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A Thermoplastic Elastomeric Nanofibrous Membrane as CFRP Modifier to Boost Both Delamination and Damping Performance

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In the present work, thermoplastic elastomeric nanofibers made up of a homogenous blend of nitrile butadiene rubber (NBR) and Ppolycaprolactone (CL), with 80% wt of rubbery component, are used to modify a carbon fiber reinforced polymer (CFRP) laminate with the aim of improving its delamination and damping behavior at the same time. Since the nanofibrous membrane is not chemically cross-linked, the fibrous morphology is lost during composite curing owing to its melting. Nonetheless, the nanomodified CFRP displays an impressive ability to improve the delamination resistance in mode I and also an enhanced damping capacity at low temperature. The use of nanofibrous membranes allows for modification of specifically selected areas, thus maximizing the toughening and damping behavior where most required, without necessarily affecting the whole bulk of the resin. Both PCL and NBR components contribute to the final performance; however, the very high amount of rubber leads to a membrane difficult to handle whose final performance in CFRP modification is not superior to membranes up to 60% wt NBR that are instead more stable and easier to deal with. Overall, the proposed results are nonetheless very promising, taking into account also that the improved delamination resistance in mode I and enhanced damping are obtained without significantly sacrificing the weight and overall dimension of the obtained composite.

1. Introduction

Nanofibers embody a powerful tool to design advanced structural and functional materials; therefore, they are gaining an increasing attention as composite modifiers, mainly to improve the toughness of the thermoset matrices and to help contrasting delamination,[1,2] with a significant increase in the energy release rate at initiation (G_C) and propagation (G_R). Nanofibrous mats can be designed to introduce additional functional properties, such as local flame retardancy,[3] self-sensing capability,[4] or catalytic activity[5] without affecting the whole bulk material. However, for these purposes, thermoplastic polymers are often used, while the application of nanofibrous systems with elastomeric characteristics might introduce some further improvements in the composite, for example, damping behavior. The issue with rubbery nanofibers production is due to the problems in handling an un-crosslinked low T_g polymer, as the liquid rubber precursor. Indeed, nanofiber processing, for example, via electrospinning, requires the polymer to be soluble, but once formed in a fibrous fashion, it tends to quickly lose the obtained shape unless a fast post-processing curing is applied.[6]

Recently, the authors presented a smart way to obtain elastomeric thermoplastic nanofibrous membranes by single-needle electrospinning of nitrile butadiene rubber (NBR) and polycaprolactone (PCL) blends that do not require cross-linking to maintain the nanofibrous

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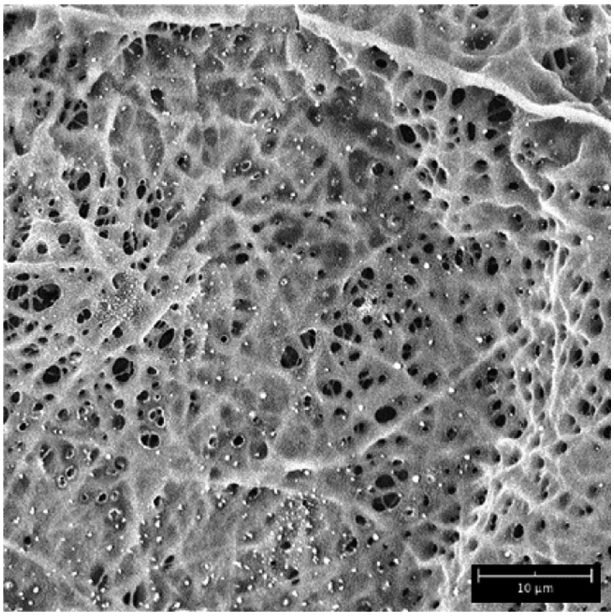

Figure 1. SEM micrograph of the electrospun NBR/PCL 80/20 w/w nanofibrous membrane. NBR, nitrile butadiene rubber; PCL, polycaprolactone.

morphology.[7] Nanofibers with up to 60% wt of rubber were successfully integrated into epoxy-based carbon fiber reinforced polymers (CFRPs) to hinder delamination, obtaining an outstanding increase of the interlaminar fracture toughness,[8] as well as an enhancement of the material damping.[9,10] Since a strong interplay of the rubbery precursor (NBR) and of the thermoplastic (PCL) components can be envisaged in the obtained results,[11] it would be of interest to explore higher rubbery fractions to evaluate their contributions to the damping and delamination behavior. Such membranes are difficult to handle, but this would be a minor drawback in the case their performance would overcome significantly the previously discussed ones. Hence, in this work, the effect of a nanofibrous mat with 80% wt of rubber on the delamination behavior of CFRP laminates is presented. Interlaminar fracture toughness was evaluated in mode I via double cantilever beam (DCB) tests. With the aim of assessing the effect of the membrane on the overall CFRP thermomechanical performance, dynamic mechanical analysis (DMA) measurements were also carried out, useful to estimate the damping capability of the nanomodified material by means of tanδ evaluation, that is, the damping factor.

