RESEARCH ARTICLE

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NBR-Rich Nanofibrous Membranes for Hindering Composite Delamination: Comparison of the Performance Obtained Using Liquid and Photocrosslinked Rubber

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This work compares the delamination behavior of epoxy CFRPs nano-modified with nitrile butadiene rubber/polyethylene oxide (NBR/PEO) blend nanofibrous membranes with a rubber content of 70 wt%. While the electrospun mat is able to retain the nanofibrous structure even without crosslinking, photocrosslinking is also carried to evaluate the potential different efficacy on the delamination hindering. Double cantilever beam (DCB) and end-notched flexure (ENF) tests show significant improvements of the energy release rates (*G*) both in Mode I (up to ≈4 times) and Mode II (up to ≈1.5 times). In particular, the presence of "liquid" rubber (uncrosslinked mat) leads to the best reinforcing action in Mode I, while the crosslinked membrane gives the highest delamination hindering in Mode II.

1. Introduction

Carbon fiber reinforced polymers (CFRPs) are currently among the most widely employed materials in structural applications as a replacement of metals. Meanwhile, due to their laminar structure, one of the main causes of structural failure is delamination.[1] Over the years, several solutions have been developed to counter this phenomenon. Specifically, the addition of rubbers, either in bulk[2] or micro-/nanoparticles,[3] works well, but often it causes a drastic decrease of the mechanical properties. The use of nanofibrous nonwovens as interlaminar fracture reinforcements may help limiting this drawback. Recently, nanofibrous mats, based on nitrile butadiene rubber (NBR), have been proposed for effectively toughening composite laminates.[4] To offset the problem of fibrous structure loss due to the low glass transition temperature (T_g) of the rubber, NBR was blended with semicrystalline polymers, such as the polyester polycaprolactone (PCL)[5] or the aromatic polyamide Nomex.[6] More recently, the thermoplastic polyethylene oxide (PEO) was proposed for reinforcing epoxy CFRP composite laminates.[7]

Here, the thermoplastic PEO is proposed in blend with NBR (70 wt%) to obtain electrospun nanofibers able to maintain the structure even without rubber crosslinking. However, to evaluate even the effect of NBR crosslinking on the CFRP interlaminar fracture toughness, the nanofibrous mat was also photocured by UV irradiation. The delamination behavior of both crosslinked and uncrosslinked-modified CFRPs was evaluated by Mode I and Mode II tests, and compared with the performance of the unmodified commercial material.

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2. Results and Discussion

The nanofibrous mat NBR/PEO 70/30 was fabricated by single-needle electrospinning, producing both membranes with and without the photoinitiator. The crosslinkable mats were also photocrosslinked by applying UV radiation for 5 and 30 min. To investigate the effect of the UV irradiation time on the nanofibers' structure, mat washes were performed in distilled water to remove the PEO fraction, and, subsequently, in chloroform to remove the potential uncrosslinked NBR. The mats' morphologies were assessed via SEM analysis after i) the crosslinking, ii) the water wash, and iii) the water and chloroform washes, as displayed in **Figure 1**. The uncrosslinked mat's morphology was also recorded for comparison purpose.

The crosslinking does not modify the nanofibrous structure and, after water washing, the morphology is practically unchanged compared to the unwashed ones. As further proof, even

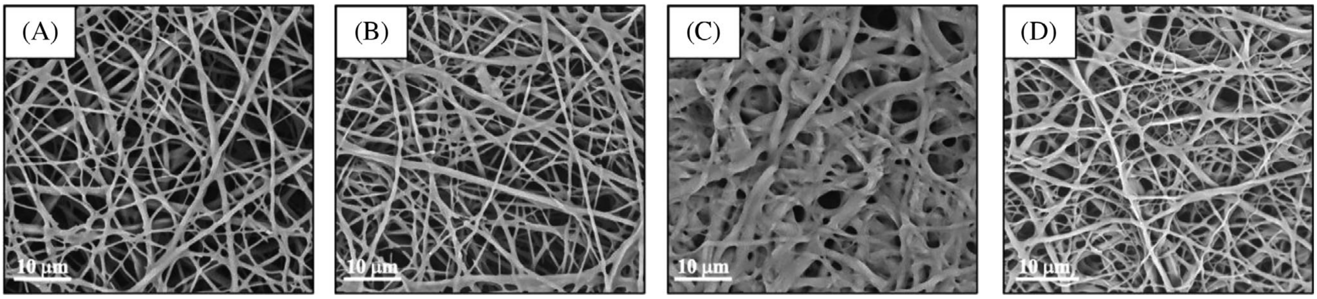

Figure 1. SEM micrographs of the NBR/PEO 70/30 mat: A) uncrosslinked; B) crosslinked for 30 min; washed in H_2O and $CHCl_3$ after C) crosslinking for 5 min, and D) crosslinking for 30 min.

