1 Introduction
Composite laminates represent one of the most important technological developments of the last decades. They find application in a constantly greater number of sectors and their importance is consequently growing up day by day. Laminates are orthotropic materials subjected to a failure mode called delamination: it happens when a fracture takes place between two plies. It is one of the most critical failure modes for laminates since it appears and grows under the surface and it is not visible from the outside. A laminate can significantly loss stiffness and strength and still remains visibly unchanged. For this reason, the interest of the research community on this problem is highly connected to the world of the industry, in particular the aerospace and aeronautical sectors.

Many efforts were carried out in the last decades to face such problem and plenty of research can be found in literature on experimental testing [1-8] and numerical modelling [9-18] of delamination. The present work deals with the use of nanofibers as an interleaving reinforce. In particular, the base idea is that a nanofibrous layer placed in particular laminate interfaces is able to affect some ply-to-ply properties and thus to control the delamination strength. Nanofibers are able to compensate the troubles caused by the mismatch of bonded adjacent plies, without a reduction of in-plane properties and without increasing either the composite weight or the laminate thickness.

Dzenis et al. [19] in 1999 were the firsts to follow this route: they interleaved into a composite laminates a polymeric nanofibrous non-woven mat obtained by the electrospinning process and demonstrated that such nano-reinforcement is able to improve the delamination resistance of the laminate. From then, many researchers started to work with nanofibers and even if electrospinning is an old-patented process, it is only in the last years that electrospun nanofibers have been used in the composite material field to improve mechanical properties and in particular to affect the delamination problem. Zucchelli et al. [20] presented a deep review of the usage of electrospun nanofibers, showing how they offer great potential in enhancing many mechanical properties in composites: delamination and impact resistance, damping, flexural strength, and fatigue are all properties which can take benefits from the introduction of nanofibers. Some of the authors already have proved the benefits brought by a Nylon 6,6 nanofibrous mat interleaved into woven carbon fiber laminates [21]. Mode I and Mode II fracture mechanics tests performed on both virgin and nanomodified specimens showed that an interleaved nanofibrous mat can enhance composite delamination strength and damage tolerance. Delamination of virgin and nanomodified interfaces is simulated cohesive zone model, which is proved to be an efficient technique to simulate the delaminating interfaces. In [22, 23] a cohesive adapting method was implemented in Abaqus. In this model, a pre-softening zone is proposed ahead of the existing softening zone. In this pre-softening zone, the initial stiffness and the interface strength are gradually decreased. Borg [11] proposed a discrete model where the interface elements softening model does not follow a linear decrease with separation but a power law. The delamination model is implemented in the finite element code Abaqus and simulation results are shown to be in
agreement with experimental results. In [24] the delamination process is validated by simulation of DCB, ENF and MMB (Mixed Mode Bending) setups, and the results are shown to be in agreement with experimental data. In ENF tests, contact introduces regions in which friction may be important. The presence of contact will influence the stability of the delamination propagation. As shown in [25, 26], the delaminations of a stable system will tend to grow together, leading to an increased capacity of the system to absorb energy and a more ductile structural response. Maimi [27] proposed damage laws that force softening as soon as one criterion is activated. Exponential damage evolution laws are used to represent the cohesive response of all the failure modes of the ply. Turon et al. [28] studied the effects of the element size on the force/displacement response of a DCB test. It is shown that accurate results can be obtained using elements with length smaller than 1 mm, and a minimum number of 5 elements within the cohesive zone is necessary for accurate simulations. It is also shown that the interface stiffness can have a huge influence on the accuracy of the solution as well. This work intends to perform both experimental and numerical analysis of Double Cantilever Beam (DCB) and End Notched Flexure (ENF) tests on non-nanomodified and nano-modified samples are done. Different configurations of nanolayers are manufactured, then interleaved into CFRP laminates and tested. Experimental results are eventually used as a base to identify delamination models of both virgin and nanomodified specimens. Simulations done using cohesive zone have a double purpose:

1) to model the presence of a nanofibrous interleave into an epoxy-based composite laminate. Different configurations of nanolayer were manufactured, and each feature affects the behavior of the whole laminate in its way; simulations have the purpose to link the geometrical feature of the nanofibrous mats to the global mechanical properties of the laminates;

2) to provide a useful tools to those designer who want to reinforce their laminates with nanofibers. Authors attempt to provide a tool capable to predict the nanointerleaved laminate behavior to be used in practical applications.

