

Electrospun nanofibers as reinforcement for composite laminates materials - A Review

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Abstract

In the last few decades nanofibers have been developed and introduced in a vast number of industrial and research applications. One of their most effective use is as interleaved reinforcement for composite laminate materials against delamination. Nanofibrous mats have the ideal morphology to be embedded between two plies of a laminate, and a vast and deep research has been carried out investigating their effect on the global behaviour of a composite laminate.

This review is the first of its kind to date which presents a detailed state-of-the-art on the effect of nanofibrous interleaves into composite laminates with focus on the mechanical performances and behaviours of nanomodified materials. A detailed description of the working mechanisms of the nanointerleave under different load cases is presented, and a comparative analysis between papers in literature will provide readers with a powerful tool to understand and use nanofibers for reinforcing purposes.

Keywords: Nanofibers, Composite Materials, Electrospinning, Delamination, Mechanical tests, Experimental Mechanics

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Acronyms

3PB	3 Points Bending
AA	Acetic Acid
AC	Acetone
BuAc	Butyl Acetate
CAI	Compression After Impact
CFRP	Carbon Fibers Reinforced Plastic
CLF	Chloroform
CNT/CNF	Carbon NanoTubes/NanoFibers
coPES	Copolyethersulfones
DCB	Double Cantilever Beam
DCPD	Dicyclopentadiene
DFM	Dimethylformamide
DMAC	Dimethylacetamide
DMSO	Dimethyl sulfoxide
ENF	End Notched Flexure
ETL	Ethanol
FA	Formic Acid
$G_{I,C}/G_{I,R}$	Mode I Critical/Propagation energy release rate
$G_{II,C}/G_{II,R}$	Mode II Critical/Propagation energy release rate
GFRP	Glass Fibers Reinforced Plastic
HLu	Hand Lay-up
HMW	High Molecular Weight
IFT	Impact Fracture Toughness
ILSS	Interlaminar Shear Stress
K_I/K_{II}	Mode I/II fracture toughness
LiBr	Lithium Bromide
LMW	Low Molecular Weight
LVI	Low Velocity Impact
MDI-TAD	4,4'-(4,4"-diphenylmethylene)-bis-(1,2,4-triazoline-3,5- dione)
MEK	Butanone
MWCNT	Multi-Walled Carbon NanoTubes
NA	Not Available
P(St-co-GMA)	Epoxy compatible copolymer
PA/PAI	Polyamide/Polyamide-imide
PAN	Polyacrylonitrile
PCL	Polycaprolactone
PEK-C	Polyetherketone
PES	Polyethersulfone
PGME	Propylene Glycol Monomethyl Ether
PP - PPS	Polypropylene - Polyphenylene sulfide
PrP	Prepreg
PSF	Polysulfone
PVA - PVB	Polyvinyl Alcohol - Polyvinyl Butyral
PVDF	Polyvinylidene fluoride
PW	Plain Wave
SBS	Styrene Butadiene Styrene
SBS _h	Short Beam Shear
SEM	Scanning Electron Microscope
TEGO	Thermally exfoliated graphene oxide
TEOS	Tetra Ethyl Orthosilicate
TFE	Trifluethanol
THF	Tetrahydrofuran
TPU	Thermoplastic polyurethane
TW	Tow
UD	Unidirectional
VARTM	Vacuum Assisted Resin Transfer Moulding
VE	Vinylester

1. Introduction

The aim of this review is to collect the research results produced on the topic of composite laminates reinforced with polymeric electrospun nanofibers, and to present a critical and comparative summary of the most significant findings, with focus on mechanical response and behaviour of the nanomodified materials.

A laminate structures is formed by stacking anisotropic plies one on top of each other, and external excessive stresses or strains may cause a damage to start (initiate) between two laminae, and then to propagate following several failure modes. Due to the anisotropic and heterogeneous nature of the composite materials, a large number of failure modes can be detected [1], with the three main ones being: (i) intra-ply cracking, (ii) interlaminar matrix delamination, and (iii) fiber failure. Other types of damage simply alter the load levels at which these three occur. Amongst the three principal damage modes mentioned above, the interlaminar matrix delamination is of major importance. Delamination is a subcritical failure mode whose effect may be stiffness loss, local stress concentration, and local instability causing its further growth and eventually failure of the manufactured. Delamination is the most prevalent failure mode for composites [2], and can be caused by many factors, as shown in Figure 1.

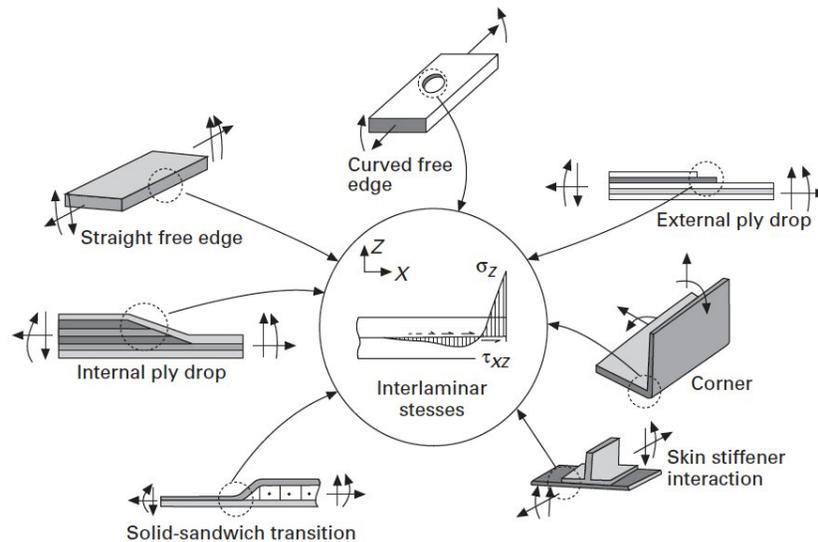


Figure 1: Causes of delamination [3].