2. Results and Discussion

In the present work, NBR/PCL 80/20 w/w membranes characterized by 50 μm average thickness and 30 g m^{-2} grammage were used. Though these fibers appear partially filmed, owing to the extremely high liquid NBR rubber content, and their handling is not easy, the membrane still maintains an overall fibrous aspect, as displayed in **Figure 1**, even with a very small PCL content, that was proved to be the responsible for the crystalline structure that guarantees the overall fibrous morphology. While partially filmed, the morphology of the nanofibrous mats is stable up to 2 years.[7]

Nanofibrous membranes with NBR/PCL 80/20 w/w were interleaved in between prepregs with two different configurations depending on testing condition requirements: a simpler configuration with one membrane positioned between two layers of seven stacked prepregs, with a Teflon inset as crack trigger for DCB tests according to ASTM D5528; in the second configuration a membrane has been interleaved in between every single prepreg in a ten prepregs and nine nanofibrous mats stacking for producing specimens for damping assessment via DMA. A reference composite without interleaved mats has also been produced for the sake of comparison in each of the two configurations (14 plies with only Teflon in the middle layer for DCB tests, and ten plies for DMA). The complete characterization of nanofibrous mats was previously done,[7] with the exception of mechanical properties. Indeed, while a reliable method (based on the specimen mass normalization of load) for analyzing tensile load-displacement curves was recently introduced by the Maccaferri et al.,[12] the tensile testing of such NBR/PCL 80/20 w/w mat is prevented owing to its poor handleability.

The nanomodified composites show an impressive increase in fracture toughness, as displayed in **Figure 2**.

Indeed, the CFRP laminate modified with the thermoplastic rubbery mat requires an impressively higher load to promote delamination in mode I (Figure 2a). When evaluating the energy release rate in mode I, (G_{I}, Figure 2b), the nanomodified samples display an energy release rate at initiation about five times higher than the pristine sample (about +550 in $G_{\mathrm{I,C}}$). The energy release rate for crack propagation is also significantly enhanced, even if to a slightly lesser extent (about +350% in $G_{\mathrm{I,R}}$). It is worth to point out that the nanofibrous mat morphology of the membrane used for CFRP modification is based only on the blending ability of the electrospinning process that helps the almost immiscible NBR/PCL pair to stay homogeneously mixed.[7] The fibrous morphology is maintained thanks to the presence of a PCL-like crystal phase, that, however, melts around 60°C. Hence, owing to the composite curing condition that required 135°C, in the final CFRP the persistence of the membrane fibrous morphology can be safely ruled out. However, the nanofibrous mat appears as an outstanding way to homogenously deliver NBR and PCL selectively in the interlaminar matrix rich region. The porosity of the membrane favors the percolation of the crude resin precursor within the fibers; the latter, prior melting, are thus well distributed in the interlaminar region, and when their morphology is lost, they allow an impressive reinforcing action by matrix toughening.[8] The presence of the NBR/PCL blends makes also possible to deliver the rubbery NBR component, that in the absence of the PCL thermoplastic counterpart would not be stable to be delivered in the significant regions without prior crosslinking. The presence of the elastomeric component promotes an impressive toughening of the composite, far higher than the sole PCL.[8] However, the performance reached by enriching the rubber fraction up to 80% wt, leads to results that are in line, if not slightly worse than previously published fibers with 60% wt rubber content[8] (about +580 in $G_{\mathrm{I,C}}$ and +440% in $G_{\mathrm{I,R}}$) accounting for a threshold in the efficiency of the rubber contribution with respect to their thermoplastic counterpart PCL. These results are also in line with the performance of the bulk NBR uncrosslinked film.[8]