2. Experiments

2.1 Testing methodology

Mode I (DCB) and Mode II (ENF) fracture mechanic tests were performed on 20 plies, 20 mm width, virgin and nanomodified composite laminate specimens according to the international standards ASTM D5528 [29] and ASTM 7246 [30] respectively (Figure 1).

![Figure 1: Experiments.](image)

(a) DCB.  
(b) ENF test.

An initial delamination is required for both the tests, in the mid-thickness of the specimen, and it was provided by a 15µm thick Teflon sheet, placed during the lay-up process. Electrospun nanointerleave is placed into nanomodified specimens in the delaminated interface during the lay-up. Experiments were performed under displacement control condition at constant crosshead rate of 1.5mm/min in a servo-hydraulic universal testing machine Instron 8033 with a force capacity in the range 5-250 kN. Load and crosshead displacement were recorded 10 times per second during the test. For each configuration, 5 specimens were manufactured and tested, and the results are given by the average of all the tests. As previously mentioned, the effect of the architecture of the nanoreinforcement is investigated by manufacturing different nanofiber configurations. In particular:

- nanoreinforce of 25 and 50 µm thicknesses were electrospun by changing the electrospinning process time;
- nanoreinforce with random and aligned fibers were electrospun. Oriented nanofibers will be placed in the direction of the length of the beams;
- nanofibers with diameters of 150 and 500 nm were electrospun. Fiber diameter distribution was determined by measuring 200 fibers per sample, with an image acquisition software (EDAX Genesis).

A full description of the electrospinning process can be found in [31]. Thus a full experimental campaign with 3 parameters and 2 factors was carried out: it leads to 8 different nanomodified configurations, each one identified with a code made by 4 characters:

- the first two digits indicate the concentration of the polymer into the electrospun solution,
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which is related to the nanofiber diameter: 14 in the case the diameter is 150 nm, 25 for a diameter of 500 nm;
• the third character is a letter related with the nanofiber orientation: R indicates Random fibers, while O is related to oriented (aligned) nanofibers;
• the last one is a letter which represents the nanolayer thickness: B indicates a 25 µm layer, C indicates the 50 µm one.
Configurations and codes are summarized in Tab. 1.

Table 1. Nanofibers configurations.

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Orientation</th>
<th>Diameter</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 µm</td>
<td>Random</td>
<td>150 nm</td>
<td>14RB</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500 nm</td>
<td>25RB</td>
</tr>
<tr>
<td></td>
<td>Aligned</td>
<td>150 nm</td>
<td>14OB</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500 nm</td>
<td>25OB</td>
</tr>
<tr>
<td>50 µm</td>
<td>Random</td>
<td>150 nm</td>
<td>14RC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500 nm</td>
<td>25RC</td>
</tr>
<tr>
<td></td>
<td>Aligned</td>
<td>150 nm</td>
<td>14OC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500 nm</td>
<td>25OC</td>
</tr>
</tbody>
</table>

Both the DCB and the ENF tests were then performed on 9 configurations: one virgin and 8 nanomodified.

2.2. Results and discussion

In Figure 2 the most representative curves of each configuration are presented. In Figure 2 the force/width vs. displacement data of DCB experiments are reported, while ENF tests are plotted in Figure 3.

Not all the nanofiber configurations yield an increase of the peak force and/or a pseudo-ductile behavior underlining a toughening of the interface. Indeed, this is true essentially in the case of the 14RB configuration only. The effect of the nanoreinforce on the global behavior of the laminate is the results of two important and complementary contributions: from one side the nanofibers bring a positive reinforce effect to the interface, but on the other side, at the same time they make a stand to the resin flow during the curing process.

The reinforcement mechanism of the nanofibers is illustrated in Figure 4, where two SEM pictures of fractured surface are shown.

It is clear that even if the matrix is broken, and cannot longer carry loads, many nanofibers still link the two layers where they are placed in between, given a self-reinforcing effect to the laminate. As previously mentioned, the presence of nanofibers represent an obstacle to the resin flow during the curing process, and it may leads to leave voids and defects, that weaken the interface. It means, for example, that increasing the nanofiber thickness, even if the reinforce is greater, may generate a weaker interface that globally decrease the laminate strenght. It was proven that aligned nanofibers are more compact and with a lower grade of porosity with respect random mats, i.e. less possibility of resin penetration. The risk is therefore that an interface with aligned nanomat will not be fully impregnated by the resin. In a similar manner, thickness of nanolayers influences the permeability of the interface and similar considerations can be also done for the diameter of the fibers.
3. Numerical modelling

The aim of this section is to identify a behavioral model based on cohesive zone for simulating delamination of the nanomodified interface under simple loads (DCB and ENF tests). The simulation is performed with FE code Abaqus using cohesive elements at the delaminating interface and implicit time integration.