Over the years many techniques have been developed to investigate and mitigate delamination, which is particularly dangerous because it appears and grows under the surface: a laminate can loose up to 60% of its compressive residual strength and stiffness and still remains visibly unchanged [4]. Among the range of solutions developed over the years targeting to solve or mitigate the delamination problem, interleaving polymeric nanofibers in interlaminar regions has proven to be one of the most effective thanks to their tiny diameter (as small as tens of nanometres), small pores (ranging from tens of nanometers to tens of micrometers) and high volumetric porosity. Nanofibers are produced by electrospinning, which first patent dates back in 1902 [5, 6], and found successful application in numerous fields, such as nanocatalysis, tissue engineering scaffolds, protective clothing, filtration, biomedical, pharmaceutical, optical electronics, healthcare, biotechnology, defence and security, environmental engineering [7–10].

In 1999, Professors Y.A. Dzenis and D.H. Reneker interleaved sheets of polymeric nanofibers between two consecutive layers of a composite laminate to improve its mechanical performances [11]. Their idea worked and the new three-phase composite material exhibited improved performances compared to the pristine configuration, and a new application for nanofibers had just been introduced.

A research on Scopus (www.scopus.com) using "Nanofibers" and "Laminate" as keywords in titles, abstract and keywords for articles, reviews and articles in press, in the areas of Material Science and Engineering, output 159 documents starting from 2002, as shown in Figure 2. Taking into account also conference papers and reviews, books and book chapters, the total number of documents rises to 298.

In the last few decades, the research community showed great interest on the potential of nanofibers as reinforcement for laminates, and three reviews have been already published on this topic [12–14]. The first one presents the mechanical improvements of interleaving a polymeric structure (either particles, films or nanofibers) between composite laminae, while the other two focus on the range of possible applications and the actual benefits of nanomodifying laminates with nanofibers.

The intent of the present review is to analyse the state-of-the art on composite laminates interleaved with electrospun nanofibers, focusing on macroscopic mechanical performances. For the first time, the state-of-the art is depicted by direct comparison of mechanical test results between pristine and nanomodified laminates. Results from literature are presented in charts which

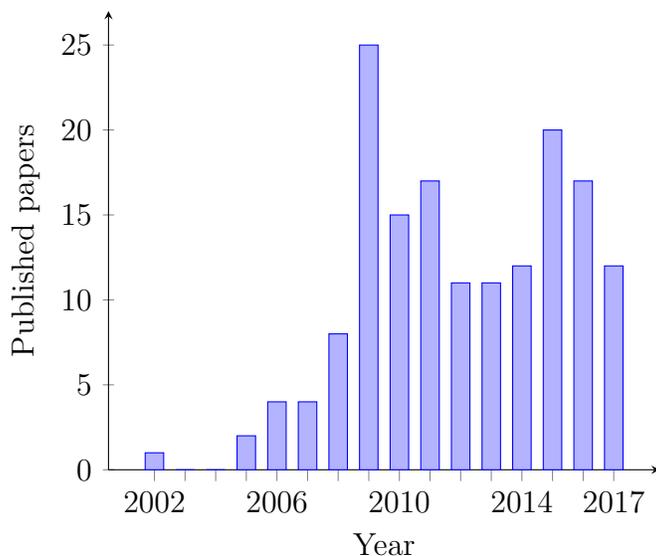


Figure 2: Published papers found using "Nanofibers" and "Laminates" keywords. Source: Scopus, August 30, 2017

relate the responses of nanomodified laminates with those of control samples, to provide the readers and the users with a clear view of the effect of the nanomodification. The same charts can also be a useful tool to select materials for practical applications.

Section § 2 after a brief introduction of the electrospinning process, lists all the polymers that have been used to date for producing nanofibers for structural and reinforcing purposes; Section § 3 presents a detailed analysis of the behaviour of the nanomodified composites classified according to 7 different mechanical tests: (i) Mode I and (ii) Mode II fracture mechanics, (iii) Tension, (iv) Bending, (v) Impact, (vi) Compression after impact, and (vii) Vibration. Each load case is individually presented: experimental results, working mechanism of the nanofibers, and any relevant information from the papers present in literature have been reported.

A dedicated section has been left to present the results of a recent and very effective nanoreinforce: nanofibers doped with CNT. Despite the topic may seem slightly out of the scope of this review, the strong effect that nano carbon-based materials have on the composites they are interleaved in, could not have been left out, and deserved a mention.

The general trend shows that nanofibers bring significant benefits to the

properties of the laminate they are interleaved in; those few documents that report negative results have been collected and presented in Section §4, aiming to identify the causes and the operations that should be avoided when working with nanofibers. Section §5 identifies the research holes that still need to be filled, and presents the future perspectives of the use of nanofibers in composites; conclusions are drawn in Section §6.

2. Electrospinning

The electrospinning process makes use of five main components to produce polymeric nanofibers: (i) a high voltage power supply, (ii) a feeding system that brings the polymeric solution from (iii) a reservoir to (iv) a dispensing unit (a needle- or a needleless-system [15, 16]), and (v) a grounded collecting plate. The high voltage applied between the collector and the polymeric solution charges and accelerates this latter, which whips travelling between the capillary tip and the collector. The unstable motion aids the evaporation of the solvent(s) and stretches the polymer, which is deposited in the form of nanofibers.

The electrical field can be tuned with devices such as deflectors, electrostatic lenses, or shaped collectors. Figure 3 shows a detailed electrospinning apparatus scheme.

