CHARACTERIZATION OF CARBON NANOTUBE DOPED CARBON FIBER PREPREG LAMINATE

J. Engström[1*], R. Joffe[2], P. Fernberg[1]

[1]Swerea SICOMP AB, Dept. of Materials and Manufacturing, P.O. Box 271, 941 26 Piteå, Sweden
[2] Luleå University of Technology, Division of Materials Science, 971 87 Luleå, Sweden
**jonas.k.engström@swerea.se*

Keywords: Carbon nanotubes, carbon fiber composite, nano-doped prepreg, damage tolerance.

Abstract

The current paper reports results from a preliminary study on PREGCYL™ NC R2HM-01 which is a carbon nanotube doped prepreg produced by Nanocyl. The work consisted of sample manufacturing in autoclave, microcopy analysis with XHR-SEM and mechanical testing. The mechanical testing consisted of tensile tests of unidirectional (in longitudinal direction) and cross-ply laminates. Test of unidirectional laminates showed that stiffness of the PREGCYL material is slightly higher than that of MTM55 composites (111GPa vs 102GPa). The results from tests of cross-ply laminates indicated that damage (transverse cracks) initiation is delayed in PREGCYL composites compare to the MTM55 material. Damage accumulation also seems to be slower in nano-doped composites.

1 Introduction

There has been a lot of research and development in the area of so-called nanocomposites over the past decade. The concept of polymeric nanocomposites involves addition of relatively small amounts – ranging from fractions of percent to up to a few percent – of very small particles to polymeric materials with the purpose to achieve and enhance certain desired property of the host matrix. A characteristic feature of nano-reinforcement is that at least one of its dimensions is in the nanometer range. Many studies in the area of thermosetting fiber reinforced nanocomposites explore the possibility to add nanofiller into the composite material to improve mechanical and physical properties (e.g. toughness or electrical conductivity) [1,2]. Nano-reinforcements with very large potential are different types of carbon nanotubes (CNT). On the nano-scale they exhibit remarkable performance, both in terms of mechanical and electrical properties [2].The main challenge in most development work related to nanocomposites is to transfer the remarkable properties from the scale of individual CNT to the macro-scale. One common difficulty is to achieve good dispersion of the CNT in the matrix. When the dispersion is less successful, CNT may gather or remain in micrometer-sized agglomerates. This implies that they fail to create a percolating network required to achieve e.g. electrical conductivity. Agglomerates may in worst case also have detrimental effect on mechanical properties of the nanocomposite by acting as stress concentrators. Moreover, adding nanofillers to the matrix also leads to difficulties during the composite manufacturing due to the often large increase in viscosity as well as problems with filtering (the preform filters the nanofillers which clog up and hinders the resin flow) [3]. As a consequence of the above mentioned challenges and difficulties, many nanocomposite materials have been available mainly at a laboratory scale and rather inaccessible to the real industrial application. During the last years the number of commercially available nanomaterials has started to increase and it becomes important to evaluate if and how the processing of such material differs from more traditional materials. Also the property enhancement provided by the nanocomposite modification needs to be evaluated and assessed. The particulate goal in this study was to:

- Evaluate the processability of a commercially available CNT modified prepreg
- Manufacture composite laminates from the CNT modified prepreg
- Characterize the resulting composites via microscopy and mechanical testing and compare with commercially available traditional prepreg composite.

2 Materials

PREGCYL™ NC R2HM-01 is a prepreg produced by Nanocyl, Belgium. It is based on a formulated epoxy resin system EPOCYL™ NC R2HM01 modified (doped) with CNT. For this study a unidirectional reinforcement based on the Toray T700 - 12K fiber was used. The reinforcement had a fiber areal weight of 150 g/m^2 and the resin weight fraction was 37%. As reference material a prepreg from Advanced Composites Group based on the MTM55 epoxy resin was used with exactly the same reinforcement and fiber areal weight as above. The resin weight fraction was 36%.

