Fiber reinforced polymers (FRPs) are widely used for high performance structural applications since they offer remarkable in-plane mechanical properties combined with a low density. One of the main limitations of these materials is their poor mechanical properties through the thickness. Internal damage caused by an out-of-plane low velocity impact can severely reduce the mechanical performance of laminated composites, even if the damage is not visible on the surface.

In the recent years carbon nanotubes (CNTs) have been used in structural composites to improve their toughness by exploiting mechanisms on the nanoscale ([1-3]). The presence of CNTs increases the matrix dominated mechanical properties of composites and, therefore, can be expected to also improve the impact damage resistance. Composites with superior delamination resistance generally perform better in compression after impact (CAI) tests. Many studies have proven in the past that properties like interlaminar fracture toughness, interfacial shear strength and interlaminar shear strength can be enhanced by the incorporation of CNTs into the matrix of FRPs. However, little is known about the effect of CNTs on CAI.

The goal of the present study is to investigate the effect of CNTs on the projected delaminated area after impact and the residual compression strength. Since the damage resistance under low velocity out-of-plane impact loading is mostly associated with mode II delamination resistance, also \( G_{\text{IIc}} \) will be measured. The latter will serve as an indication about the delamination resistance due to the incorporation of CNTs and the comparison with the compression after impact strength will highlight the correlation between damage resistance and \( G_{\text{IIc}} \). ILSS is also measured to investigate the effect of CNTs on the onset of delaminations under shear.

2 Materials and methods

The primary reinforcement used in this study is a balanced twill 2/2 woven carbon fiber fabric produced by Hexcel under the commercial name HexForce G0986 injectex. The resin used to produce composites is Epikote 828 LVEL (Bisphenol-A type) together with a 1,2-diaminocyclohexane (Dytek DCH-99) hardener. The composite made from this resin will be referred to as ECF. This resin is also used to dilute the CNT master batch to produce the CNT modified composites.

Three different master batches provided by Nanocyl were used. All the master batches are based on a liquid Bisphenol-A epoxy resin and contain a high concentration of MWCNTs with an average diameter of 9.5 nm. Two of the masterbatches are the same commercial product EpoCyl NC R128-02 with the difference of the storage time. One of them was stored for less than three months prior to the current study (the composite made from this resin will be referred to as CNT-fresh) whereas the other one was prepared almost three years earlier (CNT-old). The third type of the master batch is produced with functionalized multi-wall CNTs of the same type (CNT-func). The matrix in composites contains 0.25 wt% of CNTs. Carbon fiber/epoxy composites were produced using the resin transfer molding (RTM) technique.
The experimental setup for the impact test was chosen according to the ASTM D7136 standard. It is shown in Fig.1. Five specimens for each material system with dimension of 100x150x4 mm³ were tested. The weight of the impactor was adjusted to 5.536 kg. With a drop height of 0.49 m, an impact energy of 26.8 J was achieved. This corresponds to an impact energy of 6.7 J per mm sample thickness as recommended by the standard.

Since the number of specimens available for testing and examination was limited, only nondestructive evaluation (NDE) techniques were applied to assess the extent of delaminations after the impact. Ultrasonic inspection (C-scan) was conducted before the impact test to check the quality of the specimens and after the impact to measure the delaminated area.

The compression test was performed according to the ASTM D7137 standard. An Instron 5985 universal testing machine fitted with a 250 kN load cell was used. The test was done at a constant rate of 1.25 mm/min till specimen failure while load and displacement were recorded. The compressive residual strength and the effective compressive modulus were calculated. The setup is shown in Fig.2.

The end-notched flexure (ENF) test was used for the determination of the critical energy release rate in mode II ($G_{\text{IIc}}$). The samples were cut into dimensions of 120 mm x 20 mm x 4 mm. An Instron 5567 universal testing machine with a 1 kN load cell was used to carry out the test at a cross head speed of 1 mm/min.

2 Results and discussion

2.1 Impact tests

Inspection of the damage on the surface by naked eye indicated that the samples of all material systems fractured in a similar way. On the front side, where the impactor was in contact with the specimen, matrix cracks could be found. A dent in the contact area between the sample and the striker had a characteristic depth in the order of 0.1 to 0.3 mm. On the back side, fiber breakage was visible. These damage patterns corresponded well with descriptions in the literature. The extent of delaminations detected by C-scan was larger than one would expect from the visible surface damage. The narrow and sharp peak around 2010 indicates the high quality of the produced specimens and the impact damage is represented by the peak near the low scale value.

