INCREASING THE DAMAGE RESISTANCE OF COMPOSITES BY INTERLEAVING THEM WITH ELECTROSPUN NANOFIBROUS VEILS

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Keywords: Fracture toughness, Electrospinning, Nanofibres, Delaminaion, Damage resistance

Abstract
Delamination between reinforcing plies is one of the most important failure mechanisms encountered in composite laminates during use. Interleaving composites with electrospun nanofibrous veils is proving to be a viable technique in order to increase the delamination resistance. The veils can easily be placed in the resin rich interlayers prior to production and do not require a dispersion in the matrix resin such as traditional particle toughening techniques. Furthermore, they are easily produced by electrospinning. Although there are many expected obvious benefits, the research on composites toughened with electrospun nanofibres is still very limited.

We will give thorough insight into the toughening micromechanisms that are present in laminates interleaved with nanofibrous veils. The bridging of microcracks by nanofibres is shown to be the main mechanism resulting in an increased interlaminar fracture toughness. Upon crack extension, nanofibres will bridge the newly formed crack surfaces and take up energy by straining, yielding and fracture. Several parameters are identified which influence this nanofibre bridging, and thus the observed interlaminar fracture toughness. This allows us to accurately determine the crucial parameters and toughening mechanisms which is necessary for the design of advanced damage resistance composite materials.

1. Introduction

Delaminations between reinforcing plies remain one of the most important types of damage encountered in composite laminates during service. Hence, the susceptibility to delamination of composite laminates is a critical design factor in many applications. It is often expressed in terms of interlaminar fracture toughness (IFT) and a lot of research is dedicated to developing methods that increase the IFT of composite laminates.

Excerpt from ISBN 978-3-00-053387-7

Recently, the use of electrospun nanofibres has been investigated to increase the interlaminar fracture toughness of composites [1–13]. These nanofibres have the potential to toughen composites without any of the disadvantages related to the traditional toughening methods. They can be easily placed in the resin rich interlayer between two reinforcing plies prior to composite production. Hence, there is no need to disperse them into the resin. Their nanoscale diameter (50 - 500 nm) offers the possibility of very thin and uniform interlayers, while their macroscopic length poses no health hazards. Furthermore, their large surface area to volume ratio and superior mechanical performance only add to the advantages of using electrospun nanofibres. Although there are many expected obvious benefits, the research on composites enhanced with electrospun nanofibres is limited. A thorough understanding of the toughening mechanism is clearly needed.

In this paper, we provide thorough insights into the toughening mechanisms by analyzing the nanofibre toughening effect on three different levels simultaneously: (i) nanotoughened epoxy, (ii) nanotoughened interlaminar region and (iii) nanotoughened laminate. These levels coincide with the hierarchical nature of laminated composite materials. This multilevel approach allows us to accurately determine the crucial parameters and toughening mechanisms through the use of electrospun nanofibres on the micro- and macroscale which is necessary for the design of advanced composite materials.

2. Materials and methods

PCL (Sigma-Aldrich, M_N 80 000) and PA 6 nanofibers (Sigma-Aldrich, M_W 51 000 g/mol) were electrospun from a formic acid (Sigma-Aldrich, 98%) / acetic acid (Sigma-Aldrich, 98%) solution according to previously reported procedures [11,14]. An in-house developed multinozzle electrospinning machine was used. The PCL and PA 6 nanofibers had a diameter of 343 ± 150 nm and 195 ± 35 nm respectively.

Nanofiber/epoxy nanocomposites were made by an in-house developed VARTM setup. This setup consisted out of a two-piece flat steel mould with inner dimensions of 300 x 150 x 7 mm³. In order to make the nanocomposites, a stacking of thick nanofibrous veils with dimensions of 300 x 150 mm² was used. The amount of nanofibrous veils was selected to have approximately 17 vol% of nanofibers in the final nanocomposite. This is representative for the amount of nanofibers present in the interlayer between reinforcing plies of the nanofiber interleaved laminates. Prior to infusion, the epoxy resin (EPIKOTE MGS RIMR135) and hardener (EPIKURE MGS RIMH137) were mixed in a 100:30 mass ratio using a mechanical stirrer. The mixture was placed under vacuum for 15 minutes in order to remove any trapped air introduced during mixing. After infusion of the nanofibrous veils, the mold was cured at 23.2 °C and 50% RH for 24 hours, followed by a second curing step at 80 °C for 15 hours according to the manufacturer's recommended cure cycle. Virgin epoxy plates (without nanofibers) were made by casting the epoxy resin in an empty mold.