3 Manufacturing

To evaluate the processability of the prepregs several laminates were manufactured. The laminates were thereafter characterized, as described in Section 4. Manufacturing was performed in an autoclave at Swerea SICOMP AB. The process parameters used are presented in Table 1.

Material	Cure cycle	Autoclave pressure [Bar]	Vacuum level [Bar]
PREGCYL	1h@120°C, 2h@140°C	6	< 0.04
MTM55	1h@120°C	6	< 0.04 until autoclave pressure ~1.4, then 1

Table 1. Autoclave process parameters used during manufacturing.

Different process parameters were logged during manufacturing as can be seen in the log for sample 216 (see Figure 1).

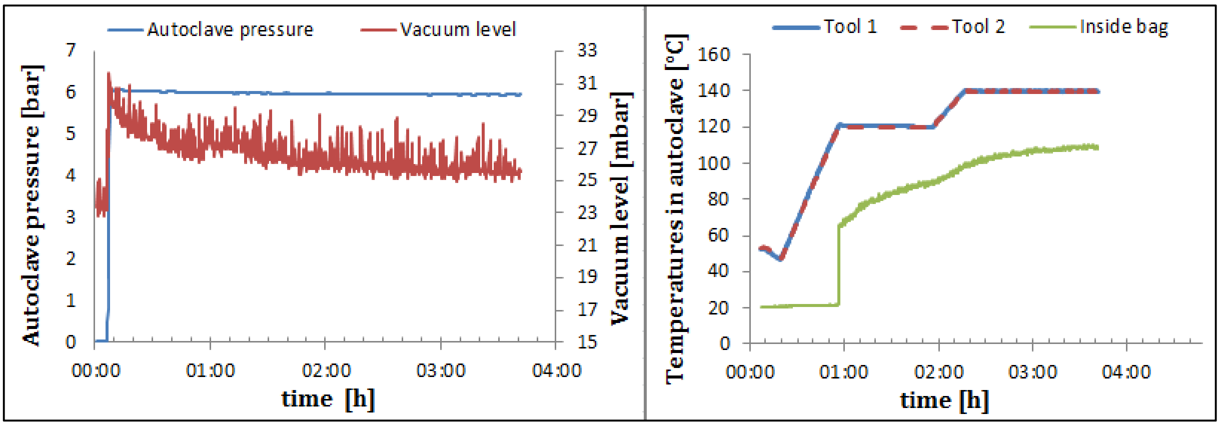


Figure 1. Log for sample 216.

The laminates manufactured for this study are summarized in Table 2.

Sample	Material	Layup	Process
197	PREGCYL	$[0_{12}]$	Vacuum bag
216	PREGCYL	$[0_{12}]$	Autoclave
229	MTM55	$[0_4]$	Autoclave
217	PREGCYL	$[0_2/90_6]_S$	Autoclave
226	PREGCYL	$[0/90_3]_S$	Autoclave
230	MTM55	$[0/90_3]_S$	Autoclave

Table 2. Overview of samples manufactured with details about material, layup and processing method.

4 Testing methods and equipment

4.1 Microscopy analysis

To analyze the dispersion of CNT in the manufactured samples a Magellan 400 XHR-SEM (Extreme High Resolution Scanning Electron Microscope) was used. The specimen was prepared by breaking it just before it was loaded into the test chamber and the fracture surface was then examined.

4.2 Mechanical testing

Tensile testing of laminates was performed using an Instron 8501 hydraulic machine with 100 kN load cell. Standard Intron extensometer 2620-601 with 25 mm gauge length was used to measure strain. Loading was performed in strain controlled mode with the strain rate of 1%/min. The load, displacement of the cross-head and strain were recorded and store on the PC (standard Instron acquisition system and software package WaveMatrix was used).

The unidirectional laminates were loaded in one single step until the failure. Whereas cross-ply laminates were loaded with stepwise increased load level in order to evaluate damage accumulation and stiffness degradation. The maximum applied tensile strain during a cycle was incrementally increased with steps of 0.2% until a maximum strain of approximately 1% was reached. During the tests acoustic emission setup (AE equipment by Physical Acoustics Corporation: preamplifier 2/4/6C and α-series sensor R15α) was used to register failure events (cracks) in cross-ply laminates. The BIOPAC acquisition unit MP100 was used to register (with 200 Hz) and store AE data on computer.

