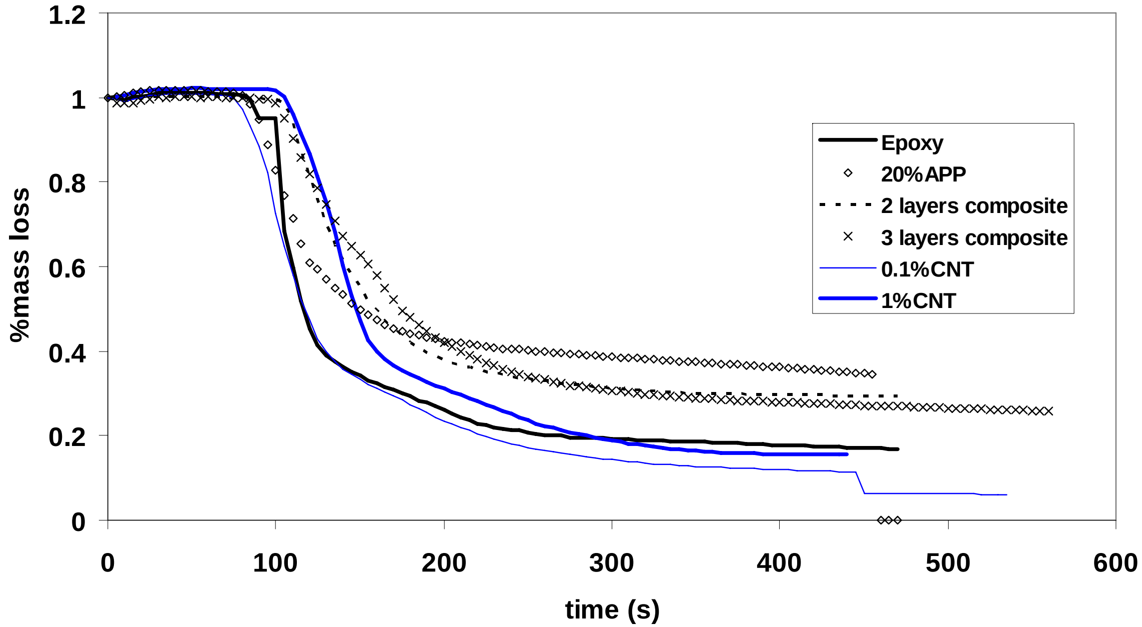
-1.0 wt% of CNT present the same effect in increasing the time-to-ignition, as the 2 carbon fibres (CF) layers;

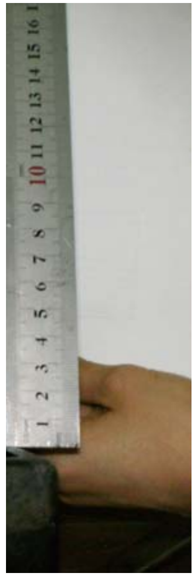
-1.0 wt% of CNT present rather the same effect in the heat release rate peak as the 2 CF layers;

-3 CF layers promote an important reduction in the heat release rate peak;

-20% of APP reduces in 60% the heat release rate peak.

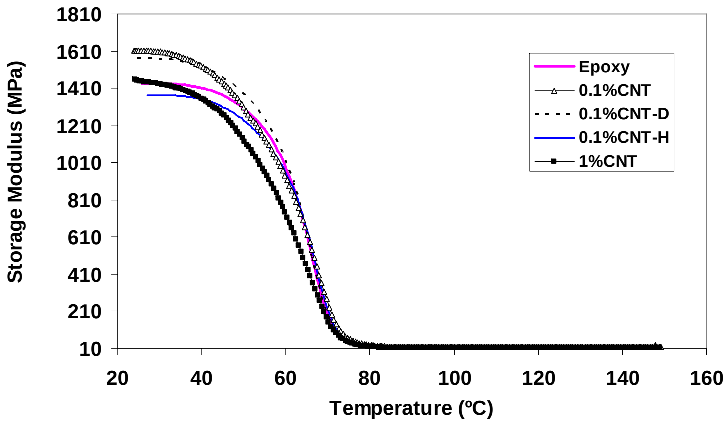
Results- comparing with the effect of carbon fibers and APP on epoxy flammability: mass loss

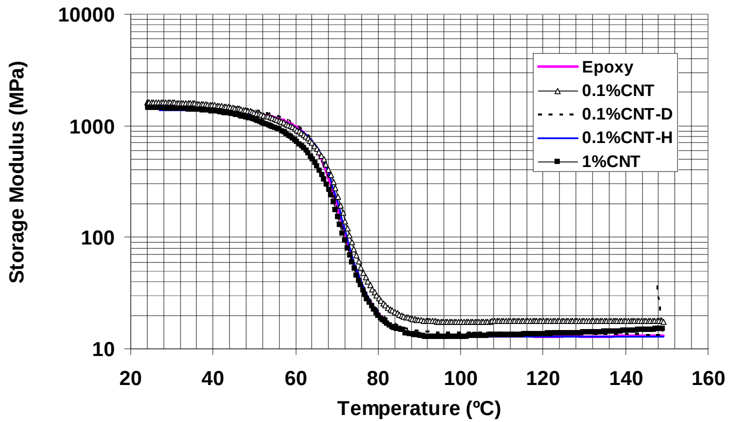




Cone Calorimeter results show:
- 2 and 3 CF layers produces the same mass residue;
-20% APP produces the higher charring residue.