Single Edge Notched Bending (SENB) experiments were carried out according to ASTM D5045. The samples had a thickness of 5 mm. A sharp natural precrack was produced by milling a starter notch in the specimens, followed by tapping a fresh razor blade in the milled notch with a dynamic precracking drop tower apparatus. The experiments were performed on an electromechanical Instron 3369 with a load cell of 500 N.

Unidirectional $[0°]_8$ laminates with PCL or PA6 nanofibers in the tested interlayer and were manufactured by VARTM using UDO ES500 unidirectional glass fiber plies. The laminates had a nominal thickness of 3 mm. The nanofibers were directly spun onto the reinforcing plies facing the midplane. The interlaminar fracture toughness was evaluated using DCB as well as ENF experiments [4].

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Low velocity impact tests were performed according to ASTM D7136 at an impact energy of 67 J (drop height of 1 m and impactor mass of 8.17 kg). The tests were executed on an in-house developed impact test machine. The test machine was equipped with a Gen. 5I oscilloscope to record acceleration, load and displacement data of the impactor. Two Photron SA4 high-speed cameras were used to observe the upper and lower face of the specimens during impact. A third AP-XRS high-speed camera was used to measure displacement, velocity and acceleration of the impactor by the use of a specific line pattern stuck on the impactor. Crossply $[0°/90°]_{2S}$ specimens with a nominal thickness of 3 mm were used. Electrospun nanofibrous veils were interleaved on each 0°/90°-interface. The damage area after impact was measured optically due to the translucence of the laminates.

3. Results and discussion

3.1 Nanotoughened epoxy

The effect of the electrospun nanofibres' properties on the fracture toughness of bulk epoxy is analysed in order to determine the toughening mechanism of nanofibres. Two types of nanofibres were selected as model systems, i.e. polyamide 6 (PA6) and poly-(ε-caprolactone) (PCL). The PA6 and PCL nanofibres were used to produce relatively thick nanotoughened epoxy plates by infusing a stacking of nanofibrous veils with epoxy resin under vacuum. The volume fraction of nanofibres was controlled to be similar to the volume fraction of nanofibres in the interlaminar region. It allowed us to accurately determine the fracture toughness via the standardized Single Edge Notched Bending (SENB) method. The SENB experiments show that while the matrix resin exhibits brittle failure, i.e. sudden and complete failure at the point of crack initiation, both PCL and PA6 nanotoughened epoxy fail by extensive plastic failure (Figure 1a). This results in an increased fracture toughness of the nanotoughened epoxy compared to the bulk epoxy resin (Figure 1b).

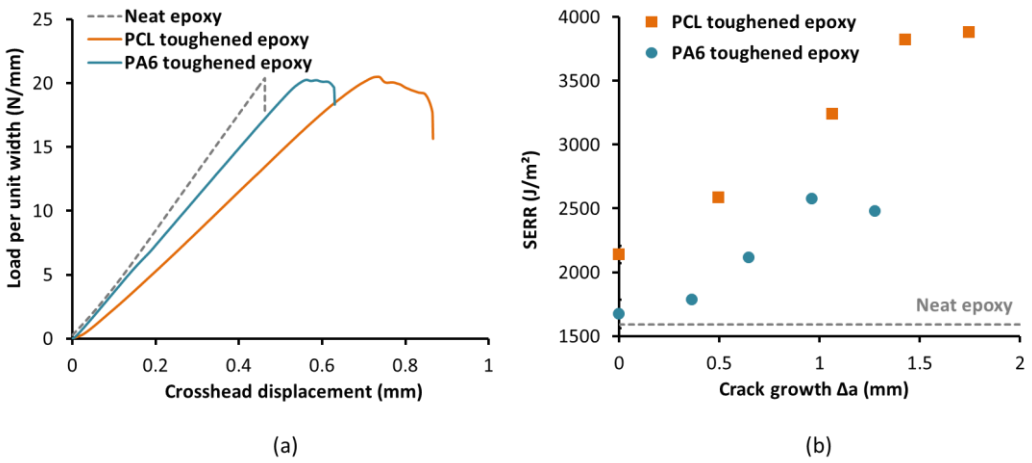

Figure 1. Load-displacements graphs for the SENB experiments (a) and the resulting strain energy release rate (b).