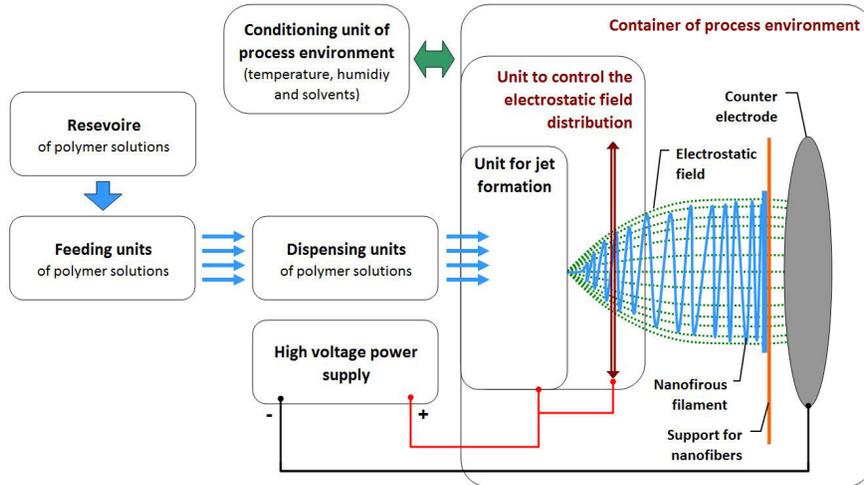


Figure 3: A scheme of an Electrospinning apparatus, making use of an elliptical collector

Polymeric solution's characteristics (polymer's molecular weight, solution's viscosity, surface tension and conductivity, and solvents' dielectric properties), process parameters (voltage, solution's feedrate, temperature, collector's motion and/or shape, capillary diameter, and capillary tip-collector distance), and environmental conditions (humidity, temperature, atmosphere and pressure), are all factors that affect the morphological properties of the final fibers, mainly the diameters, length, presence of beads and orientation [17]. The process has been used to produce nanofibers from a wide range of polymers, and Table 1 shows those used to produce nanofibers for composite laminates reinforcing purposes, by considering the structure they were interleaved in (UD, PW or TW) and the main matrix reinforce (Carbon or Glass).

	Carbon fibers			Glass fibers		
	UD	PW	TW	UD	PW	TW
coPES	[18]					
Epoxy				[19–21]		
nPVA	[22]					
PAI	[23]					
PAN	[24, 25]	[26–28]	[24]			
PA6				[29–32]	[21]	
PA6,6	[23, 33–38]	[20, 36, 39–45]		[35, 37, 46, 47]		
PA6,6+PCL				[48]		
PA6,9	[38, 49]	[49]	[38, 49]	[31]		
PCL	[23]	[28]		[29, 31, 50, 51]		
PEK-C		[52]				
PES	[23]					
Phenoxy		[53]	[54]			
PP					[21, 55]	
PPS	[56]					
PSF	[57, 58]					
PVA	[59]	[60]				
PVB	[23]					
PVDF		[28, 61, 62]	[63]	[64, 65]		
P(St-co-GMA)	[66]	[67]	[66]			
SBS				[68]		
Silk		[69]				
TEGO	[70]					
TEOS					[71–76]	[77, 78]
TPU					[21]	

Table 1: Electrospun polymers and their application

As seen, the most used polymer is the PA, sometimes also referred to with its commercial name: Nylon. The reasons for such popularity are due to that fact that it is relatively cheap, dissolves easily in a wide range of solvents, has better mechanical properties compared to other polymers at both bulk and nanofibrous level, and its melting point is usually higher than the maximum curing temperature of most of the matrix used for composites. This latter aspect makes the polymer morphologically stable during the curing process, and therefore the nanofibers maintain their geometry after the high-temperature and high-pressure cycles most composites have to go through to make the matrix polymerises.

From Table 1 it is also noteworthy that the vast majority of the nanofibers for reinforcing purposes are electrospun from thermoplastic polymers, and only few from thermosetting ones. In [79] it is shown that if a thermoplastic interleave (being particles, film of nanofibers) has a good bond with the composite's thermosetting resin, then it is possible to enhance the fracture toughness by various mechanisms. The same usually does not apply to thermosettings, and even when it does, the improvements are usually poorer than when the thermoplastics are employed.

Eventually, it is also worth mentioning that other types of interleaves rose popularity in the last few years, such as CNF and CNT [80–84] but they are not treated in this review. The main issues with the use of CNT and CNF are linked to health dangerousness [85] and difficulties in mixing and homogenizing with the matrix [86].

Authors considered out of the scope of this literature, and therefore did not treat, studies on nanofibers embedded in pure matrix [60, 87–94], on the single nanofiber [95–98], and on numerical simulations of nanomodified composites [65, 99–102].

3. Electrospun nanofibers for structural reinforcement

The present literature review reports and analyses the achievement in the field of electrospun nanofibers used as mechanical reinforcement in resin-based composite laminate materials. Nanofibrous mats are the ideal reinforcement to be interleaved between two plies of resin matrix composites because of the following main aspects:

1. thinness and lightness: nanomats can be as thin as few microns and as light as few grams per square meter, making their impact to weight and thickness of the final manufactured negligible;

2. porosity: the high porosity of the mats makes the resin flow easily through them, still maintaining a solid bonding between the two layers the nanofibers are placed between in (see Figure 4);

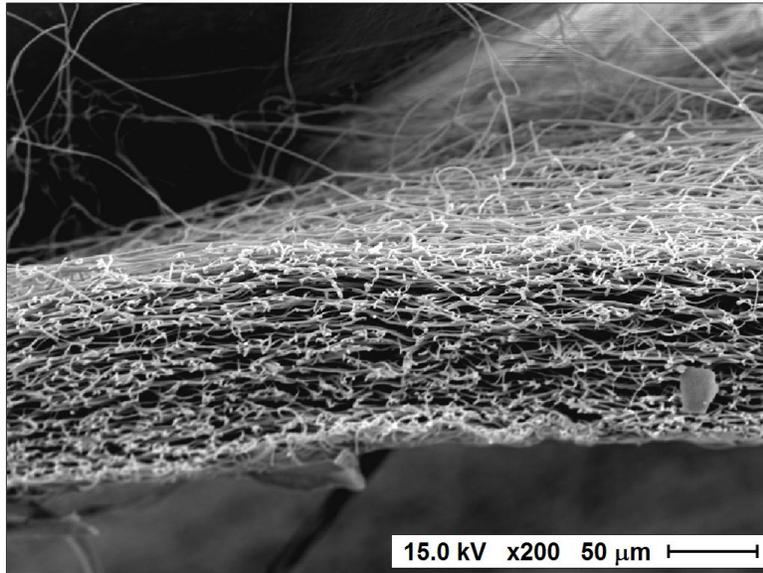


Figure 4: Section of a nanofibrous mat

3. tiny volume: the many pores of the nanomats, when interleaved, are filled with resin, and the actual volume of the nanofibers is small. The pressure applied during the curing process further shrinks the nanointerleave, and most of the papers did not register any appreciable thickness increase due to the interleave. However, in the majority of the papers, just one nanofibrous mat is used, and in some of those cases where several mats are applied, increases of few % are registered;
4. mechanical properties: nanofibers' mechanical properties can be significantly higher than those of the same material in bulk state [103].

