Epoxy composites with aligned assemblies of carbon nanotubes

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INTRODUCTION

Aligned carbon nanotubes in the form of sheets, yarns and fibres give a promise of the translation of their axial properties into the special functionality of polymeric composites.

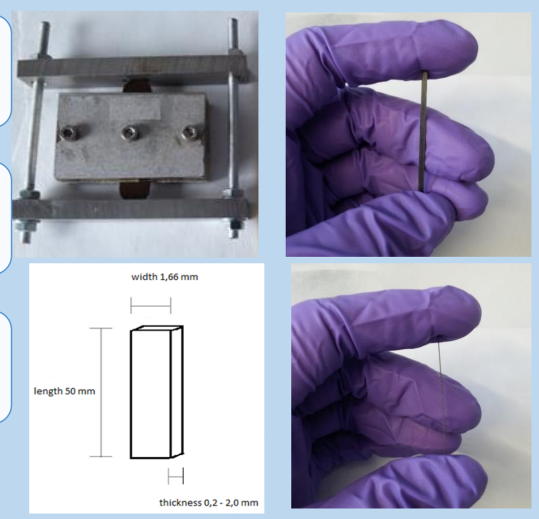
We have investigated a range of epoxy composites filled with carbon nanotube assemblies in the form of mats and fibres, synthesized by the direct single-step spinning process. Specific thermal behavior and mechanical performance of nanocomposites were found in comparison with composites filled with commercially available carbon fibres.

MATERIALS

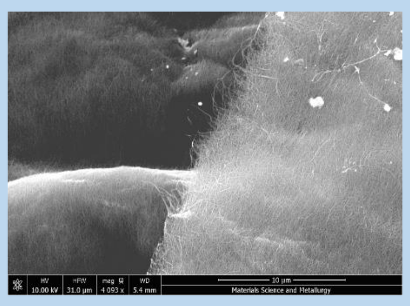
- As-produced carbon nanotube mats (CNTM) and fibres (CNTF) (ropes of ~1000 individual filaments Ø 10 µm, 0.03 tex), Cambridge University;
- PAN-based carbon fibres T300 3K (Ø 7 µm, 396 tex), Amoco;
- Araldite LY 556 epoxy resin (pot life RT 32-37 h, mix viscosity RT 5.2-6.0 Pa·s), Huntsman.

COMPOSITE PROCESSING

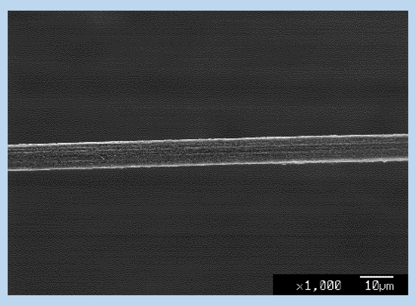
1. Epoxy system degassing 30-60 min, 60 °C, 0.1 MPa
2. Impregnation & second degassing 30-60 min, 60 °C, 0.1 MPa
3. - Curing 2h 120 °C, 0.1 MPa
   - Post-curing 4h 180 °C, 0.1 Mpa
   - Slow cooling to room temperature