The traction-separation behavior assigned to cohesive elements is exemplified in Figure 5 by a triangular law. The elements initially behave linearly. When a certain level of displacement (or stress) is reached, the stiffness and strength are progressively reduced until the complete separation is obtained. This type of cohesive law fits reasonably well to a predominantly brittle fracture, where the force/opening curve presents an initial maximum peak followed by an exponential-like decay.

![Figure 5. Example of a linear damage cohesive law.](image)

If a significant fiber bridging is present, the cohesive law can be broken up into two components, associated with matrix cracking and with fiber bridging respectively (Figure 6), which has been shown more appropriate in describing the experimental behavior than a simple linear damage law such as the one in Figure 5 [32].

![Figure 6. Schematic mode I traction–separation law used to describe fracture of composite with fiber bridging. The peak load corresponds to matrix cracking, followed by fiber pull-out [32].](image)

With reference to Figure 5, the identification of parameters starts from the initial stiffness $K_{i}^{0}$, that is determined by increasing progressively the value until the FE trend coincides with the elastic part of the experimental data. Once established the stiffness, a value of $\sigma_{22,\text{max}}$ is determined by taking the cohesive energy $\Gamma_{i} = G_{\text{fc}}$, then increasing progressively $\sigma_{22,\text{max}}$ until little, if no deviation from linearity is left before the force peak. Finally, the cohesive energy $\Gamma_{i}$ is varied until a good convergence is found on the post-peak force trend. The same procedure is used also in the case of mode II. In the case of the bi-linear damage law shown in Figure 6, $K_{i2}^{0}$ and $\sigma_{22,\text{max}}$ are determined in the same way as for the linear damage law. The value of $\sigma_{22,\text{b,max}}$, $\Gamma_{1m}$ and $\Gamma_{1}$ are then identified by trial-error process in order to reproduce as closely as possible the data in the post-force peak phase.

3.1. DCB modelling

All the simulations were carried out using a 2D plane strain finite element model: fully integrated square four-node elements (size 0.25 mm) were used to simulate the cantilevers, while square cohesive elements (size 0.1 mm) were used to simulate the delamination. The force is transmitted via rigid kinematic constraints simulating the fixtures. Figure 7 shows the model. Table 2 summarizes the elastic constants used in the simulations of the carbon/epoxy laminate.

![Figure 7. FE model of the DCB specimen.](image)

<table>
<thead>
<tr>
<th>$E_{11}$ [GPa]</th>
<th>$E_{22}$ [GPa]</th>
<th>$E_{33}$ [GPa]</th>
<th>$G_{13}$ [GPa]</th>
<th>$v_{12}$</th>
<th>$v_{23}$</th>
<th>$v_{13}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>59</td>
<td>59</td>
<td>8</td>
<td>0.8</td>
<td>0.261</td>
<td>0.261</td>
<td>0.062</td>
</tr>
</tbody>
</table>

3.2. ENF modelling

The numerical modelling follows the same general set-up described for the DCB tests. The mesh was refined only at the end of the initial delamination, in the region where the crack was expected to propagate, up to 10 mm beyond the half-length of the specimen (in the opposite side of the delamination), since it was experimentally found...
that the crack can overpass the mid-length of the specimen during loading. The mesh was only refined in the direction of crack growth. Figure 8 shows the geometry used during the study in a partially loaded state.

Figure 8. ENF model in a partially loaded state.

### 3.3. Mode I loading results

The Mode I fracture behavior of the virgin material has been as a first attempt modelled with the linear damage law represented in Figure 5, where the area under the traction-separation law is taken equal to the corresponding experimental critical strain energy release rate. Figure 9 shows the comparison between the experimental result and the numerical solution of the virgin specimen obtained using the linear damage model. Once calibrated, this law fits well to the case of the non-modified interface, where the force/opening presents an initial maximum peak followed by an exponential-like decay.

Figure 9. Comparison between experiment and cohesive zone model in the case of virgin laminate.

