

PERMEABILITY AND COMPRESSIBILITY OF CNT/CNF-GRAFTED REINFORCEMENTS

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ABSTRACT: The paper studies compressibility and permeability of a CNT/CNF-grafted woven carbon reinforcement. It is shown that the pressure needed to achieve the target fibre volume fraction of the preform increases drastically when CNT/CNF are present in the preform. This can lower the achievable fibre volume fraction for economical vacuum assisted light-RTM manufacturing and increase the pressure requirements in autoclave processing. The permeability of the preform is found to be non-affected by the presence of CNT/CNF.

KEYWORDS: Nanotubes, textile reinforcements, compressibility, permeability

INTRODUCTION

Growth of carbon nanotubes (CNT) and carbon nanofibres (CNF) on carbon fibres and fibrous substrates is one of the ways to modify interfacial properties of fibre reinforced composites (FRC), and encouraging results – increase of the material toughness – have been reported in the recent years [1-9]. If these nano-engineered FRC (nFRC) are destined to leave laboratories and enter industrial-scale production, the question of adapting the existing composite manufacturing methods will arise. The processing issues of nFRC have not been properly addressed in the literature. The papers cited above report conditions of the production of the composite plates, mention the somehow increased thickness of the grafted preform and of the sample produced under a vacuum pressure, report observations of impregnation of CNT-forest on sub-micron scale, but do not study the processing issues in detail. In [10] the processing issues of VARTM production of nFRC with CNT dispersed in the matrix are studied.

The paper covers two issues of RTM and VRTM processing of CNT-grafted woven carbon reinforcement: (1) compressibility and (2) permeability. It is shown that the pressure needed to achieve the target fibre volume fraction of the preform may increase drastically when CNT are present in the preform. This can lower the achievable fibre volume fraction for economical vacuum assisted light-RTM manufacturing techniques. For the studied fabric the permeability of the preform, on the other hand, was found to be not affected by the CNT/CNF grafting.

For this exploratory study, a common and widely used woven carbon reinforcement has been selected as base material. CNT/CNF were grown on the fabric using industrial Chemical Vapour Deposition (CVD) technology after impregnating it with Ni catalyst particles. No attempt was made in this study to optimise parameters such as processing conditions, catalyst distribution on

the fibres, weight fraction of the CNT/CNF etc. The aim was to determine, if the grafting poses any problem for manufacturing and estimate the gravity of these problems, rather than to find optimised solutions.

MATERIALS

The preform is the dry reinforcement of the Tencate Cetex® PEI composite. This 5-harness satin weave (Figure 1a) is made with 3K untwisted tows of Torayca® T300J carbon fibres (fibre diameter 7 μm). Areal density of the fabric is 280 g/m^2 . This material is commonly used for aerospace applications.

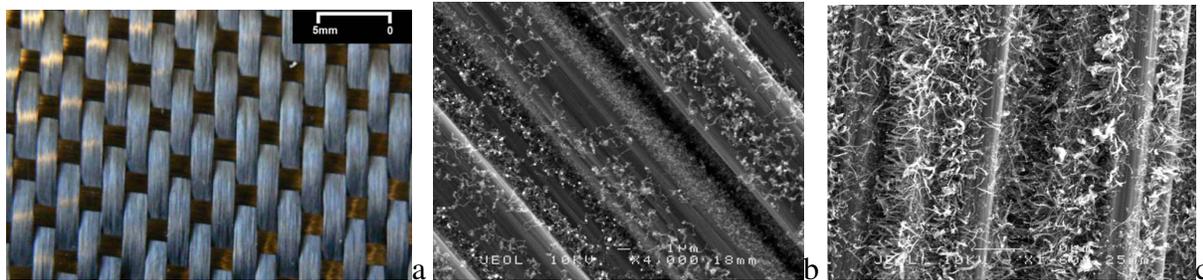


Figure 1 The fabric (a) and SEM images of the grafted preforms: (b) 5 wt%; (c) 39 wt%

