Localization of carbon nanotubes in resin rich zones of a woven composite linked to the dispersion state

Alexander Haesch\textsuperscript{2,3}, Thijs Clarkson\textsuperscript{2}, Jan Ivens\textsuperscript{1,2}, Stepan V. Lomov\textsuperscript{4}, Ignaas Verpoest\textsuperscript{4}, and Larissa Gorbatikh\textsuperscript{4}

\textsuperscript{1}Department of Materials Engineering, KU Leuven, Leuven, Belgium
\textsuperscript{2}Department of Industrial Engineering, Lessius University College, Sint-Katelijne-Waver, Belgium
\textsuperscript{3}Faculty of Materials Engineering, Georg Simon Ohm University of Applied Sciences, Nuremberg, Germany

Abstract The final position of carbon nanotubes (CNTs) in a fiber-reinforced composite and its mechanical properties can be influenced by the dispersion quality of CNTs in the resin. This topic is investigated here on the example of a woven glass fiber/epoxy composite. Two different localization states of CNTs in the composite are achieved by choosing matrices with two different dispersion states but the same CNT concentration. The two investigated states of dispersion are (1) a uniform dispersion with small CNT agglomerates and (2) an interconnected dispersion where CNTs form a network with large features. The uniform dispersion results in a better distribution of CNTs throughout the composite with CNTs also appearing inside the fiber bundles. The network-like dispersion, on the other hand, tends to localize CNTs in resin rich zones. The composite with CNTs in the resin rich zones has a higher strain-to-failure (by 10\%) and a lower density of transverse cracks (by 29\%) in comparison with a virgin composite. In the meantime, a lower strain-to-failure and about the same crack density are measured for the composite where CNTs appear in small individual agglomerates.

Keywords Composite, Carbon nanotubes, Mechanical properties, Matrix cracking, Dispersion

Cite this article A. Haesch, T. Clarkson, J. Ivens, S.-V. Lomov, I. Verpoest and L. Gorbatikh: Nanocomposites, 2015, 204–213

Introduction

Carbon nanotubes (CNTs) have been widely explored in recent years as a reinforcing component of polymers in combination with conventional fibers such as continuous glass or carbon fibers.\textsuperscript{1} Composites, which use nanoscale and microscale reinforcements together, are frequently referred to as multi-scale, three phase, hybrid or nanoeengineered fiber-reinforced composites (nFRCs). From the point of view of the mechanical performance, the benefit of adding carbon nanotubes to a composite is expected in the improvement of its overall toughness. The latter can be realized through strengthening of the fiber/matrix interface, suppressing formation of transverse cracks, hindering onset, and propagation of delaminations.\textsuperscript{2,5}

Processing parameters for the production of these nanoeengineered composites often need to be modified as CNTs can change behavior of the constituents. For example, CNTs in the resin can change its viscosity\textsuperscript{6} and CNTs grown on fibers can alter their compressibility.\textsuperscript{7}

One of the approaches to integrate CNTs in fiber-reinforced composites is to mix them in small quantities in the polymer matrix. For epoxy resins, these amounts are usually limited to 0.5–1 wt.% because of the challenges related to CNT dispersion.\textsuperscript{6,9} Attraction between CNTs due to van der Waals forces makes them prone to form agglomerates, which may further cluster into larger aggregates. The agglomerates are likely to generate stress concentrations upon material loading and lead to a poor mechanical performance of the resin (including lower strength and fracture toughness). Moreover, toughening by the CNT pull-out can only be fully exploited if cracks propagate through CNT rich areas. If cracks do not pass through agglomerates (and this is usually the case), CNTs simply do not have a chance to participate in energy dissipation. This explains why dispersion of CNTs in polymers is targeted to be homogeneous and free of agglomerates.