Interleaving a nanofibrous mat into a laminate is one of the most critical phase when nanostructuring composites. Literature papers present two main approaches: (i) direct electrospinning of nanofibers on the raw composite, or (ii) collection of the nanofibers on a support first, and then transfer to the composite. Each technique has its own pros and cons, and many aspects play an important role on the final results. Direct deposition presents advantages from the industrial implementation point of view, giving manufacturers the

possibility of implementing the electrospinning process into the production lines, improving time to production and reducing costs; on the other end, collecting nanofibers on a metallic support gives engineers the possibility to obtain nanofibers of a wider range of properties and to use lower electrical fields due to the metallic nature of the collector. However, this review shows that no clear advantages can be seen of one method over the other regarding final composite's performances.

In both cases, once the nanofibers are applied to the composite, they get impregnated. Figure 5 shows two steps of such process. Nanofibers are laid on a prepreg lamina (see Figure A), and after few minutes the resin embeds the mat (see Figure B).

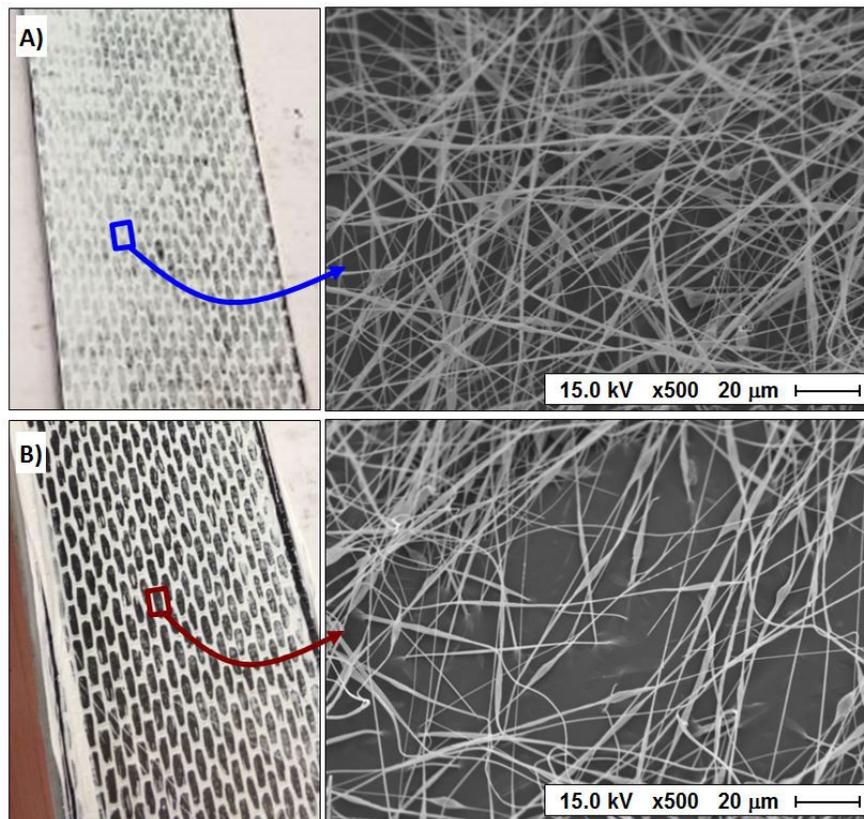


Figure 5: Nanofibers laid on a prepreg: initial time (A) and after few minutes (B)

For each type of load presented in next sections, the effect and the working mechanisms of the nanofibers have been presented, and Tables have been

built to illustrate the main characteristics and results of the tested samples for each paper. Tables have 8 columns:

1. Ref#: it indicates the paper each row is referred to;
2. Pol: it indicates the polymer(s) used to manufacture the nanofibers;
3. Solution: it indicate the composition of the polymeric solution that has been electrosun to produce the nanofibers;
4. NF_{diam}: it indicated the average diameter in nm of the nanofibers, end, when reported, the standard deviation;
5. NF_{amount}: it indicated the amount of nanofibers interleaved in the specimens;
6. Man: it indicates the way the samples have been manufactured;
7. Layup: it indicates the layup the specimens are manufactured with. Comma (,) is used to separate orientation of consecutive UD layers, while slash (/) separates the two orientation of a woven. E.g. a layup of [0,90] refers to a laminate made of 2 layers, one of which oriented at 0 degrees, and the other at 90 degrees; a layup of [0/90] refers to a single-layer laminate, made of woven fabric, which fibers are oriented at 0 and 90 degrees;
8. Results: it indicates the most relevant results presented in the paper.

Mechanical experiments give important information on the effect of the nanofibers, but other techniques are also used to further investigate their working mechanisms and are here mentioned. Most of the papers use SEM images to study and compare virgin and nanomodified fractured surfaces; other common techniques used for the same purpose, and mentioned in this review are acoustic emissions [104], X-ray spectroscopy [82], high-resolution transmission electron microscopy [105] and transmission electron microscopy [13].

3.1. Fracture mechanics

Fracture mechanics is the most common and effective approach to investigate delamination behaviour of composites [106], and it mainly relies on Mode I and Mode II loading conditions [107]. As mentioned before, delamination takes place when a crack develops and propagates between two consecutive plies (the interlaminar region) usually filled with a thermosetting resin. The resin is a brittle material, which, once cracked, tends to make the delamination propagates rapidly. Under Mode I and Mode II fracture mechanic loading conditions, two consecutive plies of a laminate are

made opening or sliding one over the other, respectively: applying a ductile, nanofibrous, interlayer in the delaminated region has proved to be a valid approach to mitigate delamination initiation and propagation since the very first publication on the topic [11].

The studies found in literature compare the results obtained from testing virgin (non-nanomodified) and nanomodified specimens with one or more delaminated interfaces and/or interleaved with nanofibers: comparing the results from both the configurations assesses the effectiveness of the nanoreinforce.