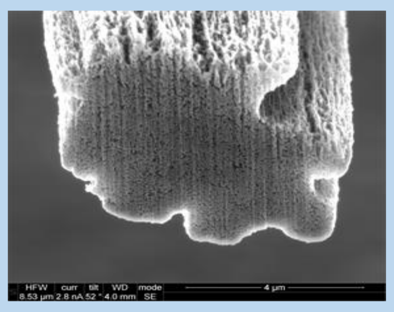


RESULTS and DISCUSSION



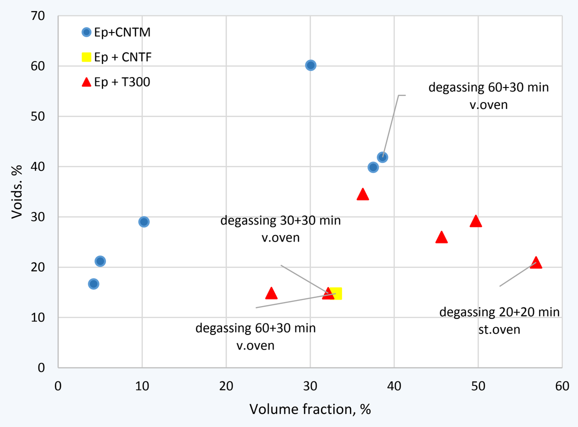
Carbon nanotube mat



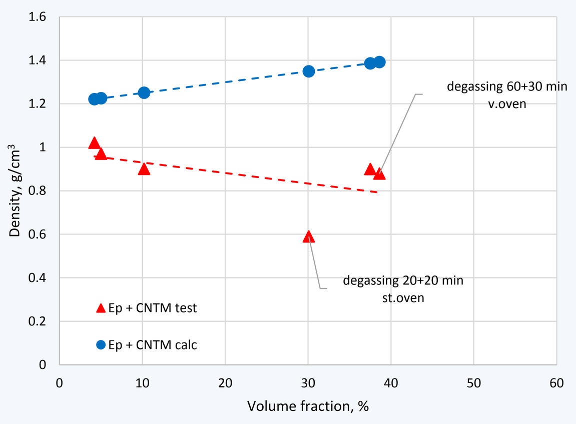


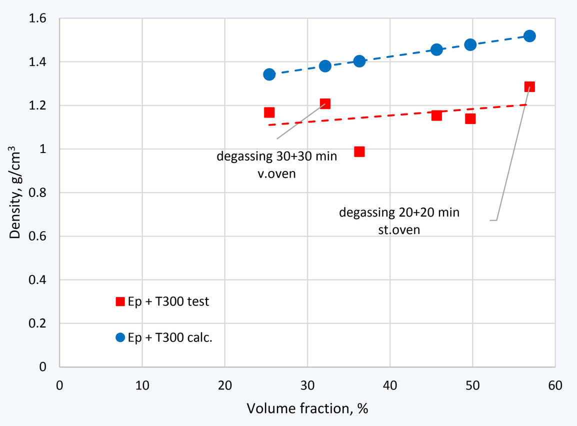
Carbon nanotube fibre

Density & Voids



Double degassing (epoxy system + prepreg), followed by curing in a vacuum allows to keep the content of voids of 12-14% vol for CF- and CNTF-composites, while for CNTM-composites it rises up to 40 % vol.

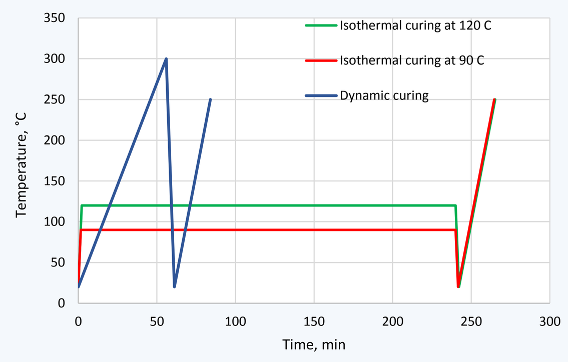




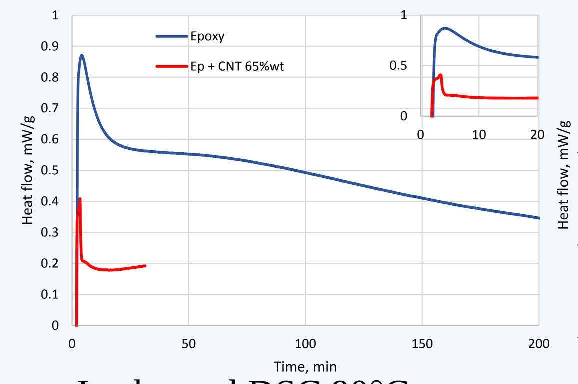
Next step:

- Lower viscosity epoxy system (0.1-0.2 Pa·s instead of 0.7-0.9 Pa·s)
- Higher vacuum pressure (0.6-0.8 MPa instead of 0.1 MPa)