When nanoreinforced polymers are used for production of FRCs, yet another consideration is important, namely how the dispersion of CNTs affects their final position in a composite. It is possible that when a CNT-containing resin flows through the fibrous medium, some CNTs become filtered out. This is particularly relevant for composites with textile reinforcement, where the distribution of fibers is highly non-uniform. There are densely packed fiber bundles with fiber volume fractions
of 60–70%, on one hand, and resin rich zones with no fibers, on the other hand. One can imagine that large agglomerates (>10–100 μm) can hinder CNT access to areas where the spacing between the fibers is a few micrometers or less. This is very likely to occur since disintegrating agglomerates completely is hardly accomplished even when special techniques such as calendering are used. There are also indications that separated nanotubes will re-agglomerate again during subsequent processing steps of a composite under raised temperatures, applied pressures, curing, etc.\(^6\)

Filtering of CNTs during injection was studied in\(^10\) on the example of random glass fiber mats. It was found that a poor dispersion with non-uniform CNT agglomerates bigger than 100 μm results in a severe global filtering of CNTs. On the other hand, for resins with uniformly distributed small CNT agglomerates and individually dispersed CNTs, hardly any filtering could be observed. The ‘global’ filtering is understood here as macroscopic distribution of CNTs on the scale of a composite plate. Filtering on the meso-scale (inside fiber bundles) was not examined, but it was argued that even for the best dispersion state, a poor distribution of CNTs inside fiber bundles was likely to occur. This was attributed to the small spacing between the fibers inside the bundles that was commonly from 5 μm down to about 50 nm for the studied material. The problem of filtering was also investigated in\(^11\) using in-plane and through-thickness electrical conductivity measurements for a glass woven and non-crimp fabric composites. The highest filtering was observed for a woven material. For a non-crimp fabric, the volume conductivity inside fiber yarns was found to be ten times lower compared to the conductivity measured between fiber yarns. This finding is in line with the previous observations from\(^10\). In\(^12\), some successful adaptations were suggested to the vacuum-assisted resin transfer molding method to control the filtering effect and CNT orientation.

The non-homogeneous distribution of CNTs in a composite on the meso-scale (for example, higher concentration of CNTs in resin rich zones combined with no CNTs inside fiber bundles) may have an important effect on composite mechanical properties. In particular, the onset and development of damage are expected to be affected by the CNT dispersion. The goal of the present work is twofold: (1) to investigate positioning of CNTs in a woven glass fiber composite for two distinctly different CNT dispersion states in the resin, and (2) to evaluate the effect of CNT localization on the composite tensile properties and damage development.

### Materials and methods

#### Raw materials

The reinforcement is a woven roving E-glass fiber fabric EWR570-1270 from Taishan Fiberglass Inc. The fabric is balanced with ends/picks count of 2.5 strands/cm and has an areal density of 579 g/m\(^2\). The resin system is a medium viscosity liquid epoxy resin Epikote 828LVEL produced from bisphenol A resin and epichlorohydrin. It is combined with a 1,2-diaminocyclohexane hardener Dytek DCH-99 in a 100–15.2 weight ratio. The nanoscale reinforcements are multiwall carbon nanotubes (MWCNTs) from Nanocyl, which were supplied pre-dispersed at a high concentration in a bisphenol-A epoxy resin as a masterbatch (EpoCyl NC R128-02). Prior to mixing with the resin, the MWCNTs had an average diameter of 9.5 nm, a length of 1.5 μm, a specific surface of 250–300 m\(^2\)/g, and a carbon purity >90%.

#### CNT dispersion states

It was noticed that prolonged storage of the CNT containing masterbatch EpoCyl NC R128-02 can influence the quality of CNT dispersion in a pronounced way. Therefore, the dispersion state in this study is controlled through aging of the masterbatch. More specifically, two masterbatches are used: a freshly made (less than a month old) and aged (almost two years old) masterbatches. The masterbatches were stored on the shelf at room temperature. No particular storage conditions were enforced. Since the aged masterbatch became a paste-like substance overtime and was difficult to process, it was heated to 60 °C on the recommendation of Nanocyl. This heat treatment was applied only once.

The two systems were characterized in\(^9\) using seven different techniques and at different stages of the composite preparation process: in the original masterbatch form, after dilution with the epoxy resin, after addition of the hardener, during the curing process and, finally, in the cured samples. Here, we only highlight main findings. The two materials were found to be distinctly different in their behavior at all stages of composite preparation. From the rheological analysis, it was found that the aged masterbatch had a significantly higher shear storage modulus compared to the fresh one. It also did not exhibit the anticipated recovery of the shear storage modulus over time, as it was in the case of the fresh masterbatch. The recovery was a lot slower and proceeded faster. This suggested that CNT agglomerates in the aged masterbatch were either very difficult to break under the applied pre-shear or they re-structured extremely fast. From characterization of these systems during the curing reaction (after dilution and addition of the hardener) using an optical microscope, it was found that CNTs in the old system formed an interconnected network with clear and well-defined borders, while CNTs in the fresh system aggregated into individually distinguishable larger clusters without formation of any macroscopic network (Fig. 1).