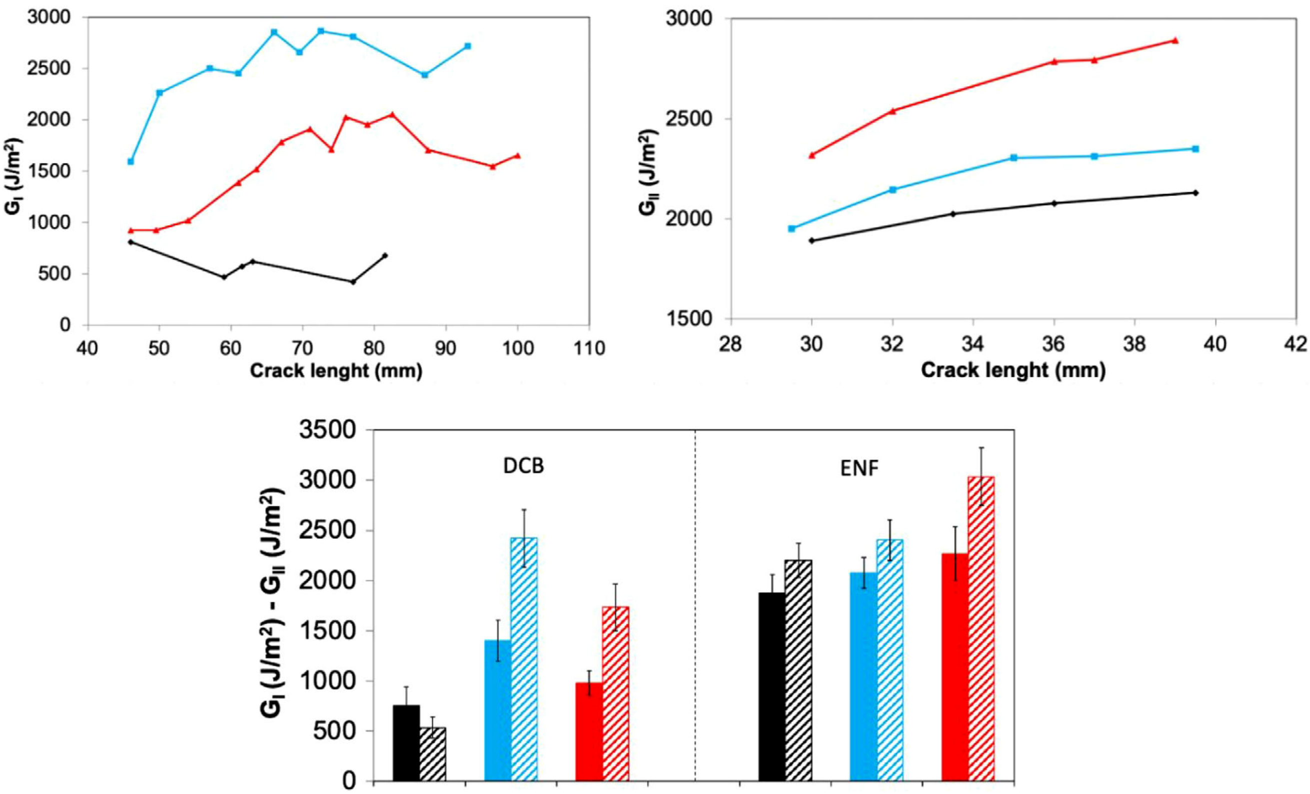

Figure 2. Top, selected *R*-curves of: reference CFRP (black), CFRP with uncrosslinked mat (light blue), and crosslinked mat (red). Bottom, average G_I and G_{II} at initial (solid bars) and propagation (dashed bars) stages (the color legend is the same).

the nanofiber diameters are unchanged, hovering around about 550 nm, in all three conditions (uncrosslinked, crosslinked, and water washed). A totally different situation is obtained when dealing with chloroform washes. The membrane is highly filmed when crosslinked for 5 min (Figure 1C). Increasing the UV exposure period to 30 min, the mat mostly retains the nanofibrous structure, tough the fiber diameter slightly increases to near 650 nm (Figure 1D).

