# CHARACTERIZATION OF CARBON NANOTUBE PAPERS INFUSED WITH CYANATE-ESTER RESIN

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## SUMMARY

Carbon nanotube skeletons were used to obtain polymer composites with high nanotube contents through resin infusion. A cyanate ester resin was used as matrix in view of prospective aerospace applications, which resulted in a satisfactory thermal behaviour, as determined by dynamic mechanical analysis. Mechanical performance was lower than expected, and discussed in light of composite defects and test method limitations.

*Keywords: carbon, nanotubes, cyanate ester resin, mechanical properties, DMTA*

## INTRODUCTION

In recent years the potential of carbon nanotubes (CNTs) has been investigated for various and highly demanding applications [1, 2]. The high mechanical performance of carbon nanotubes makes their use as the reinforcing element in composites, a very attractive development [3]. However there are difficulties associated with the effective dispersion of nanosized constituents. Several mixing techniques have been developed that result in homogeneous dispersions, still, the use of nanoparticles usually requires that content levels be kept to a minimum or dispersion problems inevitably arise. A possible and alternative solution to overcome this limitation would be the use of stable carbon nanotube preassembled structures. They could be then used as a means to obtain

polymer composites with high nanotube contents through resin infusion manufacturing techniques. The company Future Carbon GmbH has developed carbon nanotube structures labelled “skeletons”, that could be used as above described. The present work describes an effort to develop composite structures based on carbon nanotube skeletons and a high performance cyanate ester resin [4], and assess their relevance for highly demanding aerospace applications. For that purpose, the mechanical performance was evaluated through quasi-static tensile and flexural testing, while dynamic mechanical thermal analysis (DMTA) was used to assess both thermal and mechanical behaviour.

## EXPERIMENTAL

### Materials

A high performance thermoset cyanate ester (CE) resin (Primaset® DT-4000, Lonza Group Ltd.) was as used as polymer matrix, characterized by high glass transition temperature, excellent dielectric and mechanical properties, and particularly adequate for uses in electronics, aerospace, automotive and industrial composites and compounds.

The CNTs that constitute the basis of the CNT skeletons used as reinforcing element were produced by a combustion chemical vapour deposition (CCVD) method developed at Future Carbon GmbH. The CNTs can undergo different surface or thermal treatments to improve the compatibility towards the polymer resin before being subsequently used to manufacture two types of 3-dimensional CNT skeleton structures, *i.e.*, CNT papers and CNT felts. The production process can include an additional solvent treatment step that may or not be used to expand the structure thus increasing porosity. More detailed information concerning both CNT CCVD and CNT skeleton manufacture processes can be found elsewhere [5].

For comparison purposes a CNT felt from another producer (R&G) and a commercial unidirectional (UD) carbon fibre fabric were also used to produce reference composites.

### Processing

The polymer composite structures were produced by resin infiltration into the CNT skeletons through capillary action of the low viscosity heated resin. Following infiltration, composites of one or more layers were produced by stacking infiltrated CNT skeletons before final curing, which took place at a maximum temperature of 260 ºC without application of any external pressure to the composite structure [5]. The same procedure was used to manufacture composite structures with the commercial carbon fibre UD fabric.

Plates were also produced for neat cyanate ester resin cured under the same conditions as above.

The composite structures produced for the purpose of the present work are presented on Table 1, which includes CNT reinforcement production details.

Table 1. Composite structures and reinforcement production parameters.

| Composite Structure | Reinforcement | | Reinforcement Production | | |
|---|---|---|---|---|---|
| | Type | Layers | Functionalization | Solvent Treatment | |
| | | | | Solvent | Expansion |
| P-H | CNT paper | 1 | hydroxyl groups | n-hexan | no |
| P-HE | | 1 | hydroxyl groups | n-hexan | yes |
| P-C | | 2 | carboxyl groups | - | - |
| F1 | CNT felt | 3 | - | - | - |
| F2 | | 5 | - (R&G product) | - | - |
| UD | UD CF Fabric | 6 | - | - | - |

**Testing**

The present work is part of joint research project so the samples had to be divided by several partners for distinct test evaluations, and as a consequence the sample plates were *ca*. 25 to 40 mm in length by 20 to 30 mm in width. An example of specimen extraction from a plate with typical dimensions is presented in Fig. 1. The following testing methods were performed over both specimens extracted from composite and neat resin plates.

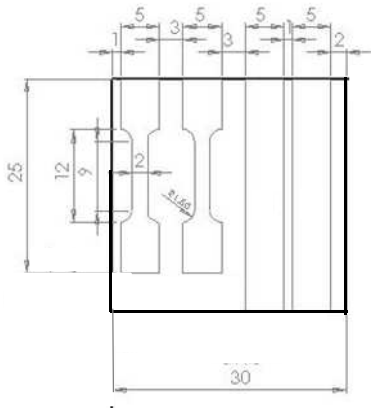


Figure 1. Example of specimen distribution in a 30 mm x 30 mm sample plate.