Comparing results of the electrical impedance spectroscopy, it was found that the CNT-reinforced epoxy prepared from the aged masterbatch had a significantly higher specific conductivity (by five orders of magnitude) in comparison with the material from the freshly made masterbatch. The diagrams of impedance vs. frequency revealed that the material from the aged masterbatch exhibited electrical percolation while this was not the case for the freshly made version, although both systems contained equal amounts of CNTs (0.3 wt.%). It was found that epoxy in the masterbatch partially crystallized during storage and this partial crystallization had a significant contribution to the agglomeration of CNTs in the aged masterbatch where they were expelled from epoxy crystallites.

The two dispersion states described above are labeled here as a Uniform state with small CNT Agglomerates (to be further referred to as the UA case) and interconnected state where CNTs form a Network with larger features (to be referred to as the N case). The largest CNT aggregates in the UA case are on the order of 10 μm. They are separated by agglomerates...
on the order of 1 μm. In the N case, CNTs are formed into a network with pathways of ~25–50 μm in width and CNT-void areas in-between that are ~50–100 μm in size.

Production of composite plates

Before composite production, the CNT containing master-batch is diluted with Epikote 828LVEL to obtain 0.3 wt.% of CNTs in epoxy. The mixture is thoroughly stirred for 5 min with a mechanical mixer and then the hardener is added. With the hardener added, the final concentration of CNTs in the resin is 0.26 wt.% For the reference composite, the hardener is directly added to the neat epoxy resin in the same ratio. All resin systems are then degassed in a vacuum oven at room temperature for 15 min. Composite plates were produced using vacuum-assisted resin transfer molding. There were two types of plates produced: (1) plates for mechanical testing, and (2) thin plates for backlight inspection and microscopy to characterize the CNT position in the composite. The plates for mechanical testing were produced with a 3.1-mm spacer and seven plies of the fabric. Production parameters were as follows: injection temperature – 40 °C, injection pressure – 1 bar, curing temperature – 70 °C, curing pressure – 4 bar, curing time – 1 h, post curing temperature – 150 °C (N case) and 100 °C (UA case), post curing time – 1 h (N case) and 2 h (UA case).

After production, the plates underwent visual inspection to check for asymmetries, cavities, improper impregnation, or thermal cracks. All plates produced for subsequent testing showed a flawless surface. No bubble type cavities or porosities were visible inside the reference plates (containing no CNTs). Some fine thermal cracks were, however, found in every plate. Because the CNT containing plates are not transparent, they could not be visually checked for cavities or cracks. The assumption was made that since they were produced using the exactly same parameters, their condition regarding cavities and thermal cracks should be similar to the reference plates. The composite plates for mechanical testing were produced and tested by two different operators. One operator worked on the UA-case study and the other one on the N-case study. The two operators worked independently of each other; therefore, the reference composites were produced twice. The achieved fiber volume fractions are listed in Table 1. They are calculated using the areal density of the fabric and the thickness of the produced plates.

The thin CNT-doped plates for backlight inspection and microscopy were produced with a 1-mm spacer and contained two plies of the glass fiber fabric. For imaging purposes, it would have been better to use a single ply but a single ply is not representative of the meso-structure inside a composite where nesting between fabric plies may be an important contributing factor to localization of CNTs in resin rich zones. The choice of two plies is a compromise to fulfill the two requirements. These plates had a fiber volume fraction of 45%. The production and characterization of the thin plates (both for the UA-case and N-case studies) was done by the same operator. The post curing temperature was kept to 100 °C for both cases.