As found in the literature [33], the linear damage model is rather insensitive to the choice of the critical stress (within some limits: extremely low values of critical stress give poor results in terms of maximum peak force). A critical stress high enough to sharpen the force-opening peak as in the experiments is used here. Concerning the fracture energy of the cohesive law, the value of $G_{Ic}$ is used. Nanomodified interfaces are modelled using the cohesive law of Figure 5 or the one of Figure 6 depending on the case: i) if the force/opening presents an initial maximum peak followed by an exponential-like decay, the type of Figure 4; ii) if the initial peak is followed by a plateau, and only afterwards it decays as an exponential-like curve, the type of Figure 6. In the latter case, the cohesive behavioral model is based on the idea that the epoxy matrix and the nanofibers work as parallel springs, following essentially the traction-separation behavior of the stronger and more brittle epoxy matrix almost until its failure. At the same time the nanofiber cohesive behavior dominates the last part of interface damage and failure. The results of the identification process are collected in a graphical form in Figure 10, while model parameters are summarized in Table 3.

As previously seen in the description of experimental results, some tests exhibited a peculiar behavior in the pre-peak regime, characterized initially by a linear behavior, followed by a deviation from linearity, then again by a linear segment, having a lower slope than the initial one, until failure. These cases were treated considering only the second linear segment for the simulation of the pre-peak behavior, implying that a longer crack length was identified in order to match the lower slope of this second linear segment.

### 3.4. Mode II loading results

In the ENF setup the crack grows rapidly. Experiments showed that, in the case of non-modified specimens, once the crack begins to grow, the delamination instantaneously overreach the centerline of the specimen. As a result, the load/displacement graph shows a sharp drop right after the maximum force peak. Experiments on the nanomodified specimens show a similar behavior. Therefore, the simulation was carried out using a linear damage cohesive law, taking as cohesive energy the value of $G_{IIc}$. Starting from the virgin material, after calibration the model allows matching the maximum force and the force drop but not the propagation phase. Indeed, the fracture energy used to match the propagation phase is significantly lower than that necessary to match the maximum load (see table in Figure 11).

On the other hand, some of the nanomodified interfaces showed the opposite behavior, that is the fracture energy used to match the propagation phase is higher than that necessary to match the maximum load. This two-ways behavior may not necessarily be explained by an underlying mechanism, but simply to an experimental scatter due to the limited number of tests. Additionally, the absence of a fatigue precrack may induce either a higher or a lower amount of energy to start crack propagation depending on the relative position of the Teflon foil with respect to the nanomat.
Figure 10. Comparison of experiments and simulations for the identification of cohesive zone parameters under Mode I.

Table 3. Cohesive zone parameters identified for Mode I loading.

<table>
<thead>
<tr>
<th>DCB</th>
<th>Cohesive Zone Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Code</td>
<td>( \Gamma_1 ) [N/mm]</td>
</tr>
<tr>
<td>Virgin</td>
<td>0.75</td>
</tr>
<tr>
<td>14 R B3</td>
<td>1</td>
</tr>
<tr>
<td>14 R C3</td>
<td>0.3</td>
</tr>
<tr>
<td>25 R B2</td>
<td>0.33</td>
</tr>
<tr>
<td>25 R C2</td>
<td>0.17</td>
</tr>
<tr>
<td>14 O B1</td>
<td>0.28</td>
</tr>
<tr>
<td>14 O C1</td>
<td>0.25</td>
</tr>
<tr>
<td>25 O B1</td>
<td>0.22</td>
</tr>
<tr>
<td>25 O C1</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The change in fracture energy is therefore simulated using two different cohesive laws depending on the position along the crack path and in particular the cohesive element close to the initial crack tip are assigned a higher cohesive energy. The size of the "tougher" zone \( L_a \) is tuned by comparing the simulations with the experimental results.

Figure 11. Result of ENF (virgin material) simulation obtained using a triangular shape cohesive law.

Figure 12. Result of ENF (virgin material) simulation obtained using two triangular shape cohesive law, the first one only for a length \( L_a \) ahead of the initial crack tip.
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<table>
<thead>
<tr>
<th>Mat with oriented fibers</th>
<th>Fiber Diameter [μm]</th>
<th>150</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mat thickness [μm]</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mat with random fibers</th>
<th>Fiber Diameter [μm]</th>
<th>150</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mat thickness [μm]</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 13. Comparison of experiments and simulations for the identification of cohesive zone parameters under Mode II.