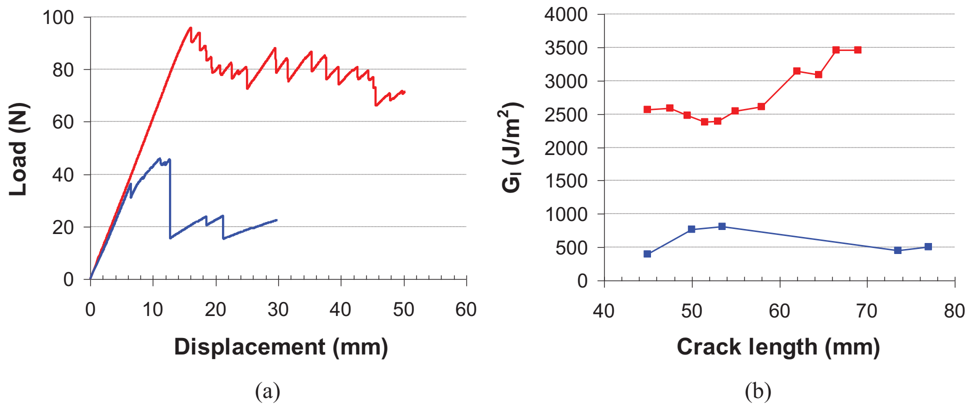

Figure 2. Selected curves representing the pristine (blue) and nanomodified (red) CFRP load-displacement curves in DCB tests a); the calculated G_I versus crack propagation for the pristine (blue) and nanomodified (red) CFRP b). CFRP, carbon fiber reinforced polymer; DCB, double cantilever beam.

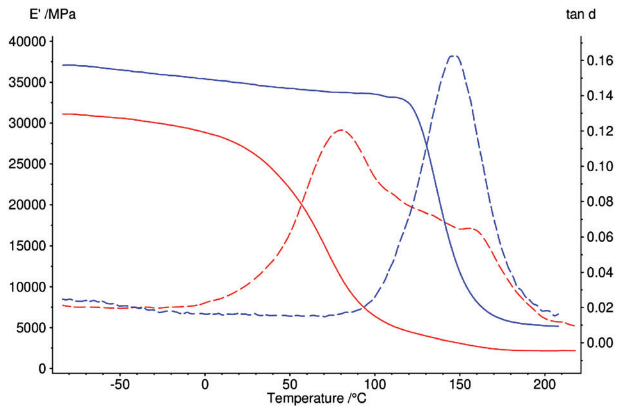

Figure 3. DMA damping factor (tanδ, dashed lines) and storage modulus (E', solid lines) curves of the pristine (blue) and nanomodified (red) CFRP. CFRP, carbon fiber reinforced polymer; DMA, dynamic mechanical analysis.

On the other side, when the damping factor (tanδ) of the pristine and nanomodified CFRP is evaluated via DMA (**Figure 3**), it is clearly observed that tanδ peak is dramatically widened.

While the end (high T) of the tanδ peak is practically unmodified upon nanofiber addition, the beginning of the relaxation process lies almost 100°C below than unmodified reference CFRP, partially covering the room temperature window. In the rubbery modified sample, indeed, the damping factor shows two peaks, one ascribable to the epoxy matrix (with a $T_\alpha = 150$°C), in perfect agreement with the expected value from the technical datasheet, and a lower temperature phenomenon that accounts for an increased low-T damping ability. Such a fact is observed even upon losing the nanofibrous morphology that, as explained above, disappears during the curing.

3. Conclusion

In conclusion, the rubbery NBR/PCL 80/20 w/w blend nanofibrous membrane, used to modify the performance of an epoxy-based CFRP laminate, displays an impressive ability to improve the delamination resistance in mode I and also an enhanced damping ability at low temperature, even if the fibrous morphology is completely lost during curing.[8] However, the nanofibers enrichment in the rubber fraction up to 80% wt did not overcome the performance of the fibers with 60% wt rubber content, thus accounting for a threshold in the efficiency of the rubber contribution with respect to the thermoplastic counterpart PCL, in a complex interplay of the two components in the reinforcing action.

4. Experimental Section

NBR/PCL 80/20 w/w blends were prepared and electrospun according to a previous work.[7] The prepreg used was GG204P IMP503Z-HT, plain weave carbon fabric with 200 g m^{-2}. Details about DCB specimens preparation and mode I fracture toughness evaluation can be found in ref.[8]

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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

blend, composite laminates, damping, delamination, electrospinning, nanofibers, rubber

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