Grafting of the fabric specimens (sheets of approximately 25x30 cm) was done using the chemical vapor deposition (CVD) technique. First, the carbon fibre material is impregnated with Ni nitrate dissolved in acetone and subsequently placed into a gas chamber and reduced with hydrogen at 600°C to obtain Ni particles needed for CNT/CNF growth. The carbon nanofibres are grown at the same temperature for 40-60 minutes in a gas mixture $\text{N}_2:\text{C}_2\text{H}_4:\text{H}_2=50:40:10$, with a total flow rate of 2 l/min. The variation of CNT/CNF weight fraction is obtained by varying the reaction time. The exact reaction time is adjusted by trial-and-error method, since the kinetics of carbon nanofibre growth at the textile fabric in these conditions and on Ni catalyst is not yet known. The specimens with two levels of the weight of the grafting were produced: low and high.

The weight percentage (wt%) of the grafting was measured by the weight increase compared to the virgin material on samples with the dimensions about 50x50 mm with the same yarn count, and found to be 5 wt% and 39 wt% for the low and high level of grafting. Figure 1b,c show SEM images of the carbon preform fibres with a 5 wt% and 39 wt% CNF content respectively.

COMPRESSIBILITY

Compression tests were done on a displacement-controlled testing machine Instron 4467 with a 1 kN load cell. The test speed was 0.5 mm/min. A compression rig, installed on the Instron lower (not moving) plate, has a ball-pivot circular platform with diameter 70 mm. When the first test is done without the sample, the platform aligns itself with the upper plate, fixed in the moving crosshead of the machine. After that, 5 tests are done without sample, to establish a calibration curve, which allows calculating the compressed sample thickness h under the load F , accounting for the compliance of the rig. Three successive cycles of compression were performed, which allows estimating of the compressibility in the relaxed and the “set” state of the preform [11]. Three specimens with the size 35x35 yarns or 50x50 mm were tested for each variant: virgin fabric, grafted fabric with 5 wt% and 39 wt% growth. The maximum pressure on the sample 0.3 MPa is defined by the limit of the used load cell.

Figure 2 presents results of the measurements. The measured values of the fabric thickness for a given pressure show quite small scatter, with the difference between the three specimens not more than 10%. The results show a consistent decrease of compressibility, or increase of the fabric thickness for a given pressure after grafting. When expressed in fibre volume fraction, the trend is as follows. For a pressure of 0.1 MPa (1 bar, corresponding to a vacuum process) the fibre volume fraction of a virgin fabric is 52% (second compression cycle). After grafting of 5 wt% of CNT/CNF it becomes 41%; for 39 wt% samples the fibre volume fraction at 0.1 MPa is 28%. Note that this higher compression resistance is not a result of just adding more material inside the fabric. When approximately recalculated with the volume of the grafting taken into account, the fibre+grafting volume fraction is changing as 52% (virgin) -> 43% (5 wt%) -> 38% (39 wt%).