The projected delamination areas measured by C-scan after impact are given in Fig. 3. The mean of the delamination area for the CNT modified specimens is larger compared to the reference composite. The largest increase in the delaminated area is found for CNT-fresh with 12.7% whereas the increase for CNT-old was only about 8.7%. The differences for all three comparisons are significant. These data indicate that CNT-old has a better resistance against impact induced delamination than CNT-fresh and CNT-func. The master batch used to produce the CNT-old composite is known to contain a network like structure of CNTs.

The differences of the absorbed energy between the tested materials are limited and no major trend can be noticed. The mean of the contact duration is larger for the CNT modified laminates. This could be a consequence of the larger delamination area and the associated loss of the composite (bending) stiffness.

The maximum contact force and the damage threshold load (DTL) are also recorded. The DTL is associated with the onset of significant damage, mainly delaminations, but can also include fibre breakage. The evolution of damage reduces the stiffness of the sample. Matrix cracks are probably introduced already below DTL. It is believed that they are the first kind of damage. Table 1 provides the recorded values for the DTL and maximum contact force. The mean values of the maximum contact force are lower for the material systems with CNTs. Since the delaminated area for these systems is also larger than for the reference composite, it is assumed that the larger delamination area results in a more severe loss of stiffness and therefore the contact force decreases. The highest DTL was found for the reference composite. It is generally accepted, that a higher DTL indicates a better impact resistance. This is also confirmed in this study where CF/epoxy with the highest DTL has the smallest delaminated area.
Within the CNT modified composites, CNT-func performs best with respect to the DTL. It is expected that functionalisation of CNTs promotes better dispersion of CNTs in the matrix. The small scatter of the DTL for CNT-func in comparison with the other two systems can be seen as an indication of that. Recalling that the CNT-old has the smallest delaminated area of the three nano modified composites, it appears that the network of CNTs promotes initiation of damage but hinders its further development.

2.2 Compression test

In the compression test after impact all material systems behave similarly and no dramatic differences could be noted. The load increases linearly with displacement and drops suddenly after reaching its maximum. This drop was associated with sudden fracture of the specimen. The final failure was always triggered by the impact damage in the center of the specimen. From the vertical strain field just before the fracture, the strain concentration in the center of the specimen was observed. The fracture then ran across the entire width of the specimen as shown in Fig. 2.

The compressive residual strength values are given in Fig. 3 along with the delaminated area data. The delaminated area for all CNT modified laminates was larger compared to the reference composite and one would expect that this would lead to a lower after impact compressive strength. The residual strength of CNT-old, however, did not degrade although the delaminated area in this material increased. The mean strength of CNT-old is even 1% higher than for CF/epoxy, although this difference is not significant. CNT-fresh and CNT-func have a lower compressive strength than the reference material, and that the decrease is statistically significant.

The fact that CNT-old has a higher residual strength despite larger delaminations area indicates that it has a higher damage tolerance than the other tested materials, even higher than the reference composite. It appears that the network-like structure of CNT dispersion in the aged CNT masterbatch has a beneficial effect on the residual compressive strength. Interestingly, one exceptionally high strength value of about 220 MPa was also recorded for CNT-old.

Functionalisation of the CNTs could not improve the residual compressive strength. The scatter of the results, however, is smallest for CNT-func among all CNT containing composites. This suggests a more homogeneous CNT dispersion as a result of functionalization.

2.3. Damage characterization

After the compression test, the damage morphology was examined under an optical microscope. For each material system, 2 sections were prepared: one was taken from the center (referred to as “center”) and another at the quarter width (referred to as “side”). The distance between the center line and the section “side” is about 25mm. At this distance, no damage from the impact test is expected to be present.

