



# Rubber Containing Nanofibers and Their Ability in Structural Modification of CFRPs: A Summary

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Rubber containing nanofiber is investigated as structural modifiers of carbon fiber reinforced polymers (CFRPs) to improve their delamination resistance. The ability to obtain long lasting nanofibrous shape from liquid nitrile butadiene rubber (NBR) has been demonstrated even without requiring instant cross-linking when a second component is used together with NBR in the process. The second component can be a thermoplastic which either melts, such as poly( $\epsilon$ -caprolactone) (PCL), or holds steady, as poly( $m$ -phenylene isophthalamide) (PMIA) or nylon 66, during CFRP curing process. Assuming that NBR is not crosslinked, during curing of low  $T_m$  thermoplastic-based rubber nanofibers, their morphology is lost, as for NBR/PCL, and both polymers blend with the surrounding epoxy resin thus leading to an outstanding toughening effect, but at the cost of the overall composite mechanical performance. When a second component is used which is preserved in nanofibrous fashion during curing (NBR/PMIA, NBR/nylon 66), instead, a good compromise is achieved, with still outstanding delamination hindering ability, together with almost fully preserved thermo-mechanical performances.

a viable solution to reduce structural vibrations, and delamination when the case.<sup>[1]</sup> Indeed, viscoelastic materials, such as thermoplastics and elastomers, are often used as additives in rigid matrices for improving toughness and damping of the bulk material. Thermoplastics are already used both as particles and, recently, arranged in nanofibrous fashion to improve the toughness of hardly cross-lined resins in CFRPs, with the former (particles) massively impacting on the whole mass of the item, while nanofibers can promote an outstanding effect in reducing composite delamination, concomitantly limiting such an impact on some specific and selected regions.<sup>[2]</sup> Nanofibers themselves can be further modified, either by addition of nanosized objects, i.e., graphene,<sup>[3]</sup> or by formulation with different types of materials.<sup>[4]</sup> While the use of nanosized objects in bulk modification is indeed strongly sensitive to the size of the modifier with an outstanding impact,<sup>[5]</sup>

## 1. Introduction

The introduction of dampening components in rigid materials, such as carbon fiber reinforced polymers (CFRPs), appears as

when graphene is deployed in CFRPs though nanofibers their final effect is not necessarily as positive, as recently proved by the authors.<sup>[6]</sup> The potential of nanofibers with different formulations, which could contain rubbery components, is instead still an open issue, probably due to the problems in rubber-based nanofiber processing. Indeed, owing to processing requirements, liquid nitrile butadiene rubber (NBR) has to be applied to be processed via electrospinning into nanofibers, and plain liquid NBR fibers coalesce fast without proper post-treatment. On the other side, the ability to obtain rubber containing nanofibrous membrane would be a highly attractive approach for hampering delamination in CFRPs. Hence in the present work, the possibility of using a liquid rubber precursor, and shape it in a nanofibrous way, has been revised addressing different approaches. In particular, it was recently demonstrated that the use of a second thermoplastic component, when conveniently selected and tailored, can lead to nanofibers that are stable in time and can be handled even without any postprocessing.<sup>[7,8]</sup> The second component can be chosen to be a thermoplastic which either melts (or anyway flows) or holds steady during the CFRP curing process. Moreover, liquid rubber can be coated onto an already established thermoplastic matrix, simply dipping the membrane in convenient NBR containing solutions.<sup>[9]</sup>

In this work, both approaches are investigated employing rubber-based nanofibers to modify epoxy-based CFRPs,

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and using as the second component poly( $\epsilon$ -caprolactone) (PCL) or poly( $m$ -phenylene isophthalamide) (PMIA, Nomex) as representative of melting or nonmelting thermoplastics, or nylon nanofibrous mats which are coated in different amount of liquid NBR and are able to maintain their fiber morphology upon curing. In none of the employed systems, the NBR has been crosslinked before lamination, and the performance of CFRPs based on the same prepreg will be compared as a function of the different rubber containing nanofibers employed.

## 2. Results and Discussion

Electrospinnable solutions containing NBR and the second thermoplastic, either PCL or PMIA, to obtain NBR/PCL and NBR/PMIA nanofibers, as well as nylon nanofibers to be further coated with different amount of liquid NBR were prepared according to previously reported procedures.<sup>[7,9,10]</sup> The obtained mats have final dimensions of approximately 30 × 40 cm and a grammage in the 10–25 g m<sup>-2</sup> range. CFRP panels for DCB, ENF, and DMA tests were produced via hand lay-up in an air-conditioned room. The nanofibrous membranes were directly applied onto the prepreg during the hand lay-up. Reference panels without nanofibrous mats, as well as panel with nanofiber mats based on the single polymeric components (PCL, PMIA, nylon, and NBR in the form of a film after fiber coalescence) were also produced for the sake of comparison.