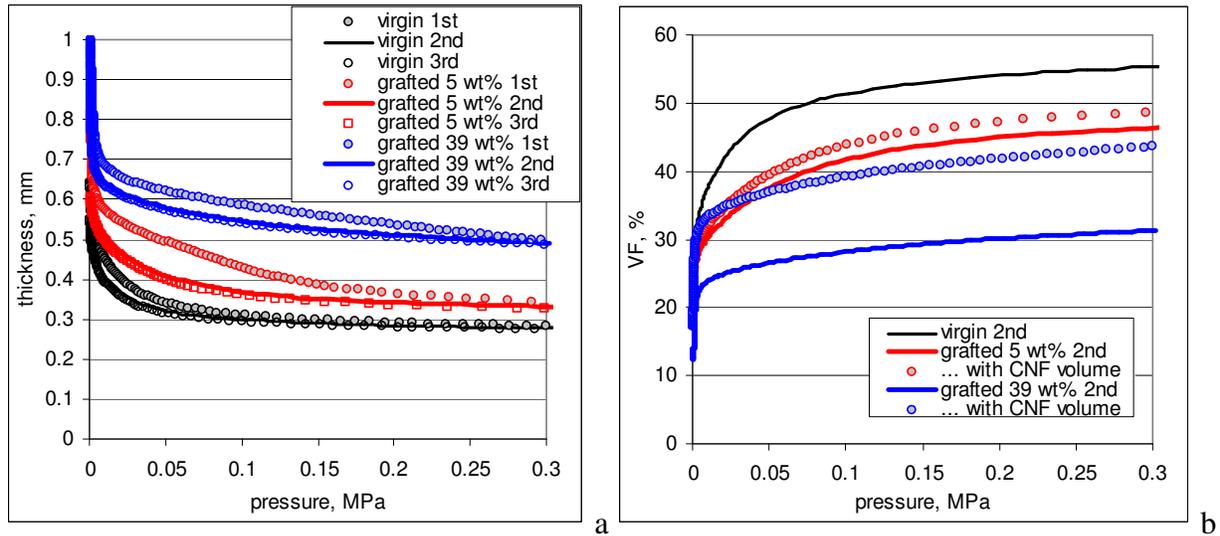


Figure 2 Compression diagrams: (a) thickness vs pressure; (b) VF vs pressure

PERMEABILITY

Permeability of the fabric was measured using a unidirectional device, shown in Figure 3.

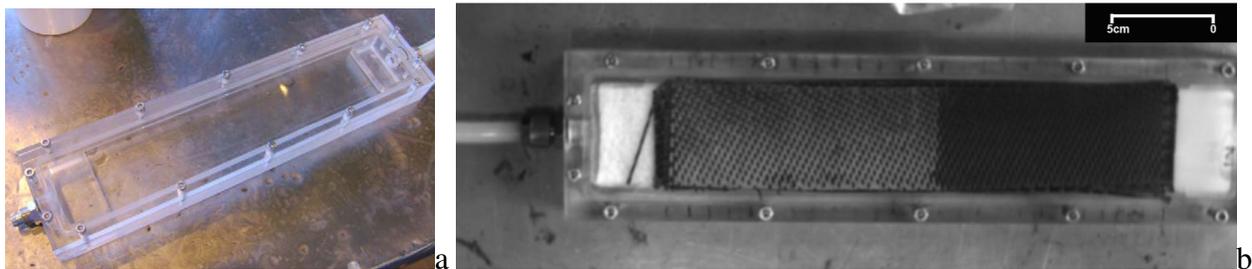


Figure 3 Permeability measurement: (a) the mould; (b) example of the registration of the progression of the flow front

The cavity size is 5x25 cm; the height of an empty cavity is 2 mm. Because of certain compliance of the silicon sealing, the actual height of the cavity (thickness of the material) has to be determined for each test. This was done by measuring the total thickness of the mould at the corners of the cavity and subtracting the thicknesses of the bottom and the top mould walls.

Axson Polyol F18 Part A was used as the measurement liquid. Its viscosity was characterized as shown in Figure 4. The test temperature was monitored using a thermocouple. The viscosity values corresponding to shear rate of 5 s⁻¹ were used for calculation of permeability.

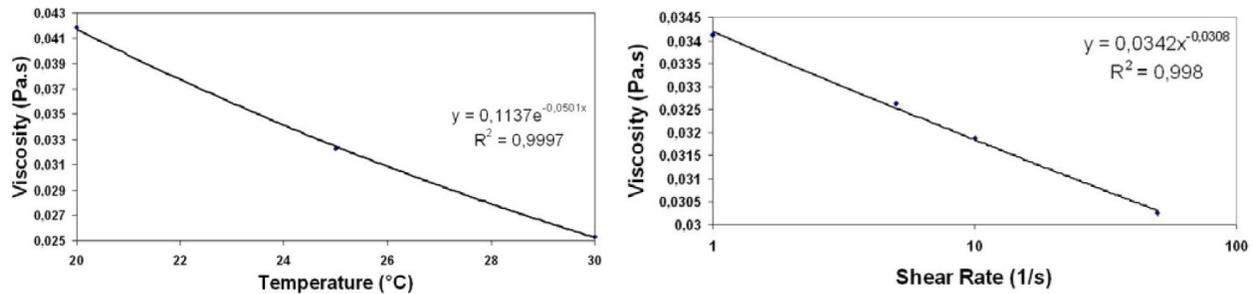


Figure 4 Viscosity of the test liquid as function of temperature at shear rate 5 s⁻¹ and as a function of shear rate at temperature 25°C

The permeability is measured by direct application of Darcy’s law. The porosity of the fabric and fibre volume fraction were calculated based on the measured fabric pile thickness (height of the mould in the closed cavity) and the fabric areal density. 8 or 9 layers of the fabric were put into the mould, which gives fibre volume fraction in the range from 47% to 55% for virgin fabric.

