



Polyamide Nanofibers Impregnated with Nitrile Rubber for Enhancing CFRP Delamination Resistance

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Delamination is the main responsible for structural failure of composites having a laminar structure. In the present work, polyamide (Nylon 66) nanofibers, even impregnated with uncrosslinked nitrile butadiene rubber (NBR), are interleaved into epoxy-based carbon fiber reinforced polymer (CFRP) laminates with the aim to counteract the delamination phenomenon. The performance of nano-modified composites using both the nanofibrous mat types, that is, Nylon 66 and NBR-impregnated Nylon 66 membranes, is investigated. Mode I loading tests show a significant improvement of the interlaminar fracture toughness of rubber-modified CFRPs, especially in the $G_{I,R}$ (up to +151%). The improvement in the $G_{I,C}$ is less pronounced, but still significant (up to +80%). The achieved results are very encouraging and pave the way to the use of such Nylon–NBR hybrid mats for hindering delamination.

one of the main reasons of structural failure during component lifetime.^[1] The use of systems able to monitor the component structural health, like the exploitation of piezoelectric nanofibers as sensors,^[2] may help preventing catastrophic events, but currently they are scarcely adopted due to the high cost. On the contrary, resin toughening approaches, as the addition of crosslinked rubbery particles^[3] or uncrosslinked liquid rubber, is common.^[4] However, these soft materials may detrimentally affect the composite structural properties, such as high strength, high modulus, and overall thermomechanical properties. A smart way to toughen the interlaminar region between prepreg plies makes use of nanofibrous membranes.^[5] Many studies report the use of Nylon nanofibers to contrast delamination.^[6]

1. Introduction

Carbon fiber reinforced polymer (CFRP) laminates are well renowned for their excellent mechanical properties, such as high specific stiffness and strength, combined with low weight. However, due to their vulnerable laminar structure, delamination is

In this case, the thermoplastic nano-reinforcement, thanks to its thermal properties, does not melt during the curing cycle, allowing the complete nanofibrous structure retention.^[7,8] The thermoplastic 3D network makes more difficult the crack to propagate, requiring additional energy to delaminate. On the other hand, the use of blend rubbery nanofibers as epoxy toughening agent is an interesting way to reinforce composite laminates (up to +480% in interlaminar fracture toughness), as already demonstrated by Maccaferri et al.^[7] In this case, the nanofibrous structure is not retained in the final laminate,^[7,8] due to the blend glass transition and melting temperature being well below the composite curing temperature.^[9] The combined action of thermoplastic nanofibers and matrix toughening provided by the rubber component mixing with the resin may help to contrast delamination more efficiently, besides potentially increasing material damping.^[8,10]

In the present study, Nylon 66 nanofibers impregnated with uncrosslinked nitrile butadiene rubber (NBR) for hindering delamination in CFRP laminates were investigated. Delamination resistance was determined via *double cantilever beam* (DCB) tests. For the sake of comparison, the action of Nylon 66-only nanofibers was also evaluated.

2. Results and Discussion

Nylon 66-only and Nylon 66 nanofibrous membranes impregnated with uncrosslinked NBR were interleaved into CFRP laminate as delamination inhibitor. Before their integration,

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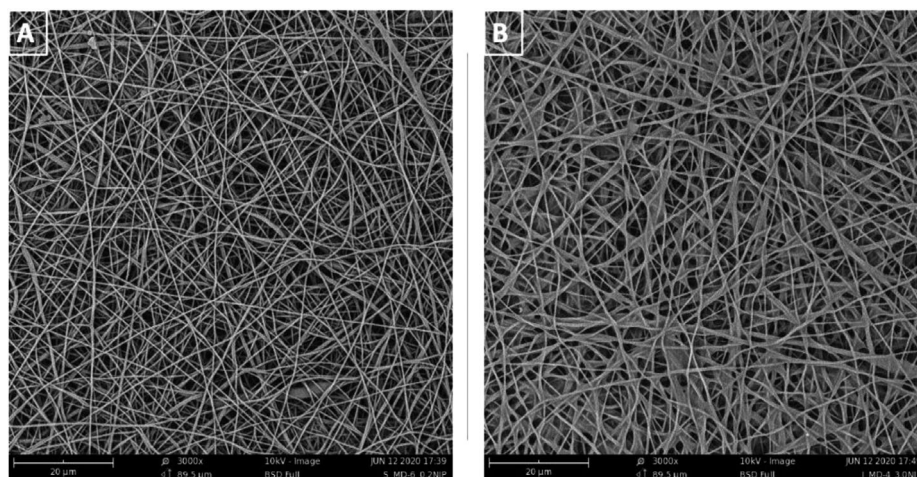