To disclose a potential different laminate toughening of mats characterized by crosslinked and uncrosslinked rubber, both membrane types were interleaved into epoxy CFRP. Regarding the crosslinked mat, the photocrosslinked one for 30 min was selected. Both the nano-modified laminates, as well as the unmodified one (reference material), were tested via DCB and ENF tests. As displayed in **Figure 2**, the toughening action of the uncrosslinked and crosslinked mats is different. Regarding Mode I delamination, the uncrosslinked membrane, able to mix with the epoxy resin, gives the best results (G_I is up to near 4× vs up to near 3× for the crosslinked mat). On the contrary, in Mode II, the crosslinked mat provides the best interlaminar fracture toughness improvement (up to near 1.5× vs up to near 1.1× for the uncrosslinked mat), probably thanks to the possibility of having a partial nanofiber bridging mechanism involved.

3. Conclusion

NBR-rich electrospun nanofibrous mats were proposed as nanomaterials for hindering delamination of epoxy composite laminates. The produced NBR/PEO 70/30 membrane was also photocrosslinked to highlight a potential different reinforcing action when interleaved into epoxy CFRP. Results demonstrate that the presence of "liquid" (uncrosslinked) rubber leads to the best reinforcing action in Mode I (full matrix toughening mechanism), while the crosslinked membrane gives the highest delamination hindering in Mode II, probably thanks to a partial nanofiber bridging mechanism.

4. Experimental Section

NBR solution (NIPOL 1072CGX, 18 wt%) was prepared in acetone under magnetic stirring at 50 °C. PEO solution (M_w = 100 kDa, 12 wt%) was prepared in $CHCl_3$ at room temperature. The NBR/PEO blend was prepared by mixing together the two starting polymeric solutions and then adding, where necessary, the photoinitiator (Irgacure 651, 5 wt% with respect to NBR, added as solution in acetone for better handling). The produced blend, called NBR/PEO 70/30, had 70 wt% of rubber content with respect to the total polymeric fraction; the resulting total polymer concentration was 12 wt%. Nanofibrous mats were produced via a 4-needle electrospinning machine (Lab Unit, Spinbow). Nanofibers were collected on a drum rotating at low speed, covered with baking paper. Electrospinning parameters were as follows: flow rate 0.40 mL h^{-1}, electric potential 19 kV, distance 8 cm. The produced mat (45–50 µm thickness) was exposed to a 254 nm UV lamp, and irradiated for two different times: 5 and 30 min. Mat washes were performed in distilled water to remove the PEO fraction, and, subsequently, in chloroform to remove the uncrosslinked NBR (each wash was carried out twice, 60 min each). SEM micrographs were acquired with a Phenom ProX scanning electron microscope. Specimens for Mode I and Mode II interlaminar fracture toughness evaluation were prepared as previously reported.[7] DCB and ENF tests were carried out using an Instron 8033 universal testing machine equipped with a 2 kN load cell.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of the present work are not available because they are part of ongoing studies. Data may be available on request from the corresponding author.

Keywords

blend, delamination, electrospinning, nanofiber, photo-crosslinking, polyethylene oxide, rubber

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[1] A. Turon, P. P. Camanho, J. Costa, C. G. Dávila, *Mech. Mater.* **2006**, *38*, 1072.
[2] D. Ratna, A. K. Banthia, *Macromol. Res.* **2004**, *12*, 11.
[3] R. Bagheri, B. T. Marouf, R. A. Pearson, *Polym. Rev.* **2009**, *49*, 201.
[4] E. Maccaferri, L. Mazzocchetti, T. Benelli, T. M. Brugo, A. Zucchelli, L. Giorgini, *Polymers (Basel)* **2021**, *13*, 1918.
[5] M. Povolo, E. Maccaferri, D. Cocchi, T. M. Brugo, L. Mazzocchetti, L. Giorgini, A. Zucchelli, *Compos. Struct.* **2021**, *272*, 114228.
[6] E. Maccaferri, L. Mazzocchetti, T. Benelli, T. M. Brugo, A. Zucchelli, L. Giorgini, *ACS Appl. Mater. Interfaces* **2022**, *14*, 1885.
[7] E. Maccaferri, J. Ortolani, L. Mazzocchetti, T. Benelli, T. M. Brugo, A. Zucchelli, L. Giorgini, *ACS Omega* **2022**, *7*, 23189.