Carbon fiber specimens were equipped with glass fiber/epoxy end tabs to prevent sliding and crashing of specimen ends. The distance between tabs (grip separation distance) was 100 mm. The width of specimens was approximately 10 mm and thickness ranging within 0.7-2.6 mm, depending on the number of layers in the laminate (4, 8, 12 or 16 layers).

The stiffness of the laminates was calculated by linear approximation of the linear part of experimental stress-strain curve within strain interval of 0.15-0.30%.

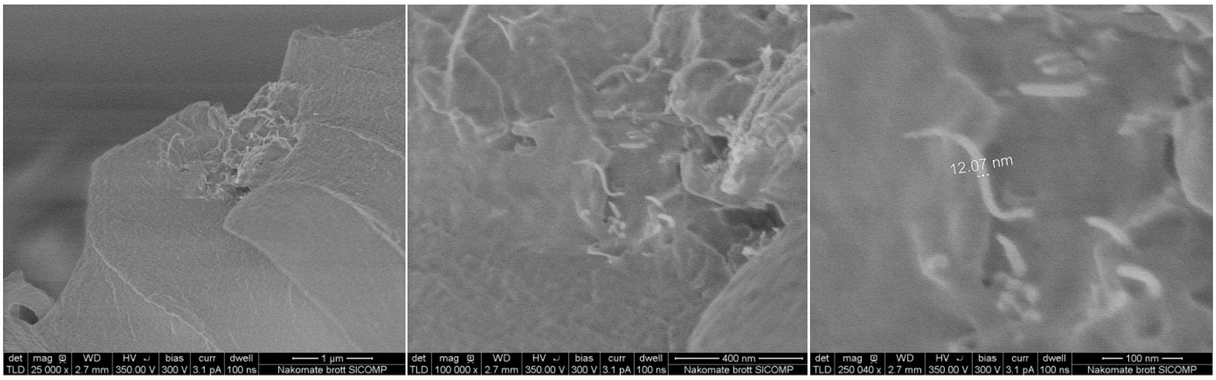
5 Results

5.1 Manufacturing

A qualitative evaluation of the processability of the CNT-doped prepreg and the reference material was performed during manufacturing. It was observed that a) no perceivable difference in tackiness between the two materials could be detected b) demoulding was performed with the same ease and there was no trace on the tool that could indicate that the CNT had affected the tool surface.

5.2 XHR-SEM

First step was to analyze the dispersion of CNT in the matrix. Three SEM micrographs with different magnifications are shown in Figure 2. The global distribution of CNT seems to be poor, as can be seen in the picture to the left (no other nano-reinforcement is visible within 2-3 micron distance from the area with nanotubes). This indicates that the mixing and dispersion is not optimal and that the CNT content is small. The dispersion on the local scale seems however to be good and on the two rightmost pictures individual CNT can be observed.



(a) (b) (c)

Figure 2. SEM micrographs with different magnifications from the same area of the fracture surface: (a) Shows a patch of CNT but also reveals that large areas lack CNT (b) Increased magnification of the patch shows that the dispersion is good (c) Dimension of an individual CNT.

The next step was to investigate the samples for possible failure mechanism/scenarios. Two types related to CNT were detected: a) CNT-pullouts (Figure 3); b) agglomerates, some of which are possibly not fully impregnated (Figure 4).