Experimental methodology

Backlight inspection and microscopy

Thin plates were subjected to backlight inspection and microscopy to visualize filtration of CNTs. This idea was mainly inspired by the work in11 where backlight inspection was used to examine CNT filtration on the level of a composite plate. In the present work, we use the same principle but on a smaller scale. For backlight inspection, the best light for imaging was
### Table 1  Tensile test results in the fiber direction for the glass fiber composites in the UA-case and N-case studies

|                     | Thickness, mm | V_f, % | E, GPa | Strength, MPa | Strain to failure, % | ε_min | ε_1 | ε_2 | ε_3 |
|---------------------|--------------|--------|--------|---------------|----------------------|------|-----|-----|-----|
|                     | Average      | St. dev | Average | St. dev | Average | St. dev | Average | St. dev | Average | St. dev | Average | St. dev | Average | St. dev | Average | St. dev | Average | St. dev |
| **UA-case study**   |              |        |        |              |                      |      |     |     |     |
| Reference composite | 3.23         | 0.03   | 48.4   | 25.1         | 0.5                  | 495.9| 15.9| 2.94| 0.16|
| Number of specimens | 50           | 25.9   | 0.5    | 511.6        | 17.9                 |      |     |     |     |
| CNT-reinforced      | 3.26         | 0.01   | 48     | 25.8         | 0.2                  | 468.6| 23.5| 2.58| 0.13|
| Number of specimens | 50           | 26.9   | 0.2    | 488.4        | 24.3                 |      |     |     |     |
| **N-case study**    |              |        |        |              |                      |      |     |     |     |
| Reference composite | 3.21         | 0.05   | 49.5   | 26.6         | 0.6                  | 451.5| 8.3 | 2.49| 0.12|
| Number of specimens | 50           | 26.7   | 0.7    | 453          | 8.8                  |      |     |     |     |
| CNT-reinforced      | 3.13         | 0.05   | 50.8   | 25.6         | 2.3                  | 487.7| 13.7| 2.75| 0.09|
| Number of specimens | 50           | 25.2   | 2.7    | 474.6        | 18.4                 |      |     |     |     |

|                     | Relative difference, % | Confidence level, % |
|---------------------|-------------------------|---------------------|
| **UA-case study**   | 3.9 −4.5 −12.2 4.3 30.8 | 97.7 100.0 58.6 98.7 |
| **N-case study**    | −6.4 4.8 10.4 −26.1 −7.1 | 87.0 96.0 99.0 71.7 61.4 |
created by using two separate light sources, the light of the small room, in which the pictures were taken, and a strong light behind the specimen. Since an area with higher CNT concentration absorbs more light and thus appears darker, it is possible to visualize the overall arrangement of CNTs on the level of a textile structure. For backlight microscopy, digital pictures were taken at two different magnifications to investigate filtration on the scale of a representative cell and at boundaries of individual yarns. In addition, several adjacent pictures were taken in a row and put together to create a 'patchwork image'. This allowed a global view of a certain area with the benefit of high magnification of the individual pictures. Both CNT-reinforced materials were imaged in the same experimental setting, so as to allow further comparison of the filtering effect. Samples for backlight microscopy were cut out of the plates from an area near to the plate boundary.

Tensile tests
The composite plates were cut into specimens 250 mm × 25 mm × 3 mm and equipped with glass fiber-reinforced end tabs of 40 mm × 25 mm × 4 mm. Tensile tests were done on Instron 4505 with a 100 kN load cell and hydraulic clamping jaws. All tensile tests were performed in the fiber direction under the displacement control and at a crosshead speed of 1 mm/min till specimen failure. The material properties obtained from the quasi static tests are the ultimate stress σ_ult, ultimate strain ε_ult, and Young's modulus E. The ultimate stress is the highest value obtained during the test and the ultimate strain is the strain corresponding to this data point. The Young's modulus is calculated according to the standard ASTM D3039 and in the range between 0.1 and 0.3% of strain. In the N-case study, the end tabs had to be tapered at an angle of 45° for the CNT-modified specimens to ensure correct failure in the middle of the specimen. The reference specimens failed in the correct fashion without end tab tapering, so did the specimens in the UA study. For accurate strain measurement, an optical extensometer (digital image correlation system) was used. The surface of the specimen was captured with a camera every two seconds and images were then processed to obtain surface strains using LIMESS Messtechnik & Software GmbH set-up (Vic-3D, developed by Correlated Solutions Inc.). The tests were also accompanied by registration of acoustic emission events using AMSYS-5 system by Vallen Systems GmbH (with amplifiers Vallen AEP4, amplification 34 dB, discrimination time 0.4 ms, real time 3.2 ms, range 0.025–1.6 MHz, sample rate 5 MHz) and two piezo-crystal sensors. A threshold value was set to 40 dB. For analysis, a curve with cumulative AE energy of events vs. strain was used. Based on this cumulative energy curve, characteristic strains (also called damage development thresholds) are identified, namely ε_threshold (AE threshold strain), ε_1 (first transition strain), ε_2 (second transition strain). The latter two reflect transition from one stage of damage development to another. The AE threshold strain, ε_threshold, is a strain level, at which low energy AE events start to occur with low frequency. The first transition strain, ε_1, is often referred to as a damage initiation threshold. It can be identified in the cumulative energy curve by a sudden increase of its slope. This increase is attributed to the onset of transverse intra-yarn cracks (or intra-ply cracks for UD-based laminates). At higher strain levels, a second knee or jump in the cumulative energy curve appears (corresponding to the second transition strain, ε_2). Depending on the material and the direction of the applied load, this transition strain may refer to the onset of delaminations on the boundaries of the fiber bundles, merging of transverse cracks from neighboring plies, etc.