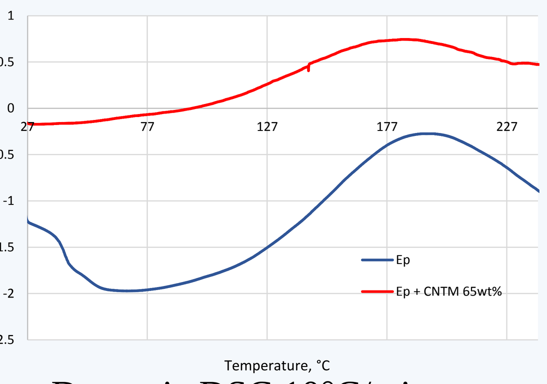
Effect on curing



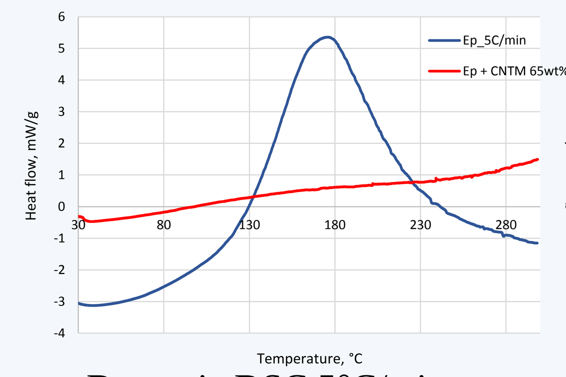
Isothermal and dynamic DSC-regimes were applied to analyse the influence of CNTM on the curing process of epoxy resin.



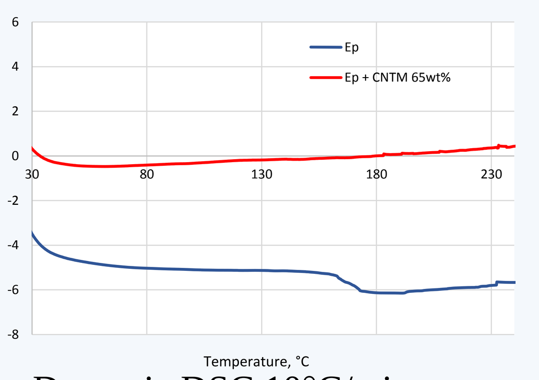
Isothermal DSC 90°C



Dynamic DSC 10°C/min



Dynamic DSC 5°C/min



Dynamic DSC 10°C/min

Cure reaction peak at lower temperature – catalytic effect of CNTM due to their high thermal conductivity (~ 1230 $Wm^{-1}K^{-1}$) (?)

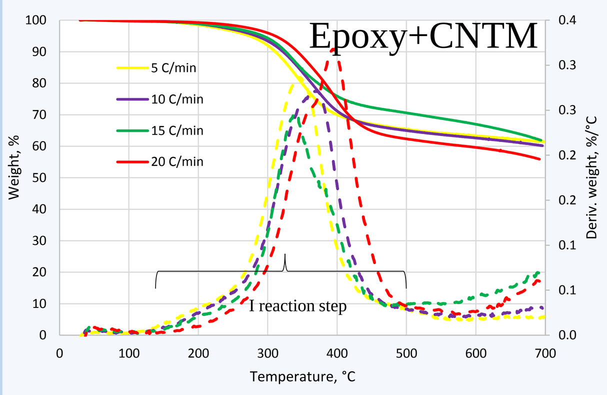
Heat transfer and heating mechanism (?)

Lower overall degree of cure / cross-link density (?)

Next step:

- Numeric evaluation of kinetics parameters
- Correlation with the volume fraction and the surface chemistry of CNTM in comparison with CNTF