The pressure gradient is established by a vacuum pump at the outlet of the mould. The pressure difference is registered by the vacuum pump and is assumed to occur only over the fabric in the cavity. This assumption is supported by the fact that no pressure difference is measured for a closed, but empty mould. The linearity of the dependency of the flow front velocity on the pressure drop was checked in the interval of pressure 0...70 kPa and was found satisfactory. The pressure of 70 kPa was used during the permeability measurements.

Measurements of the thickness of the preform (cavity height in the closed mould) correlate with the compressibility measurements reported above. The mould was more difficult to close when grafted material was used. The fibre volume fraction for 8 layers of the fabric in the mould (calculated based on the cavity thickness) changed as 47% (virgin) -> 45% (grafting 5 wt%) -> 39% (grafting 39 wt%).

A possible error in measurement of the height of the cavity is estimated to be below 0.1 mm, which for a 2 mm cavity and VF=50% can give up to ±12% scatter in the permeability value (estimation using Kozeni-Carman formula).

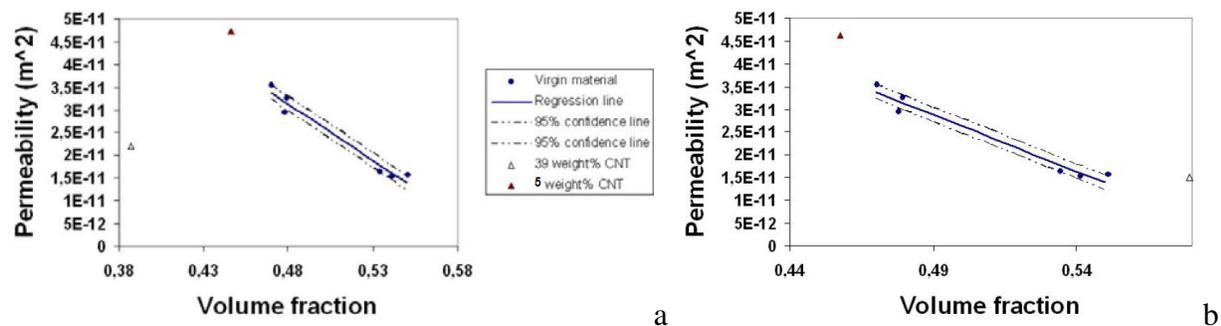


Figure 5 Permeability of the virgin and grafted fabrics as function as fibre volume fraction: (a) VF calculated for carbon fibres only; (b) VF calculated accounting for the volume of the grafting

The results of the measurements are shown in Figure 5. The dependency of permeability of the virgin fabric on fibre volume fraction is linear in semi-logarithmic scale. Grafting of 5 wt% does not change the permeability; when 39 wt% of CNT/CNF is added, the permeability changes significantly (Figure 5a). However, if the volume of the grafting is included in the volume fraction, then the points for the grafted material do not deviate from the trend for the virgin fabric (Figure 5b). It appears even that the points for the grafted material lie above the trend for the virgin fabric. This may be caused by errors in the thickness estimation; one can also speculate on the capillarity effects in the grafting “helping” the permeability.

CONCLUSIONS

After grafting 5 wt% and 39 wt% of CNT/CNF on a carbon fabric it was found that: (1) compressibility of the fabric is seriously decreased even with 5 wt% grafting; (2) permeability is not affected by 5 wt% grafting and decreased by a factor of 2 for 39 wt% grafting; however, the permeability does not change if compared for the volume fraction calculated accounting for the grafting volume.

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