Force, displacement and crack propagation are usually recorded during the tests and used to evaluate the energy release rate at initiation (G_C) and propagation (G_R) of the delamination, and the fracture toughness of the material (K).

Most of the experiments have been conducted under quasi static loading conditions (Tables 2a, 2b, 3a and 3b); only few authors tested samples under cycling loads (Tables 4a and 4b).

3.1.1. Mode I

Most of the Mode I fracture mechanics have been carried out under the guidelines provided in the ASTM D5528 [108]. From the mechanical tests, the critical and the propagation energy release rates and the fracture toughness are calculated, indicated with $G_{I,C}$, $G_{I,R}$ and K_I , respectively, where "I" indicated the Mode I.

Table 2 shows an overview of the 28 papers found in literature on this topic: 7 of them test glass fibers, 21 carbon fibers, mostly using PA as polymer for manufacturing nanofibers.

(a) Glass fibers - Papers on Mode I

Ref #	Pol	Solution	NF _{diam}	NF _{amount}	Man	Layup	Results
[29]	PCL	12% in 9:1 FA:AA	343±150	5-15g/m ²	VARTM	[0] ₈	G _{1,C} : +50%
	PA6	16% in 1:1 FA:AA	195±35	4-20g/m ²			G _{1,C} : no variation
[30]	PA6	16% in 1:1 FA:AA	150±19 230±26	5g/m ² 10g/m ²	VARTM	[0, 90] _{2s}	G _{1,C} : +14% G _{1,C} : -12%
[46]	PA6,6	14% in 1:1 FA:CLF	150±15	25±8μm (25g/m ²)	PrP	[0] ₁₀	G _{1,C} : +62%
[48]	PA6,6	14% in 1:1 FA:CLF	270	27μm	PrP	[0] ₁₄	G _{1,C} : +25%
	PCL	15% in 1:1 FA:AA	150	31μm			G _{1,C} : +4.5%
	PA6,6+PCL			30μm			G _{1,C} : +21%
[50]	PCL	14 wt% in 1:1 FA:AA	400±100	30-176μm single layer 17-89μm double layer	PrP	[0] ₈	G _{1,C} /G _{1,R} : +20/+12% G _{1,C} /G _{1,R} : +94/+27%
[68]	SBS	BuAc:SBS:MTI-TAD:LiCl 100:13:0.0585:1.3	2000±500	12-22g/m ²	VARTM	[0] ₈	G _{1,C} : +90%
[73]	TEOS	[109]	500	NA	VARTM	[0/90] ₁₀	G _{1,C} : -12%

(b) Carbon fibers - Papers on Mode I

Ref #	Pol	Solution	NF _{diam}	NF _{amount}	Man	Layup	Results
[20]	Epoxy 609	18-25% in 3:1 MEK:PGME	NA	90, 128, 144, 216μm	PrP	[0] ₂₄	no significant effects
[22]	nPVA	16, 18, 20, 22% in H ₂ O	40-80	NA	VARTM	[0/90] _?	at 0.1 % nPVA: G _{1,C} /G _{1,R} : +65/+73%
[23]	PA6,6	15% in 68:17 FA:AA	150-300	1.5, 4.5, 9g/m ²	PrP	[0] ₁₂	G _{1,C} /G _{1,R} : +33/-6%
	PVB	10% in ETH	400-700	4.5g/m ²			G _{1,C} /G _{1,R} : +13/+4%
		10.6 in ETH	700-1000	4.3g/m ²			G _{1,C} /G _{1,R} : +16/+11%
	PCL	13% in 70:17 FA:AA	150-300	4.2g/m ²			G _{1,C} /G _{1,R} : +3/+12%
	PES	20% in DMA	150-300	3.6g/m ²			G _{1,C} /G _{1,R} : -52/-52%
	PAI	15% in 77:8 DMA:DMF	150-300	4.1g/m ²	G _{1,C} /G _{1,R} : -58/-68%		
[28]	PCL	12-15-20% in 1:1 DMF:CHL	103-125-210	0.2%	PrP	[0/90] ₄	G _{1,C} : +92% with 125 nm PCL
	PVDF	16% in 1:1 DMF:AC	542				G _{1,R} : +37% with 125 nm PCL
	PAN	13% in DMF	607				
[36]	PA6,6	12% in 3:1 FA:AA	75-250	1.6-2.0g/m ²	PrP	[0] ₂₀	K _I : +150% G _{1,C} /G _{1,R} : +152/+31%
[37]	PA6,6	20% in 70:30 TFA:FA	350-400	40, 90μm	PrP	[0] ₂₀ [0/90] ₁₄	G _{1,C} /G _{1,R} : +56/+11% G _{1,C} /G _{1,R} : +250/+122%
[38]	PA6,6 PA6,9	14% 7:3 in FA:AA 16% 1:1 in FA:AA	158±19 245±28	3, 18g/m ²	PrP	[0] ₁₀ [0/90] ₂₀	G _{1,C} /G _{1,R} : +28/-41% G _{1,C} /G _{1,R} : +48/+62%
[39]	PA	20% in 1:1 FA:CLF	400-650	40μm (1.8g/m ²)	PrP	[0/90] ₁₄	G _{1,C} /G _{1,R} : +137/+124%
[41]	PA6,6	14% in 1:1 FA:CLF	150±20	25±8μm	PrP	[0/90] ₁₂	G _{1,C} : +5% - Energy absorbed: +23%
[43]	PA6,6	20% in 7:3 TFE:FA	500	70-100μm (8-12g/m ²)	PrP	[0/90] ₁₈	G _{1,C} : 280-340% - G _{1,R} : 255-322%
[44]	PA6,6	14, 25% in 1:1 FA:CLF	150, 500	25, 50μm	PrP	[0/90] ₂₀	best with thin nanoreinforce, random nanofibers, small fiber diameter
[53]	Phenoxy	30% in 3:7 DMF:THF	909±126	70μm	PrP	[0/90] ₈	G _{1,C} /G _{1,R} : +98/+106%
[54]	Phenoxy	15% in 4:1 DMF:CHL	700	35-150μm	RTM	[0/90] ₁₀	G _{1,C} /G _{1,R} : +325/+300%
[57]	PSF	25% in 9:1 DMAC:AC	230	1, 3, 5% resin content	PrP	[0] ₂₄	G _{1,C} : +158/+261/+281% with 1/3/5%
[58]	PSF	25% in 9:1 DMAC:AC	230	5% resin content	PrP	NA	G _{1,C} : 280%
[59]	PVA	15% in H ₂ O	329±58	7.10±0.70g/m ²	VARTM	[0] ₄	G _{1,C} : -27%
[61]	HMV PVDF	25% in NA	213±70	5% resin content	PrP	[0/90] ₈	G _{1,C} /F _{max} : -20/+6.0%
	LMW PVDF	30% in NA	340±150				G _{1,C} /F _{max} : -20/+3.6%
[62]	PVDF	15% in 7:3 DMSO:AC	500±110	45±5	PrP	[0/90] ₁₄	G _{1,C} /G _{1,R} /F _{max} : +98/+73/+36%
[63]	PVDF	15% in 3:7 DMSO:AC	500±110	30±3μm	PrP	[0/90] ₁₄	G _{1,C} /G _{1,R} : +43/+36%
[65]	PVDF	15% in 3:7 DMSO:AC	500±110	30±3μm 60±5μm	PrP	[0/90] ₁₄	G _{1,C} : +44% G _{1,C} : +88%
[93]	PA6,6	14% in 1:1 FA:CLF	170±30	70-100μm	PrP	[0] ₁₀	G _{1,C} /G _{1,R} : +23/-22%