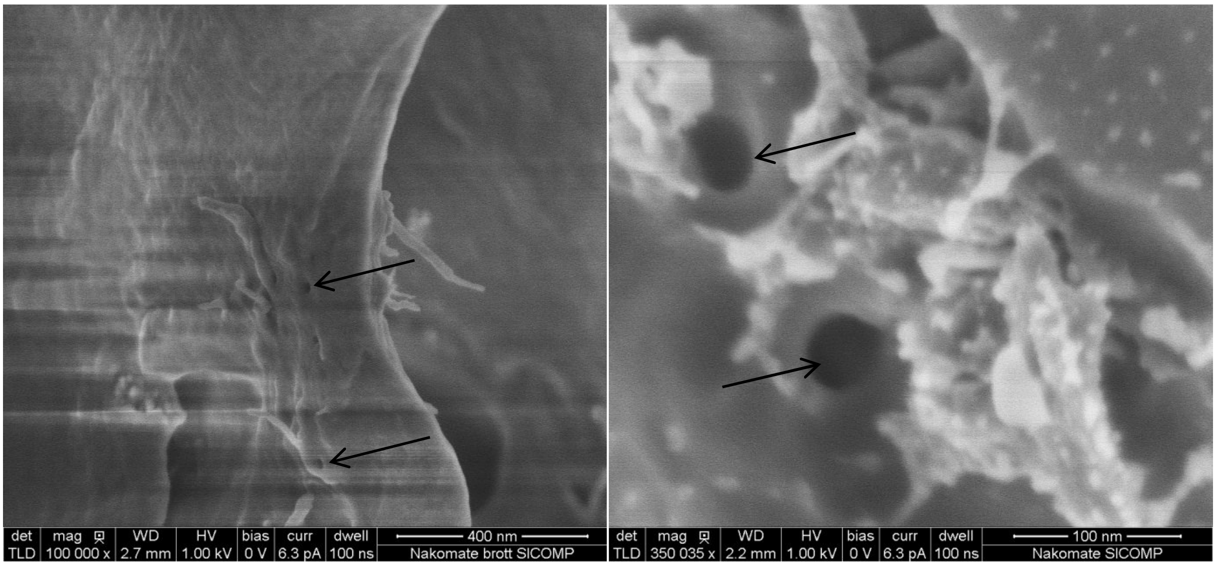


Figure 3. SEM-images of fracture surfaces of PREGCYL composites, arrows indicates traces from CNT-pullouts during fracture.

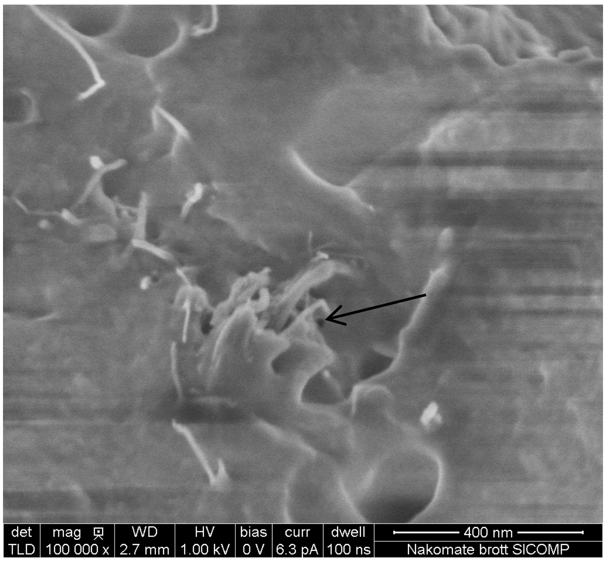


Figure 4. SEM-image of several CNT involved in fracture creating a brush-like appearance.

5.3 Mechanical testing

The summary of the initial stiffness measurements for all laminates is presented in Table 3.

Lay-up	Material	E, GPa	Number of layers	Laminate thickness, mm	Layer thickness, mm
$[0_{12}]$	PREGCYL	111.6	12	1.969	0.164
$[0_4]$	MTM55	102.6	4	0.708	0.177
$[0_2/90_6]_S$	PREGCYL	33.8	16	2.607	0.163
$[0/90_3]_S$	PREGCYL	33.7	8	1.332	0.166
$[0/90_3]_S$	MTM55	32.2	8	1.318	0.165

Table 3. Stiffness for the different materials.