The larger amount of energy required to initiate cracks in the nanotoughened epoxy indicates that the nanofibres result in intrinsic toughening, i.e. toughening mechanisms acting in the fracture processing zone in front of the crack tip. These toughening mechanisms are most likely related to yielding of the nanofibres in the fracture process zone. This effect is especially evident in the PCL nanotoughened epoxy where about 30% more energy is required for crack initiation. Additionally, the crack propagation energy increases tremendously, as can be noted from the sustained loading capability of the nanotoughened epoxy specimens after crack initiation. Basically, more and more energy is

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required to extend the crack in nanotoughened epoxy, while the brittle unmodified epoxy immediately fails when the critical load is reached. This increase in propagation fracture toughness can be related to the extrinsic toughening mechanism of nanofibre bridging: upon crack extension, nanofibres will bridge the newly formed crack surfaces and take up energy by straining, yielding and fracture. Hence, the fracture toughness of the nanotoughened epoxy increases with increasing crack growth as the zone of bridging nanofibres becomes larger. The proposed mechanism of nanofibre bridging was confirmed by SEM analysis on the fracture surface of broken SENB specimens. The SEM images showed a high degree of irregularity and plastically deformed nanofibres protruding from the epoxy as opposed to the flat mirror-like fracture surface of neat epoxy specimens (Figure 2).

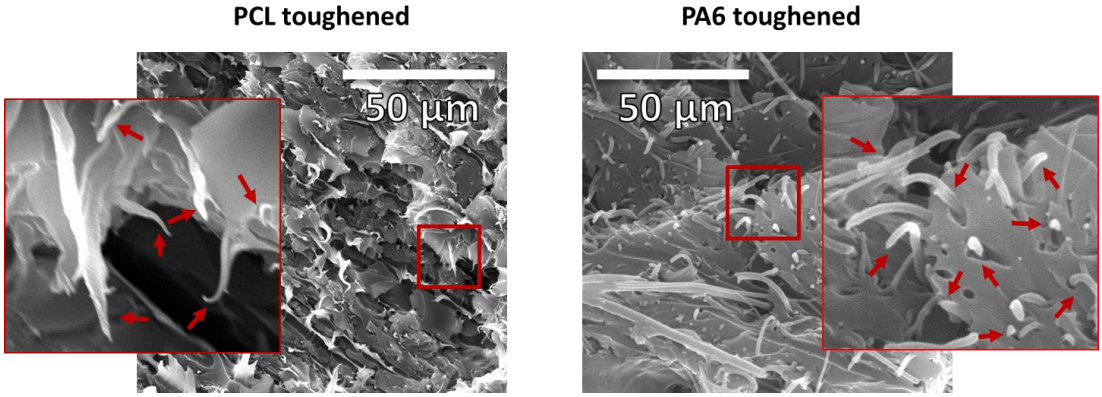

Figure 2. SEM images of failed SENB specimens show nanofibre bridging zones.