In Fig. 4 the section taken from the center of the specimen is shown. Although examination was done after the compression test, some features of the impact damage are still visible. The main failure modes are matrix cracks, delaminations and fibre breakage at the top side where the impactor was in contact with the sample. Also on the bottom side, extensive fiber failure can be recognized. In general it seems that the damage on the bottom side of the specimen is more severe for samples with CNTs. For the reference system, cracks were found only inside fibre tows and not in the resin rich areas between the tows. In CNT containing systems, however, cracks were also found in the resin rich areas. Generally, materials with CNTs appeared to contain more matrix cracks. These cracks were inclined at about 45 degrees and followed the conical shape of the impact damage. In the sections taken from the side (not shown) matrix cracks could not be found. It is, therefore, believed that these matrix cracks are damage due to impact and not a result of the compression test. Based on this damage characterization one can conclude that the matrix with the CNTs is weak under a compressive load caused by the impactor.

The “side” cross sections were also examined, examples is shown in Fig 4c. Depending on the evolution of delaminations during the compression
test, either failure under shear or buckling of the fibers can become dominant. Both types of failure could be found in all material systems without a clear tendency.

As previously noted, the impact resistance of the composites could not be improved by adding CNTs to the matrix. For all systems with CNTs, the measured delamination area was larger compared with the reference composite. A possible explanation for this might be that during the out of plane impact the matrix is loaded under compression. Under this type of loading the toughening mechanisms associated with CNTs such as pull-out and crack bridging might be less efficient. The CNTs act in this case probably more like a rigid inclusion and stress concentrator, resulting in a higher matrix crack density. The matrix cracks found by optical microscopy in the polished sections of the CNT modified composites support this assumption. The matrix cracks themselves have no severe effect on the stiffness of the laminate but they act as initiation sites for delaminations. There may be a link between the larger matrix crack density and the observed increase in the delamination area.

2.4. Mode II Interlaminar Fracture Toughness

Fig. 5 gives an overview of the measured mode II fracture toughness for all material systems. The average GIIC for all materials with CNTs is higher than for the reference composite. A statistical significant is, however, only confirmed for CNT-old. Thus, CNT-old has a higher GIIC, hence a delamination resistance under shear and this may be a consequence of the network structure of CNTs in this material. The fracture toughness was found to be independent of the crack length as expected.

2.5 SEM of fracture surfaces

The fracture surface of samples tested for the mode II fracture toughness were examined using a FEI NOVA Nanolab 600 scanning electron microscope (SEM) with a through the lens detector and an acceleration voltage of 5 kV. All samples were examined close to the tip of the starter crack. Fig. 6 illustrates SEM images of all systems. Small CNT agglomerates could be found in CNT-fresh, while much larger agglomerates were observed in CNT-old (mainly in resin rich zones). As reported previously in [4,5] the network has larger features. Just from the fracture surface, no quantification can be made about the extent of this network. The CNT dispersion for CNT-func was very homogeneous. In these composites, CNTs were found everywhere (also between fibers inside fiber bundles), which was to a lesser extent in CNT-fresh and not at all the case in CNT-old.

Pulled out nanotubes could be found suggesting an active toughening mechanism through CNT pull out. In the areas with CNTs, the fracture surface appears to be rougher, which also indicates an energy dissipating mechanism. The pulled-out CNTs appeared to be longer in CNT-old and shorter in CNT-func.

Additionally, the surface of the carbon fibres was found to be clean with no remaining epoxy matrix adhering to it in all composite systems. There were no indications that the CNTs would promote a better adhesion between fibre and matrix.

2.6 ILSS test

No differences were found in the measured ILSS values for different composite systems (Fig. 5). Interesting observations were, however, made about the failure modes. In the SBS test, specimens should fail under single or multiple shear. To observe failure development during the test, a white coating was applied on the front side of the specimen and the test was filmed. Depending on the material configuration, the observed failure modes were compression failure, single or multiple shear failure. Some samples failed partly due to shear and compression and, therefore, two failure modes were reported for these specimens.

All load-displacement curves from the reference composite show an almost linear behavior and a sudden load drop. This drop is a consequence of the delamination evolution, resulting in a single shear failure. For CNT-fresh and CNT-old a different damage morphology was observed. Compression failure in the vicinity of the central loading roller caused first discontinuity in the load-displacement
curve. The final load drop was then a result of mainly multiple shear fractures in the central area. Only a few specimens failed due to a single shear fracture. The load-displacement curves for the CNT-func samples were similar as the other systems containing CNTs. Also compression failure was found as the first failure but the final fracture for all CNT-func specimens was single shear. This is a significant difference compared with the multiple shear failure observed for CNT-fresh and CNT-old specimens. All specimens had the same dimensions and the testing setup remained unchanged during the entire test. Thus the presence of the CNTs changed the failure characteristics.