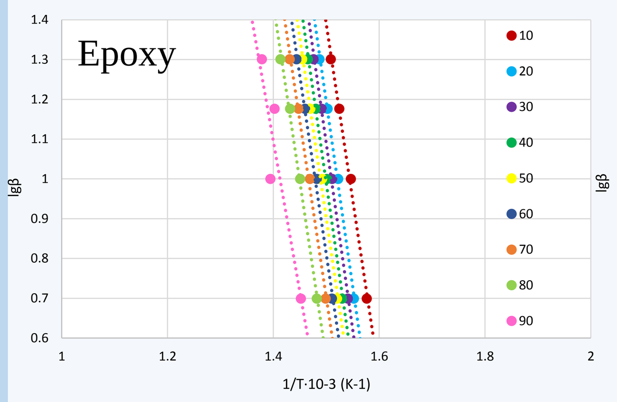
Effect on thermal behavior

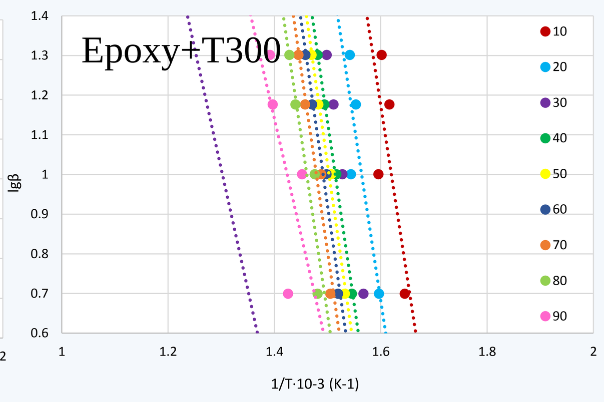


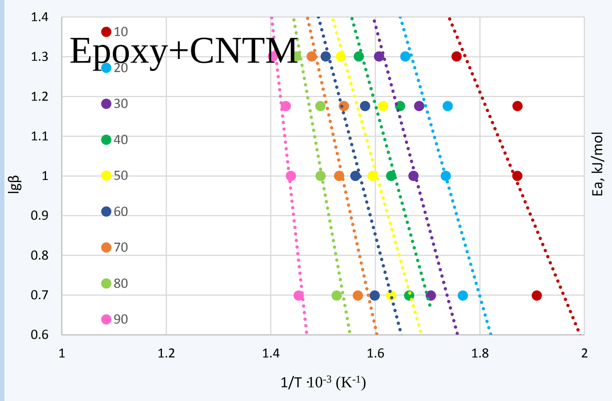
Samples were tested by TGA at four different heating rates (5, 10, 15 and 20 °C/min) and the Ozawa method was used to estimate an apparent activation energy (E_a, kJ/mol) of thermal decomposition at specific extent of composite conversion (α 10-90 %).

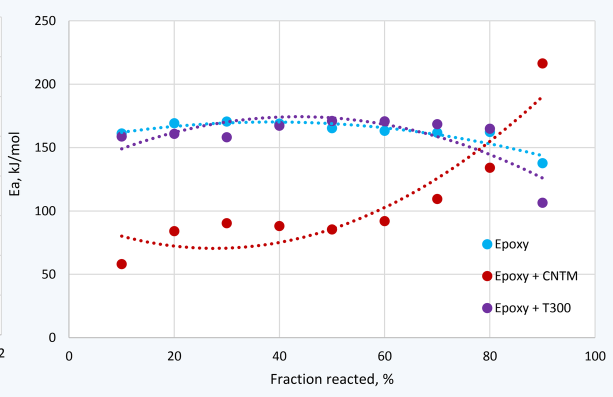
Ozawa expression:

$$\log \beta = \log\left(\frac{AE}{Rg(\alpha)}\right) - 2.315 - 0.4567\frac{E}{RT}$$







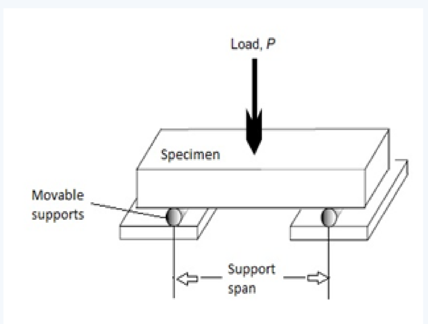


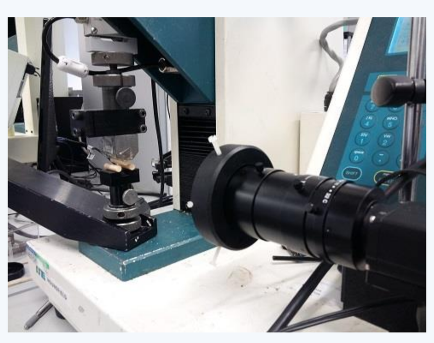
The calculated E_a of the decomposition of CNTM-composites is lower than for T300-composites and neat epoxy.