Table 2: Papers on Mode I tests

The most-right column of the table indicates that interleaving nanofibers into composites introduce significant benefits in the vast majority of the

cases. Figure 6 and Figure 7, show experimental results plotted in terms of $G_{\text{Nanomodified}}$ vs. G_{Virgin} for Glass and Carbon fibers specimens, respectively, providing a clear and immediate understanding of the effect obtained by interleaving laminate's interfaces with nanofibers. The solid lines identify configurations with identical virgin and nanomodified energy release rates; all the points above (below) these lines identify experiments with improved (reduced) Mode I energy release rate, due to the use of nanofibers. Figure 6 shows that only 2 out of 14 sets of experiments (14.3% of the total) on glass fiber specimens resulted in a reduction of energy release rates when nanofibers are employed. In the other 12 sets (85.7% of the total), nanofibers had positive (11 cases, 78.6% of the total) or negligible (1 case, 7.1%) effects on the performances of the samples. The highest registered improvement was 94% (UD glass fibers, PCL nanofibers, [50]).

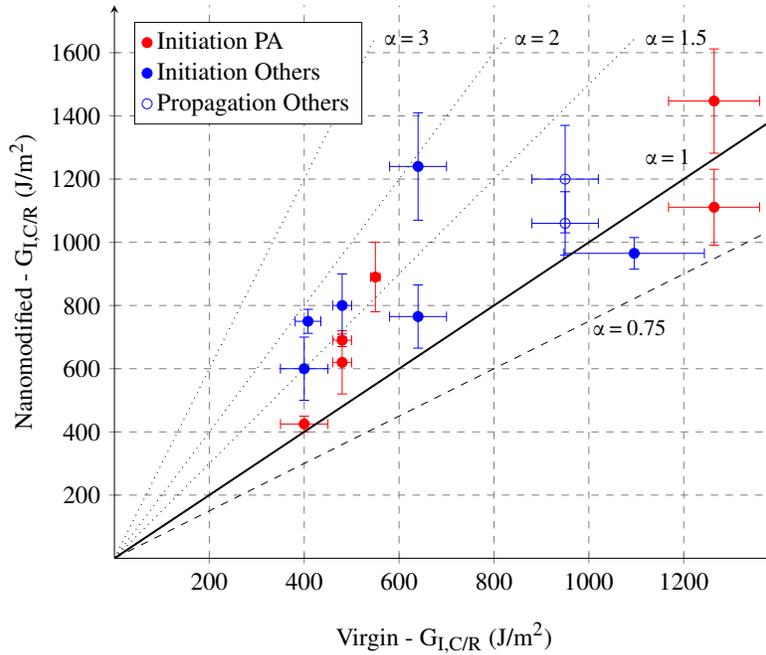
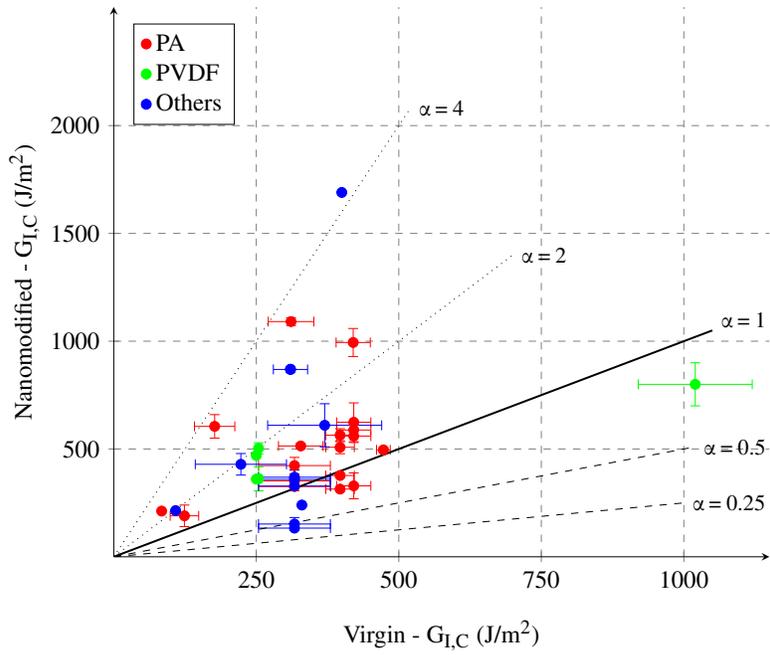


Figure 6: Mode I energy release rates for GFRP. $\alpha = \frac{G_{\text{Nanomodified}}}{G_{\text{Virgin}}}$. No data available on crack propagation for PA-modified specimens