Results- Effect of CNT functionalization and amount on Storage modulus, E’





Compared to neat epoxy, DMTA results indicated:

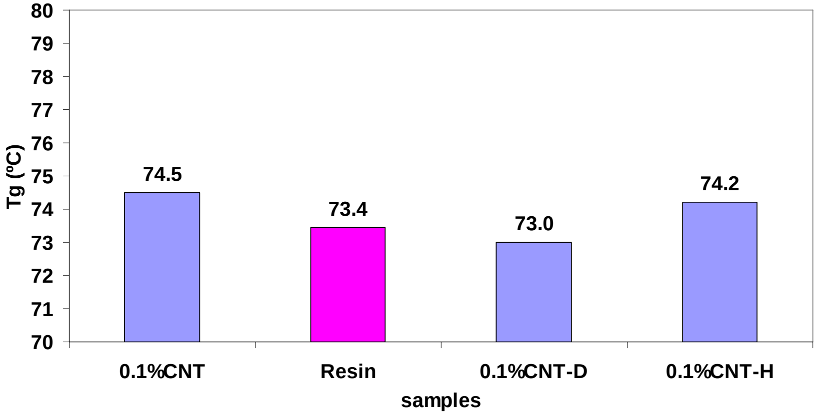
- a significant increase in storage modulus for 0.1 wt% CNT/epoxy at room temperature for no treated and D treated samples;

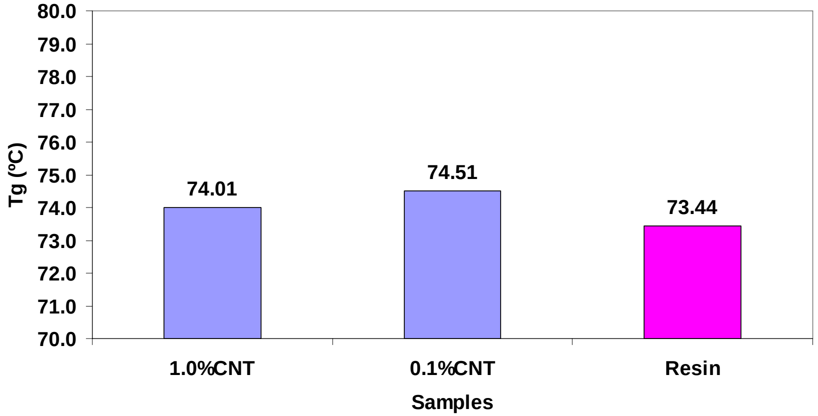
-a drop in storage modulus for H treated samples;

- a small improvement in storage modulus for 1 wt% CNT/epoxy at room temperature;

-an important increase in the elastic properties of the 0.1 wt% and 1wt% CNT/epoxy epoxy system at elevated temperatures.

RESULTS- Effect of CNT functionalization and amount on Glass transition temperature, Tg





Compared to neat epoxy, DMTA results show no significant improvements in *T*g, either by the use of 0.1wt% of CNT (functionalized and no-functionalized) either by the use of 1wt% amount of CNT.

CONCLUSIONS

- The most homogeneous dispersion in the matrix was achieved with amine functionalized CNT. (few agglomerates remaining).
- Compared to epoxy resin, cone calorimeter results show:
  - No significant changes in flammability by the use of 0.1wt% of CNT (functionalized and no-functionalized);
  - Some important changes in flammability by the use of 1wt% of CNT: a significant increase in time-to-ignition and a decrease in heat release rate peak;
  - 1.0 wt% of CNT present the same effect in increasing the time-to-ignition, as the 2 carbon fibres (CF) layers;
  - 3 CF layers promote an important reduction in the heat release rate peak;
  - 20% of APP reduces in 60% the heat release rate peak;
  - 2 and 3 CF layers produces the same mass residue.

CONCLUSIONS

DMTA results indicated:

- a significant increase in storage modulus for 0.1 wt% CNT/epoxy at room temperature for no treated and D treated samples;
- a drop in storage modulus for H treated samples;
- a small improvement in storage modulus for 1 wt% CNT/epoxy at room temperature;
- an important increase in the elastic properties of the 0.1 wt% and 1wt% CNT/epoxy epoxy system at elevated temperatures;
- no significant improvements in *T*g, either by the use of 0.1wt% of CNT (functionalized and no-functionalized) either by the use of 1wt% amount of CNT.

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