These results show that UD laminate made out of standard prepreg has by 10% lower stiffness than composite made out of PREGCYL. However, initial stiffness of the cross-ply laminates differs only by approximately 5% (higher for PREGCYL). It can be attributed to the fact that PREGCYL contains certain amount of CNTs. On the other hand, the quantity of nano-tubes in the PREGCYL material is too low to influence significantly the longitudinal modulus of carbon fiber laminate. Most likely the reason for different modulus is dissimilar content of fibers in the PREGCYL and MTM55 composites. Since both prepregs have the same areal weight and similar resin content, the comparison of thickness of the single ply in different laminates can be used as indication of relative fiber volume fraction. As a matter of fact a layer in MTM55 UD composite is thicker than in PREGCYL material, thus MTM55 contains fewer fibers and has lower stiffness. This is not the case for the cross-ply laminates, where layer thickness is practically the same for all laminates (0.163-0.166 mm) but stiffness slightly differs.

It is well known that first damage event occurring in cross-ply laminate loaded in tension is transverse cracking. Such cracks are also detected in PREGCYL and MTM55 cross-ply laminates. The evolution of applied strain with time and corresponding AE response for tested cross-ply laminates are presented in Figure 5.

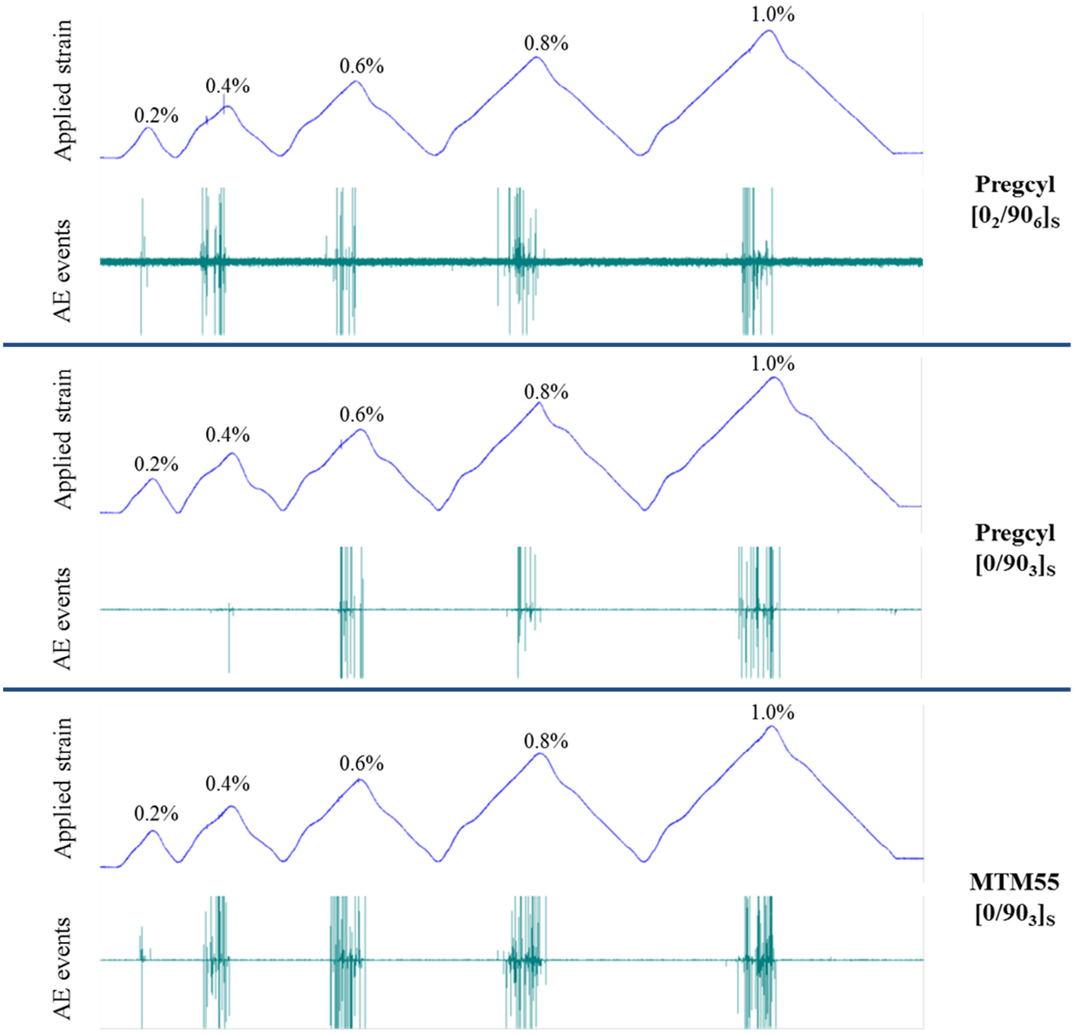


Figure 5. Applied strain as a function of time and corresponding AE response.

The results in Figure 5 indicate that cracks in thicker PREGCYL laminate develop earlier than in laminate with thinner 90-layer (at 0.2-0.4% vs 0.4-0.6% strain), which is expected for this type of materials. However, more interesting conclusion can be made from comparison