Figure 1. SEM micrographs of the electrospun nanofibrous membranes: a) Nylon 66 and b) Nylon 66 impregnated with NBR. NBR, nitrile butadiene rubber; SEM, scanning electron microscopy.

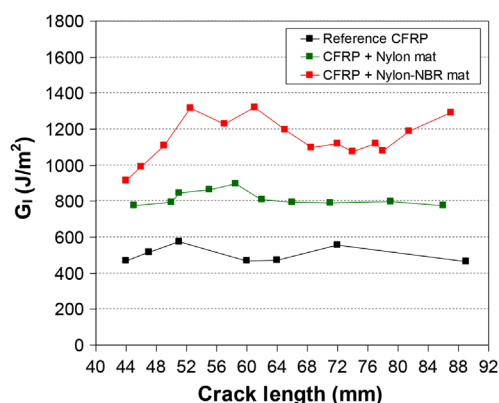


Figure 2. G_I versus crack length trends: selected R -curves representing the Reference CFRP (black), the laminate reinforced with Nylon 66 mat (green) and with NBR-impregnated membrane (red). On the right, mean values and relative standard deviations of $G_{I,C}$ and $G_{I,R}$. CFRP, carbon fiber reinforced polymer; NBR, nitrile butadiene rubber.

Sample	$G_{I,C}$ J/m ²	$G_{I,R}$ J/m ²
Reference CFRP	508 ± 19	506 ± 62
CFRP + Nylon mat	708 ± 59	773 ± 81
CFRP + Nylon-NBR mat	935 ± 126	1270 ± 158

the mats were morphologically characterized via electron microscopy.

As shown by the scanning electron microscopy (SEM) micrographs (Figure 1), the membranes display a well-defined nanofibrous structure, with no evident filming signs, even in the NBR-impregnated Nylon 66 membrane. Indeed, the porosity provided by the nanofibrous pattern is still present and clearly visible (Figure 1b). It is to highlight that the nitrile rubber is “liquid”, that is, not cross-linked.

Both nanofibrous mats were interleaved in between epoxy CFRP prepregs, and the resulting laminates tested via DCB test. The nano-modified composites significantly increase the energy release rate in mode I (G_I) up to +151% with respect to the Reference CFRP (Figure 2).

More specifically, the Nylon 66 mat boosts the G_I up to +39% at the initiation ($G_{I,C}$) and +53% in propagation ($G_{I,R}$). The NBR-impregnated Nylon 66 mat gives even better results: +84% in $G_{I,C}$ and +151% in propagation ($G_{I,R}$).

The NBR-impregnated polyamide mat gives the best results: the rubber enhances the resin toughness, improving laminae adhesion and increasing the interlaminar fracture toughness.

Concluding, the combined effect of the two polymers, that is, the polyamide and the nitrile rubber, in the form of nanofiber is a promising solution for hindering delamination.

3. Conclusion

Nylon 66 and NBR-impregnated Nylon 66 nanofibrous mats were produced and proposed as nanomaterials for reinforcing composite laminates.

Both the membranes, used to modify an epoxy-based CFRP laminate, showed an outstanding ability to improve delamination resistance in mode I without significantly affecting the weight and dimension of the final laminate. The resulting CFRP interlaminar fracture toughness, evaluated in Mode I via DCB tests, demonstrates the superior ability of NBR-impregnated Nylon 66 membranes to contrast delamination with respect to commonly used polyamide nanofibers.

Such results are very encouraging and pave the way to the use of such Nylon-NBR hybrid mats for hindering delamination.