Tensile behaviour was characterized using minitensile dumbbell specimens (Fig. 1) tested at a speed of 0.20 mm.min$^{-1}$. The tests were performed using both a TIRAtest® 2805 table unit electromechanical universal testing machine and an INSTRON® model 4208 electromechanical universal testing machine.

The flexural apparent modulus was determined by three point bending tests performed on the DMTA specimens before that analysis, by loading at a speed of 0.25 mm.min$^{-1}$ up to a maximum strain of 0.3%, using a span-to-thickness ratio of 16, and 5 mm

diameter loading and support members. The tests were performed on an INSTRON® model 4208 electromechanical universal testing machine.

The thermal mechanical behaviour of the material was evaluated from room temperature (*ca.* 23 ºC) up to 295 ºC at a heating rate of 1.5 ºC.min$^{-1}$, and a frequency of 1 Hz, on a Polymer Laboratories Mk II dynamic mechanical thermal analyzer fit with Composites Head unit. The specimens were loaded in single cantilever mode with a free length of 22 mm, and with one exception (*i.e.*, reference composite with commercial UD carbon fibre fabric), all materials had their specimens tested edgewise. This was done to maintain the same testing conditions for the highest possible quantity of available materials. Testing flatwise lead to low signal resolution due to low specimen stiffness in the case of the lower thickness structures. The very high stiffness of the reference UD composite ruled out testing it edgewise.

## RESULTS AND DISCUSSION

The small size of the sample plates determined that minitensile specimens had to be used. Several alternatives were considered and both the ASTM [6] and JIS [7] standards were discarded because their dumbbell specimens required a gripping region with a large width that would in most cases preclude obtaining more than a single tensile specimen. The ASTM microtensile specimen was also too long (length $\geq$ 38 mm) for some of the existing sample plates. The choice for specimen geometry (Fig. 1) was one proposed in a study addressing metals tensile testing [8, 9] in situations where not enough material is available to extract standard tensile specimens, as in the case where welded joints have to be characterized or in case of component failures with not enough material available for investigation. With this geometry it was possible to obtain two tensile specimens for most samples in addition to two specimens for flexural/DMA testing. The remaining material could be used for other analyses not addressed in the present report (*e.g.*, differential scanning calorimetry and microscopy studies).

The tensile resistance and apparent flexural modulus results from tensile and three point bending tests, respectively, are presented in Fig. 2. It seems clear that the modulus values for the obtained composite structures are either similar or only slightly higher than that of the polymer matrix, with the exception of that obtained for the UD composite, which yielded a modulus value about ten times higher. The proximity of modulus values renders useless any trend analysis for this property between composite structures with CNT reinforcements. The tensile resistance for the UD composite is also much higher than those of the CNT-based composites - *ca.* 7 to 15 times higher, depending on the particular composite. However, the tensile resistance property shows greater amplitude of values for the CNT composites and some observations are possible. It should however be taken into consideration that strength values are usually associated to higher scatter then modulus values, and that a maximum of only two specimens were tested for each structure. With that in mind, a decrease in strength is observed from the P-H to the P-HE composite. The later having an expanded structure results in a lower CNT volume fraction which can explain the observed trend. The P-C composite shows the lowest strength among the CNT paper reinforced composites and may indicate that infiltration is more effective for the hydroxyl functionalized CNTs. However, the P-C composite refers to a double layer structure whereas both the P-H and P-HE composites are monolayer ones, and this may influence the observed results. In fact, it has been

observed in ongoing studies (*e.g.*, microscopy) the existence of resin rich layers outside and between the CNT reinforcing structures which can influence the CNT volume fraction and therefore make inadequate any conclusions resulting from observations for

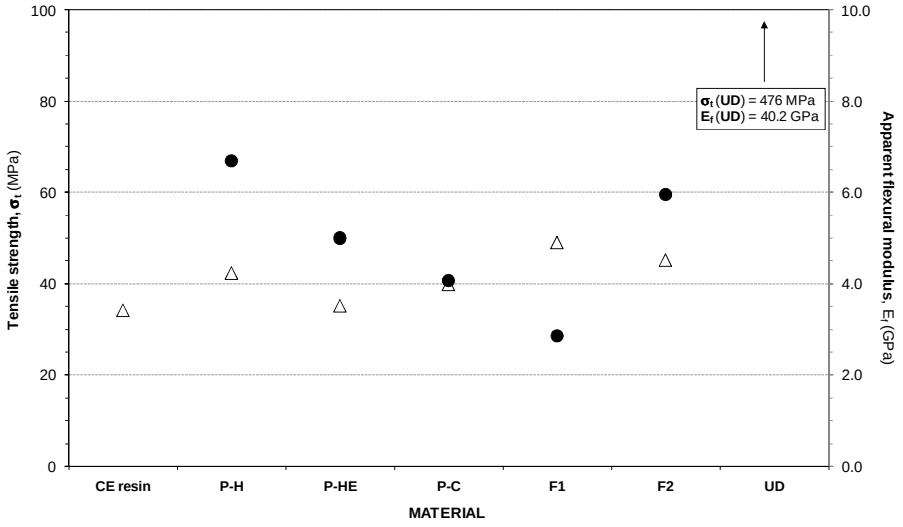


Figure 2. Results for tensile resistance (●) and apparent flexural modulus (△).