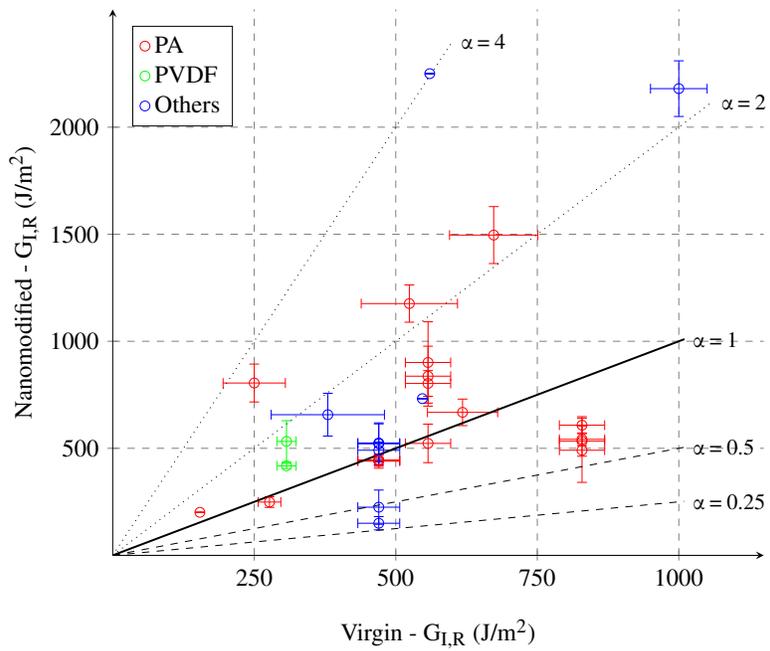
Given the larger number of papers found for carbon fibers, Figure 7 has been split in two: Figures 7a and 7b show delamination's initiation and propagation's results, respectively. Furthermore, due to the large number

of paper using PA and PVDF nanofibers compared to the other polymers, these are indicated with a different colors, as shown in the legends. Results from [20] have been omitted because authors only test one sample per configuration, and the results lack on statistical significance.

Similarly to what has been said for glass fiber samples, the vast majority of the results (82.5%) report a non-negative effect of the nanointerleave, and only 17.5% of the cases shows a reduction of properties. $G_{I,C}$ and $G_{I,R}$ of nanomodified specimens has been registered up to 4 times higher than pristine ones ([54], Phenoxy resin as polymer for the nanofibers).



(a) $G_{I,C}$



(b) $G_{I,R}$

Figure 7: Mode I energy release rates for CFRP. $\alpha = \frac{G_{I,C}^{\text{Nanomodified}}}{G_{I,C}^{\text{Virgin}}}$

Figure 7 shows similar result distributions for initiation and propagation: most of the improvements are clustered in the area $1 < \alpha < 2$, followed by the $2 < \alpha < 3$. The aspect of major concern is that of delamination initiation, for when a crack starts, it is easier to propagate and the laminates is compromised and unrepairable; on the other end, reducing the crack propagation improves the safety of the component, and increases its use-life. Several reinforce mechanism have been discovered by the authors, and are here presented, with focus to the crack's initiation and the propagation phases:

- nanofiber bridging [14, 25, 29, 37, 38, 46, 68, 69], mostly found when using ductile PA nanofibers. The phenomenon is well presented in [29], where authors present a detailed analysis of the fracture surface of their tested samples, using SEM: an extensive interlaminar crossings have been observed, besides the usual glass fiber-epoxy debonding. Interlaminar crossing happens when a crack propagates inside the same interlaminar region (between the same plies), but moving from one side of the nanointerlayer to the other passing through it. When this happens, some nanofibers survive intact, and they are those that are still able to connect the two sides of the crack, increasing the residual interlaminar's fracture toughness. It is easy to understand that it is a phenomenon that mitigates the delamination propagation, improving the G_{II} of the laminate, compared to the control samples;
- resin reinforcement [23, 60, 87–94], detected by several authors, using a different type of polymers. In [94] it is demonstrated that using an hybrid electrospinning-electrospraying method (electrospraying uses polymers with much shorter chains which end deposited as particles rather than fibers), a resin containing 0.13% weight content of fiber was 700% stronger, 250% stiffer, and more ductile than the non-modified one. As mentioned by few authors [89, 91, 93], a main aspect to take into consideration when interleaving nanofibers in a laminate is their adhesion with the resin: it is affected by several factors (moisture of the nanofibers, process conditions such as pressure, temperature, and vacuum grade, etc.) and strongly influences the final performances of the laminate. Resin reinforcement is the most desirable reinforce mechanism, for it actively reduces the risk of crack initiation, and developing an optimum, repeatable and reliable interleaving process that realise a good bonding between the nanofibers and the resin is crucial for a

positive effect of the reinforcement. Similar conclusions are drawn in [23], where authors identify in the nanofibers-resin compatibility one of the main reasons for the better properties they found for nanomodified samples;

- crack path modification [37, 39, 45, 62, 93], observed mainly when using PA nanofibers, but also with phenoxy, PCL and PSF. Those papers investigating the crack path during delamination propagation, discovered that the presence of nanofibers hinders the motion of the crack, which is then forced to follow a tortuous path, thus increasing the energy required to propagate, compared with a neat interface. It is one of the most effective reinforcement mechanisms to hinder crack propagation, for it forces the delamination to follow longer and harder paths, sometimes also crossing plies [45].

It is worth mentioning that among all papers, only one used a combination of polymers [48]: PCL and PA6,6. Those two polymers have different glass transition temperatures resulting in PCL nanofibers melting during curing cycles. The PSU-modified epoxy matrix has lower rigidity and strength compared to neat matrix, but higher fracture toughness [110], and at the same time PA kept its properties: as a result, the combination of two types of nanofibers efficiently reinforced the sample under both Modes I and II loading types.

3.1.2. Mode II

Mode II fracture mechanics has been standardised only in 2014 [111], and most of the earlier works found in literature refer to either other papers, or to the guidelines provided by the European Structural Integrity Society [112]. Different kinds of tests can be found for investigating Mode II fracture mechanics such as ENF, ISS and SBSH; for all the cases the specimen is pre-delaminated, with the purpose of generating concentrated shear stress at the crack tip. The critical and propagation energy release rates and the fracture toughness are indicated with $G_{II,C}$, $G_{II,R}$ and K_{II} , respectively, where "II" indicates the loading Mode II.