3.2 Nanotoughened interlaminar region

This section analyses the interlaminar region of nanofibre interleaved composites which consists of the nanofibre toughened epoxy of Section 3.1 in between reinforcing plies. The interlaminar fracture toughness is analysed under both Mode I and Mode II loading, G_{Ic} and G_{IIc} by the DCB and ENF method respectively, for an extensive set of composites interleaved with PCL and PA6 nanofibres. The improvement in interlaminar fracture toughness for PA6 and PCL interleaved composites with identical nanofibrous veil areal density, reinforcing ply architecture and interleaving method is shown in Figure 3. The G_{Ic} and G_{IIc} values were both obtained at the point of macroscopic delamination initiation. Both PCL and PA6 nanofibres show an extraordinary increase in G_{IIc}. The increase in G_{Ic} is slightly lower than the increase in G_{IIc} for the PCL toughened laminates, whereas PA6 nanofibres seemed to have hardly any effect on G_{Ic}. Based only on the results of Section 3.1, one would not expect such a different behavior between Mode I and Mode II loading conditions. However, under Mode I loading, crack growth subjects the nanofibres to normal forces. When the nanofibre-matrix adhesion is low, e.g. in case of PA6 nanofibres, this causes extensive peeling of the nanofibres. This mechanism results in minor to no improvements in G_{Ic} for PA6 interleaved laminates. Under Mode II loading conditions, adhesion between nanofibre and epoxy resin poses less of a problem as the shear adhesion strength of all nanofibres is relatively high due to their high surface area to volume ratio [15]. As a result, high improvements in G_{IIc} are obtained for PCL as well as PA6 nanofibre toughened composites.

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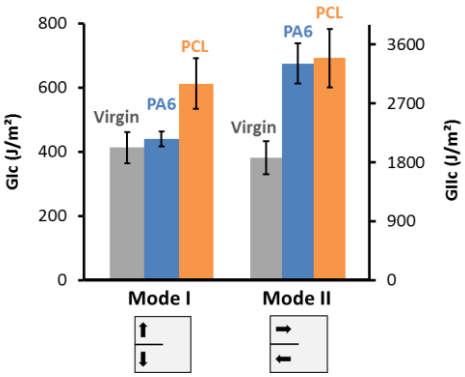

Figure 3. Improvement in Mode I and Mode II interlaminar fracture toughness for nanofibre interleaved composite laminates.

Microscopic analysis of tested DCB and ENF specimens showed the presence of additional micromechanisms related to the interlaminar region which affect the fracture toughness of the nanofibre toughened composites. Figure 4 schematically presents the observed delamination path for Mode I and Mode II loadings. Contrary to the common assumption that delaminations propagate in the middle of the interlaminar region, microscopy showed that delaminations in virgin composites progress almost exclusively at the glass fiber-epoxy interface. The delaminations in nanofibre interleaved composites show the same glass fiber-epoxy interfacial failure, but additionally show regular crossings of the interlaminar region through the nanotoughened interlayer. The amount of glass fiber-epoxy interfacial failure remains similar to that in virgin laminates as the interlaminar crossings are oriented transversely to the macroscopic delamination plane (Figure 4). However, the interlaminar crossings result in a crack through the nanotoughened epoxy which causes nanofibre bridging. Each interlaminar crossing corresponds to a crack through nanotoughened epoxy similar to the material studied in Section 3.1.

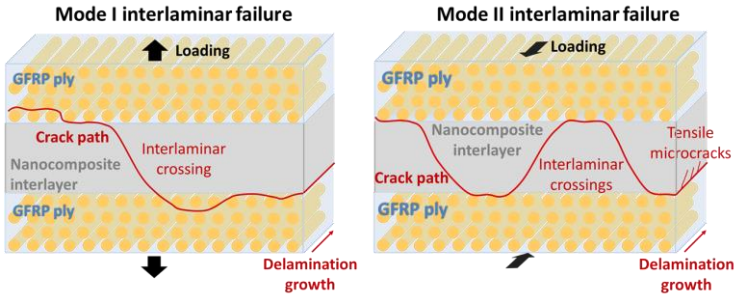

Figure 4. Schematic illustration of the delamination path in a nanofibre interleaved laminate under Mode I and Mode II loading conditions.

The interlaminar crossings are very important in order to obtain highly toughened composites as they are the main cause of nanofibre bridging on the interlaminar level. One important parameter which can drastically affect the obtained interlaminar fracture toughness is the nanofibrous veil areal density [16]. On the one hand, the interlaminar fracture toughness increases with increasing nanofibrous veil areal density as the interlaminar thickness increases linearly with veil density. On the other hand, the

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amount of interlaminar crossings under Mode I loadings quickly declines with increasing nanofibrous veil density. Under Mode II loadings, the amount of interlaminar crossings is much less affected and G_{IIc} increases with increasing nanofibre veil density.