The performed damage characterization suggests that composites with CNTs are more sensitive to in-plane compressive stresses during impact. CNTs and their agglomerates appear to act more as stress concentrators and less as reinforcements. The multiple shear failures observed in CNT-old and CNT-fresh appear to be due to larger CNT agglomerates in these materials that initiate damage at multiple locations. Although specimens of CNT-func were also sensitive to in-plane compressive stresses, they all failed due to single shear fracture in the mid plane similarly to the reference composite. The single shear fracture is another confirmation that the CNT dispersion is more homogeneous in CNT-dunc.

### 3. Discussion and concluding remarks

To highlight the relation between the different experimental results, Fig. 7 is presented. An increase in delamination area was found for all three CNT containing composites whereas for CNT-old the smallest increase was recorded. The residual compressive strength decreased for CNT-fresh and CNT-func, and remained the same for CNT-old. The fact that CNT-old has a higher residual strength despite a larger delamination area indicates that it has a higher damage tolerance than all other tested materials including the reference material.

The values measured for ILSS are very similar for all the systems. Interesting conclusions, though, were made by observing the type of failure during the ILSS test. From the observations made during the experiments, it was concluded that the presence of CNTs in the matrix makes the material more sensitive to matrix failure under in-plane compressive stresses. CNTs can improve the properties of composites due to toughening mechanisms such as bridging of cracks and CNT pull out. These mechanisms are probably less efficient if the matrix is loaded under compression. In this case, the CNTs may act more as a stress concentrator and not as reinforcement. This was observed by examining specimens after impact and compression tests where more impact induced matrix cracks were found for CNT containing composites. These matrix cracks act as initiation sites for delaminations during the impact. Therefore it is not surprising that the delaminated areas for the CNT containing composites were larger, based on the fact that also more matrix cracks were present.

The results of this study imply that the dispersion state of the CNTs influences the mechanical properties of the material. From the experimental results it can be concluded that this CNT network has a positive influence on the properties of the composites. This statement is further supported by the results of the $G_{IIc}$ test where CNT-old performed best of all tested materials and $G_{IIc}$ was improved by 22% compared with the reference material. As described in the literature review, $G_{IIc}$ plays also an important role during the growth of delamination in the compression test. The higher delamination area due to impact can be probably compensated by the improved $G_{IIc}$ during the compression after impact test, and the compressive strength (CAI) did not degrade for CNT-old. All these facts indicate that the network like morphology of CNTs can have a positive influence on the properties of the composite.

Whilst this study did not confirm better mechanical performance of composites modified with functionalized CNTs over non-functionalized ones, a clearly more homogeneous distribution was found. The scatter of the results was in general lower for the samples containing functionalized CNTs and this is an indication for a more homogeneous dispersion. This conclusion is further supported by SEM investigation where no agglomerates of functionalized CNTs could be found.
Acknowledgement

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Table 1. Results impact test: maximum contact force (F\text{max}) and damage threshold load (F\text{1})

<table>
<thead>
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<th>F\text{max} [N]</th>
<th>F\text{1} [N]</th>
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<td>avg</td>
<td>min</td>
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<td>6650</td>
</tr>
<tr>
<td>CNT-func</td>
<td>7105</td>
<td>6833</td>
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Fig. 1 Experimental set-up for the impact test.

Fig. 2 Experimental set-up for the compression after impact test.

Fig. 3 Mean values for delamination area and residual compressive strength.

Fig. 4 (a) Cutting of samples for optical microscopy, (b) sample taken from the center of CNT-fresh, (c) sample taken from the side of CNT-fresh.

Fig. 5 Mean values for mode II interlaminar fracture toughness (G\text{IIc}) and interlaminar shear strength (ILSS).
Fig. 6 SEM images of fracture surfaces

Fig. 7 Overview of the obtained results.

References