composites with dissimilar number of layers. The same remark can be made in relation to a comparison of strength values between both CNT felt reinforced composites (*cf.* Table 1). Additionally, the felts have different manufacturers and a better knowledge of morphology differences between both CNT felts is also required. A last remark on the subject of mechanical characterization to state that long unidirectional fibres in the UD composite may partially explain its much higher performance, but not entirely. As stated above, the modulus values for all CNT based composite structures are not significantly higher than that of the neat CE resin and therefore problems with infiltration may be playing an important role. We hope to clarify this issue with microscopy studies in progress.

The dynamic mechanical thermal analysis curves depicted in Fig. 3, reveal room temperature bending storage modulus ($E_f'$) values that are consistent with the results for flexural modulus presented earlier, *i.e.*, very close values between the CNT composites which are only slightly above that of the CE resin, and a much higher value for the UD composite. However as temperature raises and we move away from the matrix glassy region, through the glass transition and into the rubbery plateau a quite different situation is portrayed. The gap between storage moduli in the rubbery phase temperature range is now clear between different composites and all composites show values clearly above the one of neat resin.

The values for glass transition temperature ($T_g$) were assigned as the temperature of the peak value in the *tan* δ curves (*tan* δ = $E_f''$(loss modulus) / $E_f'$ (storage modulus) obtained from DMTA, and are presented in Table 2. The values show some differences

that may be due, to some extent, to small variations during curing, reflecting slightly different degrees of cure. In fact, different runs for neat resin specimens produced $T_g$ values with differences reaching about 10 ºC.

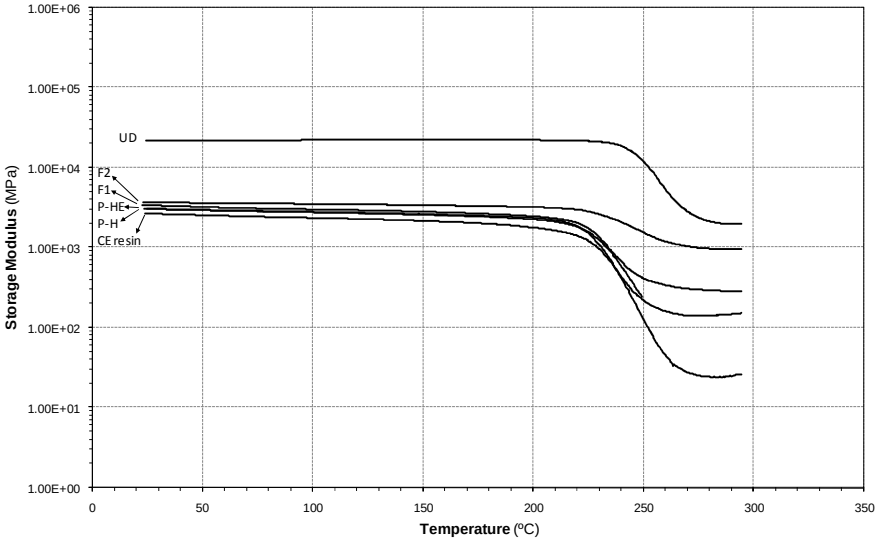


Figure 3. Dynamic mechanical thermal analysis spectra.

Table 2. Glass transition temperature.

| Material | Glass Transition (ºC) |
|---|---|
| CE resin | 247 |
| P-H | 238 |
| P-HE | 246 |
| F1 | 237 |
| F2 | 250 |
| UD | 260 |

## CONCLUSIONS

The mechanical performance of the manufactured composites was below the one expected for a well impregnated composite and indeed the ongoing microscopy analyses show resin rich regions around the CNT skeletons that help explain the outcome. The DMTA results confirmed the high thermal performance of the selected cyanate-ester resin system. Further work to improve impregnation during resin infusion processing is currently on progress. It should be noted that other uses besides structural applications are envisaged for CNT composites (*e.g.*, improved electrical conduction), where the obtained structures might encounter successful application.

**ACKNOWLEDGEMENTS**

This work was performed in the frame of project *Non-conventional Matrix / CNT Reinforced Composite for Applications in Space (NACO)*, contract 20521/06/NL/SFe, funded by the European Space Agency (ESA).

The authors wish to thank Mário J. A Pinto (Machining and Prototypes Unit of INEGI) and Fábio D. L. Neto (Composite Materials and Structures Unit of INEGI) for their support in specimen manufacture.

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