4. Experimental Section

Electrospinnable Nylon 66 solution (13% wt) was made dissolving polyamide pellets in TFA/formic acid/ CHCl_3 solvent system, according to a previous work.^[11]

NBR solution at 3% wt concentration for impregnation of Nylon 66 mat was prepared using acetone as solvent, favoring rubber dissolution by magnetic stirring and mild heating (maximum 40°C) until forming a homogeneous solution.

Nanofibrous mats were produced using a 4-needle electrospinning machine (Lab Unit, Spinbow) equipped with 5 mL syringes. Needles (internal diameter 0.84 mm, length 55 mm) were joined to syringes via Teflon tubing. Nanofibers were collected on a drum rotating at low speed (tangential speed 0.39 m s^{-1}), covered with poly(ethylene)-coated paper. Electrospinning parameters were as follows: flow rate 0.80 mL h^{-1} , electric potential 23 kV, distance 11 cm, temperature 23–25°C, and RH 22%–25%. The produced membranes had final dimensions of approximately $30 \times 40 \text{ cm}$ and $20 \mu\text{m}$ thickness. The mat thickness was measured using an analog indicator under 360 g m^{-2} pressure. Nanofibrous mat impregnation with rubber was manually carried out by dropping with a Pasteur the impregnating NBR solution onto Nylon 66 membrane. The resulting mat thickness was practically unchanged.

Both Nylon 66 mats (pristine and NBR-impregnated) were analyzed by SEM to determine nanofibers morphology. Pristine nanofibers had diameters in the 300–400 nm range.

Specimens for the mode I interlaminar fracture toughness evaluation (DCB tests) were prepared via hand lay-up, stacking 14 prepreg plies, interleaving a single nanofibrous mat in the central interface, and adding a Teflon film as a crack trigger, according to ASTM D5528. A reference panel without interleaved nanofibrous mat (Reference CFRP) was also produced for the sake of comparison. DCB tests were carried out using a two-column hydraulic universal testing machine (Remet TC-10) equipped with a 1 kN load cell, at 3.0 mm min^{-1} crosshead separation rate. At least three specimens for each CFRP sample were tested.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data will be made available upon request

Keywords

composite laminate, delamination, electrospinning, interlaminar fracture toughness, nanofiber, nylon 66, rubber

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- [1] A. Turon, P. P. Camanho, J. Costa, C. G. Dávila, *Mech. Mater.* **2006**, *38*, 1072.
- [2] T. M. Brugo, E. Maccaferri, D. Cocchi, L. Mazzocchetti, L. Giorgini, D. Fabiani, A. Zucchelli, *Compos. Part B Eng.* **2021**, 108673.
- [3] R. Bagheri, B. T. Marouf, R. A. Pearson, *Polym. Rev.* **2009**, *49*, 201.
- [4] D. Ratna, A. K. Banthia, *Macromol. Res.* **2004**, *12*, 11.
- [5] Y. A. Dzenis, D. H. Reneker, *US* **6,265,333**, **2001**.
- [6] R. Palazzetti, A. Zucchelli, *Compos. Struct.* **2017**, *182*, 711.
- [7] E. Maccaferri, L. Mazzocchetti, T. Benelli, T. M. Brugo, A. Zucchelli, L. Giorgini, *Mater. Des.* **2020**, *195*, 109049.
- [8] E. Maccaferri, L. Mazzocchetti, T. Benelli, T. M. Brugo, A. Zucchelli, L. Giorgini, *Polymers (Basel)* **2021**, *13*, 1918.
- [9] E. Maccaferri, L. Mazzocchetti, T. Benelli, T. M. Brugo, A. Zucchelli, L. Giorgini, *Mater. Des.* **2020**, *186*, 108210.
- [10] M. Povo, E. Maccaferri, D. Cocchi, T. M. Brugo, L. Mazzocchetti, L. Giorgini, A. Zucchelli, *Compos. Struct.* **2021**, 114228.
- [11] E. Maccaferri, D. Cocchi, L. Mazzocchetti, T. Benelli, T. M. Brugo, L. Giorgini, A. Zucchelli, *Macromol. Mater. Eng.* **2021**, 2100183.