Table 4. Cohesive zone parameters identified for Mode II loading.

<table>
<thead>
<tr>
<th>Code</th>
<th>$\Gamma_2'$ [N/mm]</th>
<th>$\sigma_{13,\text{max}}$ [MPa]</th>
<th>$K'$ [MPa/mm]</th>
<th>$\Gamma_2''$ [N/mm]</th>
<th>$\sigma_{23,\text{max}}$ [MPa]</th>
<th>$K''$ [MPa/mm]</th>
<th>$L_a$ [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>2.7</td>
<td>48</td>
<td>55000</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>14 R B1</td>
<td>3.3</td>
<td>40</td>
<td>55000</td>
<td>4.6</td>
<td>51</td>
<td>55000</td>
<td>20</td>
</tr>
<tr>
<td>14 R C2</td>
<td>1.1</td>
<td>17.5</td>
<td>55000</td>
<td>2</td>
<td>35</td>
<td>55000</td>
<td>25</td>
</tr>
<tr>
<td>25 R B3</td>
<td>1.65</td>
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<td>55000</td>
<td>1.45</td>
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<td>25</td>
</tr>
<tr>
<td>25 R C1</td>
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<td>55000</td>
<td>3</td>
<td>48</td>
<td>55000</td>
<td>25</td>
</tr>
<tr>
<td>14 O B2</td>
<td>3.1</td>
<td>45</td>
<td>55000</td>
<td>3.45</td>
<td>48</td>
<td>55000</td>
<td>10</td>
</tr>
<tr>
<td>25 O B1</td>
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<td>14</td>
<td>55000</td>
<td>0.28</td>
<td>7</td>
<td>55000</td>
<td>10</td>
</tr>
<tr>
<td>25 O C3</td>
<td>1.25</td>
<td>17</td>
<td>55000</td>
<td>0.35</td>
<td>8</td>
<td>55000</td>
<td>20</td>
</tr>
</tbody>
</table>

The procedure followed for the tuning of the cohesive zone parameters is:
1. identify those parameters needed to predict the maximum load (superscript ‘’ in Figure 12);
2. identify those parameters needed to predict the propagation phase (superscript “” in Figure 12);
3. assign the parameters obtained after step 1 to the cohesive elements for a length $L_a$ from the crack tip. The set of parameters coming from step 2 is given to the remaining elements.

Fitting simulations to experiments identifies the value of $L_a$.

The same approach in cohesive law identification has been adopted in the case of the tests on nanomodified interfaces. The results of the identification process are collected in a graphical form in Figure 13, while model parameters are summarized in Table 4.

4. Conclusions

In the present paper, the presence of electrospun nanofibrous mat as interleaving material in composite laminate interfaces by Mode I and Mode II fracture tests has been experimentally tested and numerically simulated using cohesive zone. From the experimental point of view, only a reinforcement mat with random fiber arrangement, fine fiber diameter and very low thickness (14RB Code) gives better results than the virgin material, with an increase ranging from 20 to 35% depending on loading mode and the propagation instant (beginning or steady). The reason is that aligned nanofibers are more compact and with a lower grade of porosity with respect random mats, i.e. less possibility of resin penetration. The risk is therefore that an interface with aligned nanomat will not be fully impregnated by the resin. In a similar manner, thickness of nanolayers influences the permeability of the interface and similar considerations can be also done for the diameter of the fibers.

This finding highlights the importance of a correct optimization of the architecture of the nanoreinforce and designers who want to introduce nanofibers into composites must take care of these aspects. On the other hand, mats can be used to decrease locally delamination toughness in order to tailor the overall
energy absorption of the laminate according, for example, to the impact energy.

From the numerical point of view, in Mode I a bilinear damage law came out to be necessary in several cases to match the experimental behavior of the nanomodified interface, while the virgin material can be represented through a simple linear damage law. The necessity of using a bilinear damage law has been related to the crack bridging and obstacle to crack growth caused by nanofibers. Under Mode II loading instead, virgin and nanomodified materials behaved similarly until the initiation of fracture, which was matched by a simple linear damage law. However, in order to match both the starting and steady-state crack propagation phases, a specific procedure for the cohesive parameters identification has been developed, as initial and steady-state cohesive energy values were in general different.

References


The effect of nylon 6,6 electrospun nanofibrous mats to the delamination strength of CFR-epoxy composite laminates.