of AE data from PREGCYL and MTM55 $[0/90_3]_S$ laminates. The results show that standard prepreg laminate is more prone to cracking than laminate doped with CNTs. The AE data in Figure 5 show that cracks appear at lower strain and are accumulating faster in standard material than in nano-doped. Yet, it can't be stated with certainty that the delay in damage accumulation is due to presence of nano-tubes in the PREGCYL material. This difference in damage accumulation might be as well attributed to the different matrix in the composite. In order to explain the difference, the fracture properties (e.g. fracture toughness) of neat resins should be compared. Nevertheless, it can be concluded that presence of CNTs in composite does not cause premature cracking. This is an indication of absence of stress concentrations, such as agglomerated nano-tubes, in the PREGCYL composites. Such statement correspond well with micrographs obtain from SEM.

The transverse cracks often run through the whole thickness of the 90-layer and cause delaminations at the crack tip between longitudinal and transverse layers, although this happens at higher load levels. The example of the crack in PREGCYL laminate is shown in Figure 6(a,b). These cracks cause degradation of the stiffness of the whole laminate. The results of stiffness degradation with applied load are shown in Figure 6(c). As seen from these results, the stiffness of laminate is not considerably affected by the transverse cracks. This is rather common for carbon fiber cross-ply laminates, since stiffness of lamina in longitudinal direction is significantly higher than for transverse (10-15 times). Moreover, delamination between layers that might have stronger impact on the properties of laminate is not present at these strains (see Figure 6 (a,b)).