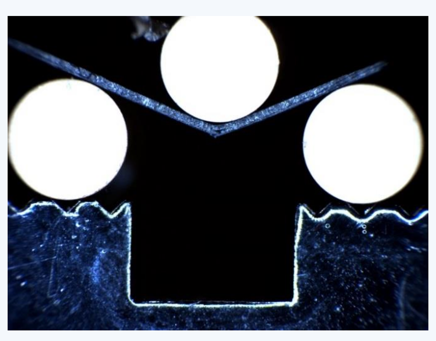
Next step:

- Coats & Redfern method (reaction mechanism and kinetics)
- Thermal decomposition of CNTF-composites

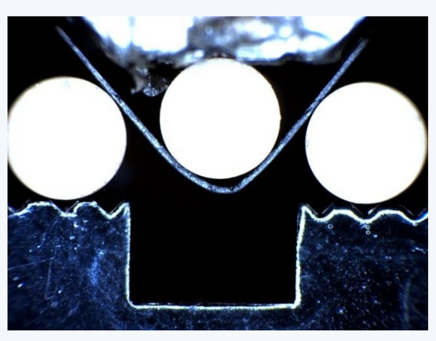
Flexural properties







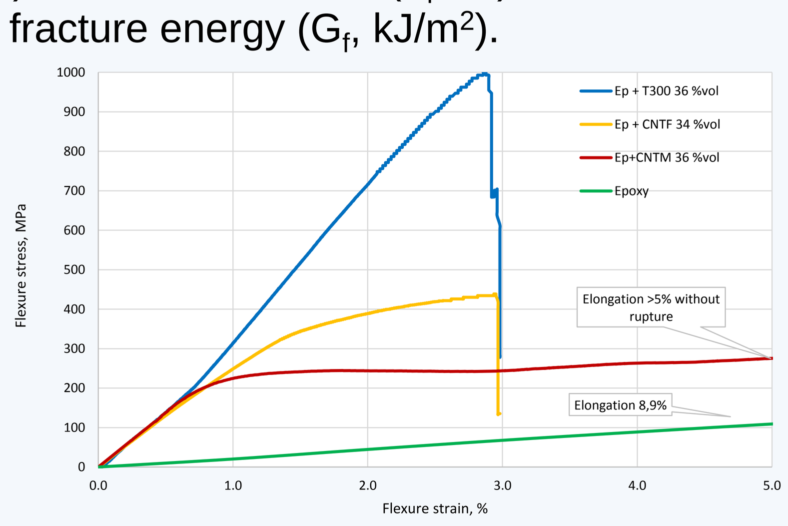
CNTF-composite

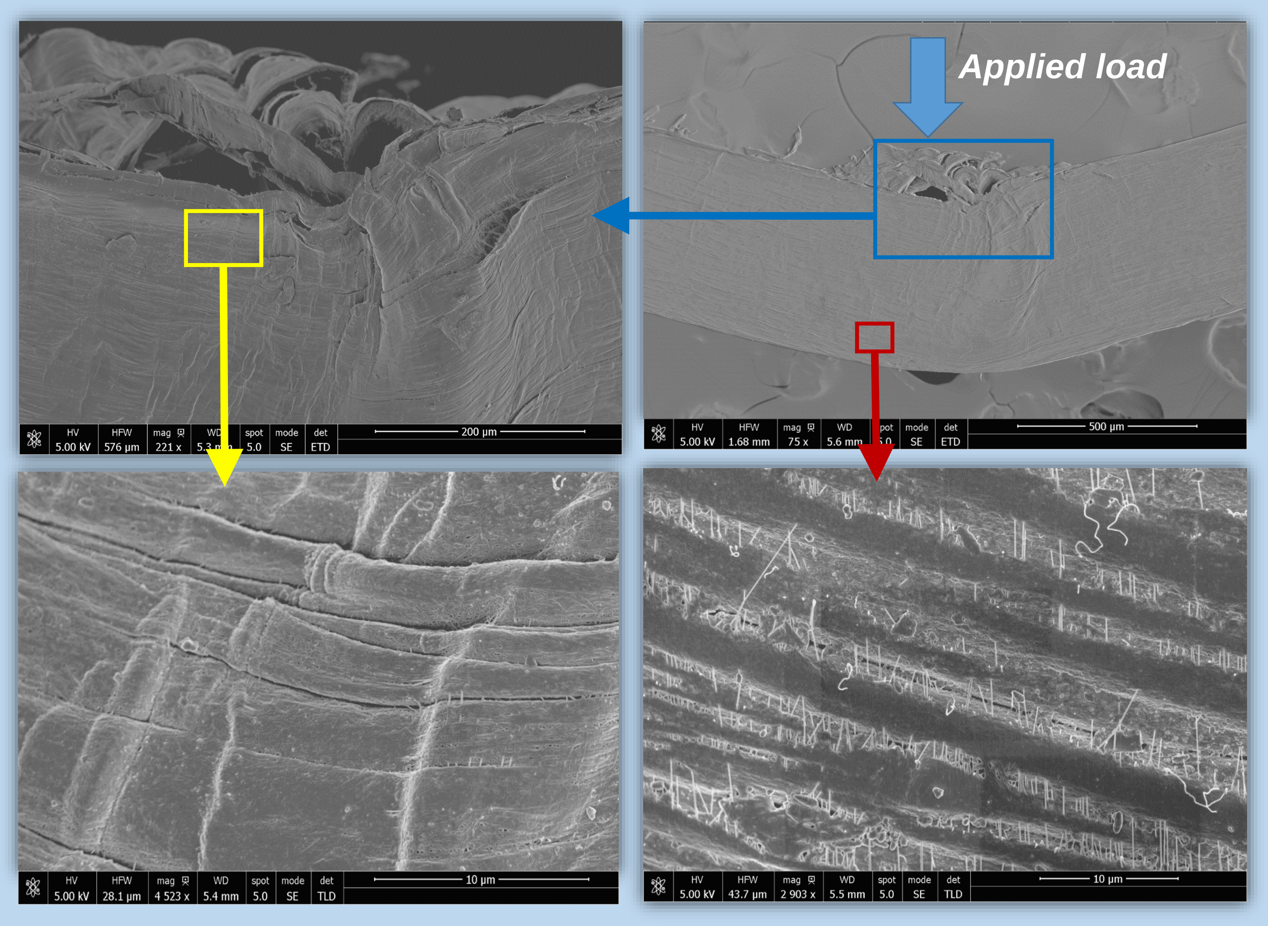


CNTM-composite

The mechanical performance of composites was analysed by a three-point bending test according to the ASTM D 7264 with a span-to-depth ratio of 40:1. Each specimen was deflected until rupture occurred in the outer surface or until a maximum strain of 5% was reached, whichever occurred first. Obtained load-deflection curves were used to calculate the flexural strength ($σ_f$, MPa), the flexural strain ($ε_f$, %), the modulus of elasticity (E_f, GPa) and the fracture energy (G_f, kJ/m²).

Incorporation of more than 10 %vol CNTM increases the flexural stress less than T300, but gives a significant plasticity to the composite performance.





Sample	% Vol	$σ_f$, MPa	$ε_f$, %	E_f, GPa	G_f, kJ/m²
Epoxy	-	163	8.7	2.0	9.0
Ep+T300	26	597	2.1	30.2	12.9
	36	1000	2.9	30.1	16.8
	52	2068	2.2	112.2	36.6
Ep+CNTM	4	113	4.2	2.7	2.7
	10	140	> 5	10.7	>2.9
	36	276	no rupture	27.2	>14.2
Ep+CNTF	34	434	3.0	24.9	14.5

For all samples with more than 10 % vol of carbon nanotube mats bending tests were stopped without rupture occurred in the outer surface. SEM images show that the composite started to damage in compression and buckling failure modes, but not in tension.

This specific performance needs further evaluation, and can be interesting for applications where bending ability without rupture is highlighted.

Next step:

- Numeric evaluation of compression and shear stress
- Tensile properties

CONCLUSIONS and FUTURE STEPS

- ✓ DSC / TGA results and kinetic analysis show the significant influence of carbon nanotubes on the curing process and thermal degradation behavior.
- ✓ Composites with high amount of carbon nanotube mats exhibit plasticity without rupture under bending, and start initial damage in compression and buckling, which can be interesting for practical applications.

- Understanding the role of carbon nanotube mats and fibres in curing reaction and thermal decomposition processes
- Evaluation of compression behavior
- Investigation of tensile properties
- Ability to transfer flexibility from CNTM to conventional CFR materials through the hybrid structure of CNTM-CF prepreg

ACKNOWLEDGEMENTS

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