Damage characterization
Different characterization techniques were used to characterize crack densities. Specimens were examined post-mortem using X-ray radiography. Before examination, samples are submerged in a bath of diiodomethane for four hours. The radiography was done using an X-TEK VTX160 device. The taken images were used to evaluate the density of transverse cracks (number of cracks per cm²) at a set distance from the rupture plane. Cracks of different lengths were not differentiated. Damage patterns were then studied in more detail with optical and/or scanning electron microscopy (SEM) on polished cross sections. For the SEM examination, samples were coated with a layer of gold and imaged with a Philips XL30 FEG microscope at an acceleration voltage of 15–25 kV. Because the study was performed by two operators who worked independently of each other, the choice of characterization techniques was different for the N and UA cases.

Results and discussion
CNT localization in the composites
During the RTM process, no obvious filtering of CNTs was noticed as could be judged by the naked eye: the resin appeared to be of the same consistency and color at the outlet (after passing through the glass fabric) as it was at the inlet (right before the injection). Composite plates of ~3-mm thickness were not at all transparent and could not be used for assessment of CNT distribution. Therefore, thin plates with only two plies were produced and examined for possible filtration of CNTs (first, under strong backlight and then with optical microscopy).

The produced composites were firstly visually inspected for macroscopic filtration. In both UA and N case, plates showed darker areas on the outside (close to the edges) with lighter areas toward the center of the plate where the outlet was situated. Some differences in the gradation from dark to light gray were observed for the two materials. In the N case, the darker areas appeared larger and more stretched out toward the center. Because, only one plate for each material was produced and examined, no solid conclusions on the difference in the macroscopic filtration could be drawn.

On the meso-scale, for both states of CNT dispersion (the UA case and N case), a black and white checked pattern is observed as shown in Fig. 2. Since glass is transparent, the white areas are attributed to the fiber yarns, while the dark crisscross lines represent the resin rich areas in between. The through thickness alignment of the two plies was not controlled during the production; thus, resin rich zones from the two zones are not always perfectly aligned. For examination, however, those parts of the material were selected where such an alignment was better achieved. The change in
of 240 times. The very thin white lines mark directions of the aligned glass fiber yarns. CNT agglomerates are clearly visible for the UA case (Fig. 3a). Most of them can be found between yarns in resin rich zones and on the yarn boundaries. Many of the smaller agglomerates also managed to get inside the yarns and are situated in-between fibers. Nevertheless, the CNT concentration inside the yarns is lower. Hence, a local filtering effect on the yarn boundaries can be identified, hindering large CNT agglomerates to penetrate the yarns and thus lowering CNT concentration around individual glass fibers.

Figure 3 Backlight microscopy images of a one representative cell of the glass fiber fabric for two dispersion states; b a close up on the resin rich areas for the same dispersion states
boundaries act as barriers for CNT agglomerates. This leaves only a small fraction of CNTs being able to penetrate the yarns and situate themselves around individual fibers. The majority of CNTs is left behind in the resin rich zones with no contact to the primary reinforcement structure.