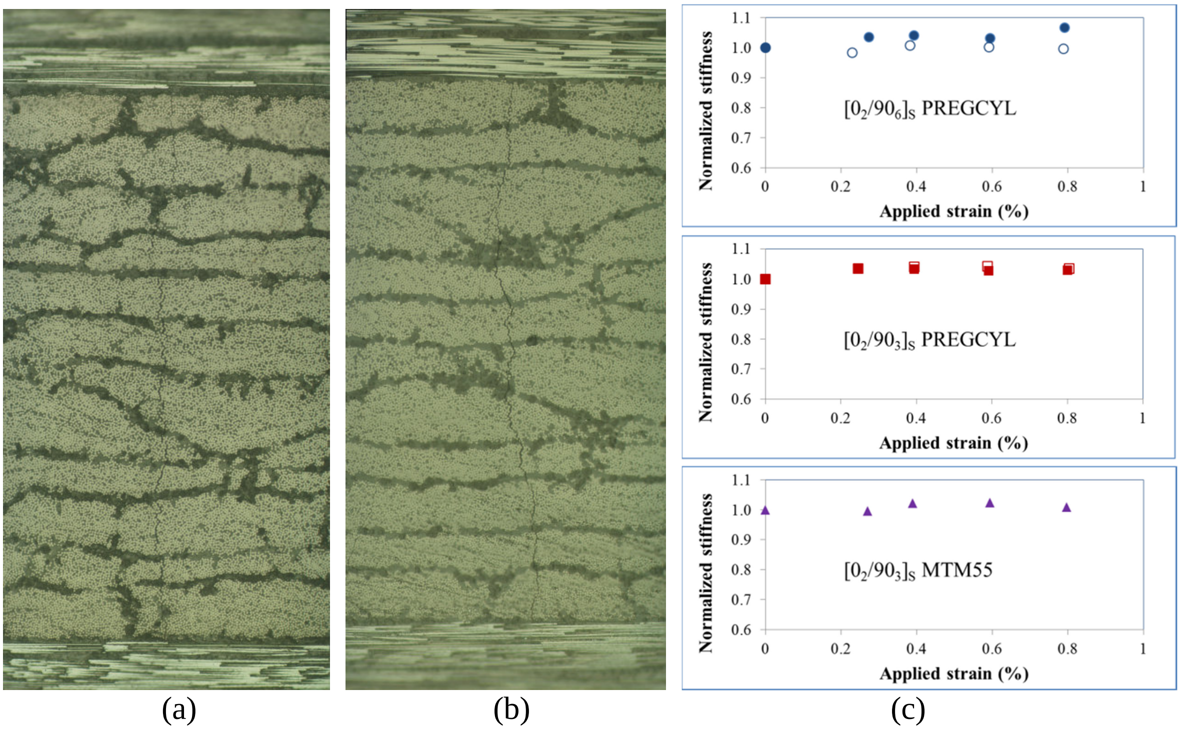


Figure 6. The micrograph showing crack in cross-ply laminate at 0.7% (a) and 0.9% (b) applied strain. The normalized stiffness as a function of applied strain for cross-ply laminates (c).

6 Summary and Conclusions

Results from the microscopy analysis shows that the local dispersion of CNT in the PREGCYL material is good in the sense that very few agglomerates were observed and it was possible to detect individual CNT. The mechanical tests also supports this fact since cracking would have developed at lower strains if the material contained a lot of agglomerates (they act as crack initiators). The global distribution of CNT is however poor since large areas with no traces of CNT were observed.

Pull-outs were observed on the fracture surfaces. This shows that the CNT can contribute to the enhanced toughness of the material.

The mechanical testing consisted of tensile tests of unidirectional (in longitudinal direction) and cross-ply laminates. Test of unidirectional laminates showed that stiffness of the PREGCYL material is slightly higher than that of MTM55 composite (111GPa vs 102GPa). However, these differences most likely should be attributed to the fiber content in the laminate rather than presence of nano-tubes. The results from tests of cross-ply laminates indicated that damage (transverse cracks) initiation is delayed in PREGCYL composites compare to the MTM55 material. Damage accumulation also seems to be slower in nano-doped composites. But because tested composites are based on different resins it cannot be fully concluded that nano-tubes are the reason for better damage tolerance. Nevertheless, it can be stated that nano-tubes do not agglomerate and cause premature damage initiation.

7 Acknowledgements

This work was performed within Interreg IV Nord project NAKOMATE funded by EU and local governments in Finland and Sweden. Authors would like to thank Mr. Greger Nilsson and Mr. Alexander Proy for help with experiments.

References

[1] Gojny F.H., Wichmann M.H.G., Kopke U., Fiedler B., Schulte K. Carbon nanotube-reinforced epoxy-composites: enhanced stiffness and fracture toughness at low nanotube content, Composites Science and Technology 64, pp 2363–2371 (2004).

[2] Chou T.-W., Gao L., Thostenson E.T., Zhang Z., Byun J.-H. An assessment of the science and technology of carbon nanotube-based fibers and composites, Composites Science and Technology 70, pp 1–19 (2010).

[3] Hsiao K.-T., Processing and mechanical properties characterization of hybrid thermoset polymer composites with micro-fiber and carbon nano-fiber reinforcements. In: Processing and properties of nanocomposites, Advani (Ed), World scientific Publishing (2007).