In the case a thermoplastic with a melting temperature below the curing temperature of the composite is used, such as in the case of PCL ( $T_m = 60$  °C approximately) the nanofibrous structure is expected to disappear during CFRP processing.<sup>[10]</sup> In the specific case of NBR/PCL mixtures, when processed via electrospinning, the two polymers were able to form a miscible blend only with PCL-like crystalline domains which melt around 60 °C or slightly lower, depending on the NBR load in the mixture. The obtained structure behaves similar to a thermoplastic elastomer (TPE) and once inserted in the CFRP contributes to the local toughening of the matrix, limited to the regions in which the membrane is applied.<sup>[11]</sup>

The interleaving of such nonwovens in epoxy CFRP laminates provides an extraordinary enhancement of the interlaminar fracture toughness in Mode I ( $G_I$  up to +480%) and a slight improvement in Mode II, besides a better damping behavior. However, the resulting laminates suffer from some important  $T_g$  lowering, strongly depending on the nanomodification extent and the nanofiber rubber amount and location.<sup>[10]</sup> Such results suggest the need for a compromise between improved interlaminar fracture toughness, damping, and overall mechanical properties. NBR/PCL blend nanofibers act exclusively as matrix toughening since the crystalline fraction melts ( $T_m \approx 60$  °C) and the polymers' pair mixes with the epoxy resin during the curing cycle. When the second component is, instead, a thermoplastic not able to undergo significant phase changes during the CFRP curing, such as in the presence of PMIA, stable noncrosslinked nanofibers with up to 60% wt of NBR are produced via single-needle electrospinning. In this circumstance however, no homogeneous blend of the two polymers is detected, with just a tiny fraction of the rubber mixed with polyaramid, and the morphology of the nanofibrous mat strongly changes with the operational parameters. NBR and Nomex mainly phase-separate, and

their relative arrangement in the nanofiber, investigated via selective removal of the rubber fraction, shows the formation of peculiar self-assembled structures resembling quasi-core-shell nanofibers or fibril-like hierarchical structures, depending on the applied electrospinning flow rate.<sup>[8]</sup> Mode I and Mode II loading tests show a significant improvement of the interlaminar fracture toughness of rubbery nanofiber modified CFRPs, especially  $G_I$  (up to +180%), while  $G_{II}$  enhancement is less pronounced but still significant (+40% in the best case). In this circumstance, two different phenomena can be contemporarily invoked to explain the reinforcing ability. First the rubbery component is expected to be released in the matrix during the curing, thus contributing to toughening the epoxy continuous phase, while PMIA nanofibers stay unmodified and help upon potential crack formation to keep together the diverging sections.<sup>[4]</sup> Moreover, it was found that the two nanofibrous morphologies (quasi-core-shell and fibril-like ones) improve the delamination resistance differently, also suggesting that the way the rubber is located in the nanofibers plays a role in the toughening action. The quasi-core-shell nanofiber morphology provides the best reinforcing action, that is also associated with the highest flow rate, i.e., highest nanofiber productivity. By contrast, pure Nomex nanofibers dramatically worsen the interlaminar fracture toughness (up to -70% in  $G_I$ ), acting as a release film.<sup>[8,12]</sup> The achieved delamination resistance improvements are also combined with the retention of both the original laminate stiffness and  $T_g$ .

In this frame, it was not possible to find a common solvent to address single needle electrospinning to obtain mixed fiber made of nylon 66 and NBR, hence a different approach was implemented for producing rubber/thermoplastic membranes, where premade nylon nanofibers were coated with liquid NBR. The starting polyamide mats were electrospun using two different solvent systems: plain nylon 66 mats electrospun from formic acid/chloroform perform better than the ones obtained from a solvent system containing trifluoroacetic acid, showing up to +64% versus +53% in interlaminar fracture toughness ( $G_I$ ), respectively. The effect of NBR coating benefits both nanofiber types, significantly raising the  $G_I$ . The best results are obtained when interleaving medium-thickness and lightweight mats (20  $\mu$ m, 9–10 g m<sup>-2</sup>) with 70%–80% wt of loaded rubber, achieving up to +180% in  $G_I$ .

## 3. Conclusions

Here, it was demonstrated that application of liquid rubber containing nanofibers significantly enhances the ability of typically brittle CFRPs to better resist delamination. The use of a second component together with liquid NBR is able to guarantee to the uncrosslinked rubber sufficient handling and stability to be implemented in the composite at the lamination stage. This process allows also for specific and optimized localization of such membranes to impact only in the most sensitive areas prone to delamination, instead of modifying the whole bulk of the composite. Moreover, the specific tool used for such a nanomodification, i.e., low or high  $T$  melting thermoplastic with respect to the curing temperature, plays a significant role in the final composite performance since the ability to retain the nanofibrous structure leads to a slightly lower delamination resistance, but at the same time is also able to retain mechanical performance almost

intact with respect to unmodified counterparts. The latter approach has also been demonstrated valid with different processing techniques, both of them easy and viable for a scale-up application, thus paving the way to the extensive and reliable application of NBR containing nanofibers in CFRPs modification.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Keywords

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

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