**Tensile test results**

Table 1 gives an overview of the tensile properties for the UA case. The Young’s modulus and tensile strength are both normalized to $V_f = 50\%$. The normalization is done for each individual specimen and the average is taken over the number of specimens tested for the specific property. It can be seen that CNTs in the matrix have no influence on the Young’s modulus of the composite. This is an anticipated result since the stiffness of the neat epoxy is only increased by 10% with the addition of 0.26 wt.% of CNTs and the composite stiffness is a global property that is mainly controlled by the stiffness of the fibers. The strength is also not affected by the presence of CNTs in the present case. The only property affected by the presence of CNTs is the strain to failure, which is decreased by 12.2%. The observed decrease in this property is statistically significant with the confidence level of 100%.

The accumulated energy of AE events recorded during tensile tests is plotted over strain for all specimens and summarized in a single diagram, as shown in Fig. 4a. These plots are used to extract characteristic damage development thresholds.

To conclude, the textile structure filters nanotube agglomerates above a certain size during the RTM process. Due to the dense packing of glass fibers inside fiber yarns, the yarn boundaries act as barriers for CNT agglomerates. This leaves only a small fraction of CNTs being able to penetrate the yarns and situate themselves around individual fibers. The majority of CNTs is left behind in the resin rich zones with no contact to the primary reinforcement structure.

**Figure 4** The UA-case study: a cumulative AE energy vs. strain curves for the composite; b representative stress vs. strain curves showing the distinctly different slopes after the onset of damage in the two composite systems

**Figure 5** The N-case study: a cumulative AE energy vs. strain curves for the composite; b representative stress vs. strain curves showing no difference in the slopes after the onset of damage in the two composite systems

Note: Red curves are for the CNT-containing composite and blue curves are for the corresponding reference composite.
Alexander Haesch et al. Localization of carbon nanotubes in resin rich zones

Nanocomposites 2015  VOL. 1  NO. 4

There is no statistical difference in $\varepsilon_1$ and $\varepsilon_2$ for the CNT containing and the reference composites. These results are well anticipated since in the N case, CNTs did not manage to get inside fiber bundles, but localized in resin rich zones. Since transverse cracks are formed inside the fiber bundles and CNTs are not there, no change for the onset of transverse cracks is expected. Thus, the AE data indirectly confirm that CNTs remain outside the fiber bundles. The lowest threshold $\varepsilon_{\text{min}}$, on the other hand, is decreased by 26%. This threshold is not always directly linked to the onset of transverse cracks, but to the ad hoc appearance of first damage in the material. For example, in15, the authors showed that first damage in a composite may onset at the boundaries of yarns, where transverse cracks rarely develop. The formation of transverse cracks is controlled by the stress distribution on the meso-level, defined by the architecture of the textile reinforcement, while fiber debondings (observed prior to the onset of transverse cracking) are formed as a result of local irregularities/non-uniformities in the distribution of fibers and yarn geometry. The reduction of $\varepsilon_{\text{min}}$ may be related to the inhomogeneities introduced by CNT agglomerates around the yarns. In contrast to the UA case, there is no difference in the slope of the stress–strain curves of the reference and CNT containing composites after the knee point. It is interesting to note that in the N case, the AE curves are more smooth (Fig. 5) in comparison with the UA case (Fig. 6) indicating a more gradual damage development. The formation of transverse cracks is controlled by the stress distribution on the meso-level, defined by the architecture of the textile reinforcement, while fiber debondings (observed prior to the onset of transverse cracking) are formed as a result of local irregularities/non-uniformities in the distribution of fibers and yarn geometry. The reduction of $\varepsilon_{\text{min}}$ may be related to the inhomogeneities introduced by CNT agglomerates around the yarns. In contrast to the UA case, there is no difference in the slope of the stress–strain curves of the reference and CNT containing composites after the knee point. It is interesting to note that in the N case, the AE curves are more smooth (Fig. 5a) in comparison with the UA case (Fig. 6a) indicating a more gradual damage development. Due to CNT localization in resin rich zones, a mismatch in the transverse stiffness of the yarn and the resin rich zone is reduced in this case. This may lead to a more gradual development of transverse cracks, which propagate not only through the width of the yarn but also along the yarn, crossing resin rich zones and then stopping at the yarn intersections. In the UA case where CNTs are distributed homogeneously in the
composite, the AE curves are similar to those of the reference composite.