3.3 Nanotoughened laminate

The toughening capability of electrospun nanofibres is shown on a large scale laminate with a more realistic stacking sequence which is subjected to a low-velocity impact. Crossply $[0°/90°]_{2S}$ composite laminates were produced with PA6 or PCL nanofibrous veils placed in between reinforcing plies on every 0°/90° interface. The effect of nanofibre toughening can clearly be noted from looking at the damage area as it decreases dramatically for nanofibre interleaved composites (Figure 5). Furthermore, the virgin composites showed large indentations at the point of impaction due to excessive failure of the composite, while this indentation and associated damage are limited for nanofibre interleaved composites. Hence, the nanofibres effectively toughen the composites when subjected to impact loadings. This is especially evident in composites interleaved with PCL nanofibres where a reduction in damage area of approximately 50% is obtained.

As opposed to the standard DCB and ENF methods which are optimized to measure interlaminar fracture toughness between 0°/0° interfaces in unidirectional specimens, delaminations will naturally occur at interfaces with dissimilar orientation during impact due to the mismatch in elastic properties. Hence, the delamination mechanism of a nanofibre interleaved laminate can be affected by the reinforcing ply orientation at the delamination interface. Microscopy on impacted specimens and SEM images of the fracture surfaces in the delamination region show a mixed mode delamination behavior, exhibiting fracture mechanisms which are typical for Mode I as well as for Mode II loadings like extensive peeling of PA6 nanofibres and hackle formation. There are many similarities with the results obtained in Section 3.2 such as sporadic interlaminar crossings in which nanofibre bridging zones develop.

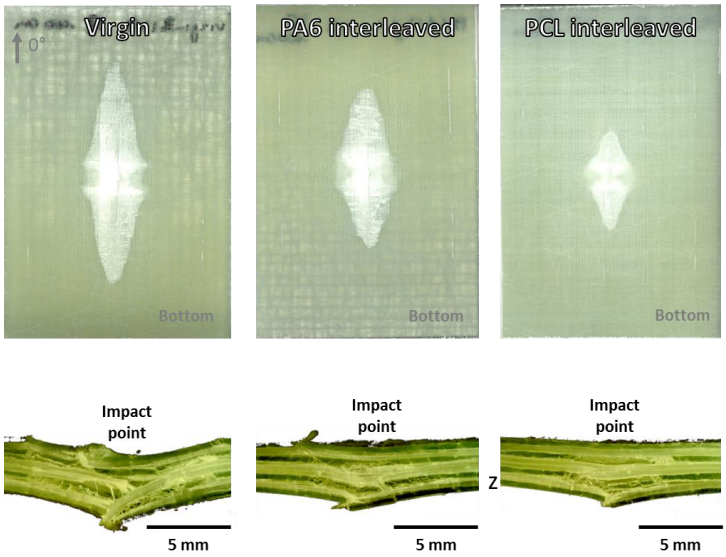

Figure 5. Damage geometry after low velocity impact.

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4. Conclusion

This paper shows that electrospun nanofibrous veils are a viable option to design advanced composite materials with a very high damage resistance. The electrospinning process is relatively simple, scalable and can be used to produce nanofibres from a whole set of polymers ranging from traditional polymers like polyamides to specially designed polymers for toughening purposes. Their effect is shown to be significant, not only on a microscopic level in nanotoughened epoxy, as is the case for most other nanotougheners, but also on an interlaminar and laminate level. The insight gained throughout the analysis is crucial in order to advance the research for these novel materials. It allows for optimizing and designing highly toughened advanced composite applications. Furthermore, uncovering the important parameters through the multiscale analysis allows more dedicated future research on specific parameters.

Acknowledgments

Financial support from the Agency for Innovation by Science and Technology of Flanders (IWT) and the Special Research Fund (BOF) Ghent University is gratefully acknowledged. Results in this paper were obtained within the framework of the IWT Strategic Basic Research Grant 141344 and the BOF 13/24J/020 project.

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Excerpt from ISBN 978-3-00-053387-7