**Damage characterization**

In the UA study, the density of transverse cracks was estimated using two approaches: (1) from the surface of tested specimens and (2) from polished cross sections of tested specimens. A typical view of surface cracks is shown in Fig. 6a–c. Cracks were counted on specimens of 25 mm × 25 mm (Fig. 6b) that were cut out from specimens tested till failure more than 1 cm away from the failure plane. There were seven specimens examined for each material system. The areas under investigation included four representative cells and each representative cell included five locations on transverse yarns that were cracked (Fig. 6b). Only distinct cracks were counted when calculating the crack density per visible part of a yarn. The crack density was then calculated per cm length of a specimen. The density of surface cracks was found to be 11.9 ± 2.0 cracks/cm in the reference composite and 10.5 ± 2.4 cracks/cm in the CNT-reinforced composite, which corresponds to the decrease in 11.8% with the confidence level of 98.8%. During this exercise, it was noted that cracks in the reference composite extended further away from the yarn centers than in the CNT-containing composite and some of these cracks merged with transverse cracks from a unit cell further. The CNT composite, on the other hand, seemed to also contain smaller defects but their quantity was difficult to assess with this approach. The crack densities quantified from polished cross sections were as follows: 15.4 ± 3.5 cracks/cm in the reference composite (9 samples) against 16.5 ± 5.7 cracks/cm in the CNT reinforced composite (10 samples). According to the statistical analysis, there is no apparent difference in these crack densities. Transverse cracks in the CNT-reinforced composite, however, looked different than the same cracks in the reference composite (9 samples) against 16.5 ± 5.7 cracks/cm in the reference composite and 10.5 ± 2.4 cracks/cm in the CNT reinforced composite, which corresponds to the decrease in 11.8% with the confidence level of 98.8%. During this exercise, it was noted that cracks in the reference composite extended further away from the yarn centers than in the CNT-containing composite and some of these cracks merged with transverse cracks from a unit cell further. The CNT composite, on the other hand, seemed to also contain smaller defects but their quantity was difficult to assess with this approach. The crack densities quantified from polished cross sections were as follows: 15.4 ± 3.5 cracks/cm in the reference composite (9 samples) against 16.5 ± 5.7 cracks/cm in the CNT reinforced composite (10 samples). According to the statistical analysis, there is no apparent difference in these crack densities. Transverse cracks in the CNT-reinforced composite, however, looked different than the same cracks in the reference material (Fig. 6d and e). They were less straight and often changed trajectory in places where there was no obvious reason for it. This can be understood if one imagines that the matrix has a heterogeneous structure. Indeed, CNT agglomerates are expected to change crack paths upon approach, as cracks are likely to go around the CNT agglomerates following higher stress concentrations than to enter them.

For the N case, damage in the composite is characterized with X-ray radiography. The images are taken from specimens tested till failure. A very homogenous distribution of transverse cracks along the length of the sample was observed. An overall reduction of 29% is noted for the CNT reinforced samples (11.2 ± 2.2 cracks/cm² against 15.8 ± 4.2 cracks/cm² in the reference composite) and shown to be statistically significant (with the confidence level of 99.9%).

**Overview of the results**

All results were combined together to see interrelations. The main differences between the UA- and N-case studies are summarized in Table 2. The state of the CNT dispersion has an effect on the position of CNTs in the composites. The CNT localization further affects the damage development and final properties of the composites. The presence of CNTs inside fiber bundles is found to delay damage development and to reduce compliance contribution due to transverse cracks. The CNT localization in resin rich zone, on the other hand, has shown not to affect the AE diagrams and the slope of stress–strain curves after the onset of damage. These are well-expected results. The effect on the composite strength and strain-to-failure is difficult to analyze as the failure process is also controlled by the onset and propagation of delaminations, but they were not characterized in the scope of the present study. It is hypothesized that the higher concentration of CNTs outside fiber bundles and in the interlaminar space in the N case may have influenced the delaminations’ resistance of the composite and therefore improved its strain-to-failure.

**Conclusions**

In the course of the work, the following conclusions have been made:

- Backlight inspection and microscopy revealed filtering of CNTs on the scale of the fabric architecture. This effect is attributed to the difference in the original dispersion state in the resin. For the case of small isolated CNT agglomerates, CNTs are able to enter fiber bundles. This conclusion is also supported by the AE measurements, which indicate a shift in damage development thresholds toward higher strains. For the state of dispersion where CNTs form a network with large features, it is found that CNTs tend to localize in resin rich zones without (or hardly) entering fiber bundles. The AE registration data are consistent with this observation as no change in the onset of transverse cracks is recorded.
- The presence of CNTs in a composite has no effect on the Young’s modulus, only minor effect on the strength,

| Table 2 Main differences in the UA- and N-case studies | UA-case study | N-case study |
|------------------------------------------------------|---------------|--------------|
| Dispersion state of CNTs | Uniform with small isolated agglomerates | Interconnected, network-like structure with large features |
| CNT localization in a composite | Partially filtered at the yarn boundaries, but also present inside yarns | Fully filtered at the yarn boundaries, hardly present inside yarns |
| Stiffness | No change | No change |
| AE diagrams | Shifted to higher strains indicating delay in damage development | No change |
| Stiffness after the onset of transverse cracks | Decreased | No change |
| Number of transverse cracks in the failed specimens | No change | Decreased |
| Delaminations | Not examined | Not examined |
| Strength | Slightly decreased | Slightly increased |
| Strain-to-failure | Decreased | Increased |
and pronounced effect on the strain-to-failure. The composite with CNTs in the resin rich zones has a higher strain-to-failure and lower density of transverse cracks in comparison with a virgin composite. In the meantime, a lower strain-to-failure and about the same crack density are measured for the composite where CNTs are clustered in small individual agglomerates.

Acknowledgements

We thank Nakul Prasad for characterization of surface cracks and Mohammad Ali Aravand for optical microscopy images in Fig. 1. The help of technicians Bart Pelgrims, Kris Van de Staey and Manuel Adams is also gratefully acknowledged.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

The work at KU Leuven was performed in the scope of the GOA/10/004 project ‘New model-based concepts for nano-engineered polymer composites’, funded by the Research Council of KU Leuven. The CNT containing masterbatch was received from Nanocyl S.A in the framework agreement between the Department of Materials Engineering, KU Leuven and Nanocyl S.A.

References

1. H. Qian, E. S. Greenhalgh, M. S. P. Shaffer and A. Bismarck: J. Mater. Chem., 2010, 20, 4751–4762.
2. F. L. Shan, Y. Z. Gu, M. Li, Y. N. Liu and Z. G. Zhang: Polym. Compos., 2013, 34, (1), 41–50.
3. V. M. Drakonakis, C. N. Velisaris, J. C. Seferis, C. C. Doumanidis, B. L. Wardle and G. C. Papanicolaou: Polym. Compos., 2010, 31, (11), 1965–1976.
4. W. Wu, Q. Chen, Y. Zhao, X. Ma, M. Tian and H. Fong: Polym. Compos., 2014, 35, (7), 1229–1237
5. M. Siegfried, C. Tola, M. Claes, S. V. Lomov, I. Verpoest and L. Gorbatikh: Compos. Struct., 2014, 111, 488–496.
6. A. Aravand, S. V. Lomov, I. Verpoest and L. Gorbatikh: Express Polym. Lett., 2014, 8, (8), 596–608.
7. S. V. Lomov, L. Gorbatikh and I. Verpoest: Carbon, 2011, 49, 2079–2091.
8. M. Ya and R. Pyrzy: Polym. Compos., 2014, DOI 10.1002/pc.23133.
9. Z. Spitalsky, D. Tasis, K. Papagelis and C. Galiotis: Prog. Polym. Sci., 2010, 35, (3), 357–401.
10. Z. Fan, K.-T. Hsiao and S. G. Advani: Carbon, 2004, 42, 871–876.
11. G. Rieber, T. Grieser, P. Grad and P. Mitschang: ‘Processing and evaluating CNT doped laminates,’ Proceeding of the SAMPE, Long Beach, California, 23–26 May 2011, Society for the Advancement of Material and Process Engineering.
12. J. J. Qiu, C. Zhang, B. Wang and R. Liang: Nanotechnology, 2007, 18, 275708.
13. Z. Fan, M. H. Santare and S. G. Advani: Compos. Part A, 2008, 39, 540–554.
14. S. V. Lomov, D. S. Ivanov, T. C. Truong, I. Verpoest, F. Baudry, K. Vanden Bosch and H. Xie: Compos. Sci. Technol., 2008, 68, 2340–2349.
15. N. De Greef, L. Gorbatikh, A. Godara, L. Mezzo, S. V. Lomov and I. Verpoest: Carbon, 2011, 49, (14), 4650–4664.