Table 3 shows an overview of the 18 papers found in literature studying Mode II fracture mechanics on nanomodified samples: carbon and glass fibers are investigated in the same number of papers (9), and the most used polymer is PA.

(a) Glass fibers - Papers on Mode II

Ref #	Pol	Solution	NF _{diam}	NF _{amount}	Man	Layup	Results
[19]	Epoxy	18-25% in 3:1 MEK:PGME		80-257 μ m	PrP	[0] ₂₄	G _{II,C} from -41% to +17% G _{II,C} , F max at 0.1281 mm nanomat thick
[29]	PCL PA6	12% in 9:1 FA:AA 16% in 1:1 FA:AA	343 \pm 150 195 \pm 35	5-15g/m ² 4-20g/m ²		VARTM [0] ₈	G _{II,C} : +81% G _{II,C} : +76%
[31]	PCL PA6 PA6,9	1:1 FA:AA	650 \pm 150 195 \pm 35 250 \pm 30	14 \pm 0.5g/m ²		VARTM [0] ₈	G _{II,C} : +25/+42% CCP/ENF G _{II,C} : +28/+30% CCP/ENF G _{II,C} : +31/+46% CCP/ENF
[35]	PA6,6	14% in 1:1 FA:CLF	100	9g/m ²	PrP	[0] ₁₀ [0] ₁₆ [0] ₁₈	G _{II,C} : +85% G _{II,C} : +75% no effect
[46]	PA6,6	14% in 1:1 FA:CLF	150 \pm 15	25 \pm 8 μ m (25g/m ²)	PrP	[0] ₁₀	G _{II,C} : +109%
[48]	PA6,6 PCL PA6,6+PCL	14% in 1:1 FA:CLF 15% in 1:1 FA:AA	270 150	27 μ m 31 μ m 30 μ m	PrP	[0] ₁₆	G _{II,C} : +24% G _{II,C} : +68% G _{II,C} : +56%
[49]	PA6,9	20% in 1:1 FA:AA	457 \pm 53 random 464 \pm 110 aligned	11 \pm 0.5g/m ²	PrP	[0] ₁₂	G _{II,C} : +400%
[68]	SBS	BuAc:SBS:MTL-TAD:LiCl in 100:13:0.0585:1.3	2000 \pm 500	12-22g/m ²		VARTM [0] ₈	G _{II,C} : +100%
[71]	TEOS	<i>see reference</i>	200	6 μ m (2.5g/m ²)		VARTM [0/90] ₆	G _{II,C} : +56.1%

(b) Carbon fibers - Papers on Mode II

Ref #	Pol	Solution	NF _{diam}	NF _{amount}	Man	Layup	Results
[23]	PA6,6 PVB PCL PES PAI	15% in 68:17 FA:AA 10% in ETH 10% in ETH 13% in 70:17 FA:AA 20% in DMA 15% in 77:8 DMA:DMF	150-300 400-700 700-1000 150-300 150-300 150-300	1.5, 4.5, 9g/m ² 4.5g/m ² 4.3g/m ² 4.2g/m ² 3.6g/m ² 4.1g/m ²		PrP [0] ₁₂	G _{II,C} : +29, 69, 54% with NF _{amount} G _{II,C} : -6% G _{II,C} : -8% G _{II,C} : +7% G _{II,C} : +20% G _{II,C} : +56%
[35]	PA6,6	14% in 1:1 FA:CLF	100	9g/m ²	PrP	[0] ₁₈	no significant effect
[37]	PA6,6	20% in 70:30 TFA:FA	350-400	40, 90 μ m	PrP	[0] ₂₀ [0/90] ₁₄	G _{II,C} : +62% G _{II,C} /G _{II,R} : +99/+34%
[38]	PA6,6 PA6,9	14% 7:3 in FA:AA 16% 1:1 in FA:AA	158 \pm 19 245 \pm 28	3, 18g/m ²	PrP	[0] ₁₀ [0/90] ₂₀	G _{II,C} /G _{II,R} : +20/+211% G _{II,C} /G _{II,R} : +211/+65%
[41]	PA6,6	14% in 1:1 FA:CLF	150 \pm 20	25 \pm 8 μ m	PrP	[0/90] ₁₂	σ_{max} : +6.5% - Absorbed energy: +8.1%
[44]	PA6,6	14, 25% in 1:1 FA:CLF	150, 500	25, 50 μ m	PrP	[0/90] ₂₀	no thickness effect, aligned nanofibers, smaller nanofibers improved absorbed energy, bigger diameters improved the maximum tension
[53]	Phenoxy	30% in 3:7 DMF:THF	909 \pm 126	70 μ m	PrP	[0/90] ₈	G _{II,C} : +31%
[61]	HMV PVDF LMW PVDF	25% in 8:2 DMF:AC 30%	213 \pm 70 340 \pm 150	5% resin content	PrP	[0/90] ₈	G _{II,C} : +57%
[69]	Silk	13% in FA	50-100	0, 3, 5, 10% _{cc} resin content	VARTM	[0/90] ₁₀	G _{II,C} : +30% at 5% _{cc}

Table 3: Papers on Mode II tests

Similarly to the Mode I, also for the Mode II a general improvement can be observed due to the use of the nanofibers.

Figure 8 presents the results on tests on GFRP: only 1 out of 20 sets of experiments resulted in a clear reduction of properties. In the other 19 sets (95% of the total), the researchers found positive (15 cases, 75% of the total) or unclear (4 case, 20%) effects resulting from the interleaved nanofibers. Properties' improvement up to 3 times have been registered (TW carbon fibers, PA6,9 nanofibers, [49]).

Results generally show a low standard deviation, but in [19]; unfortunately the authors have not provided an explanation for the large scatter they found. It is worth mentioning that no papers have been found dealing with Mode

II delamination propagation in glass fiber samples, probably due to the fact that it happens suddenly and it is difficult to register.

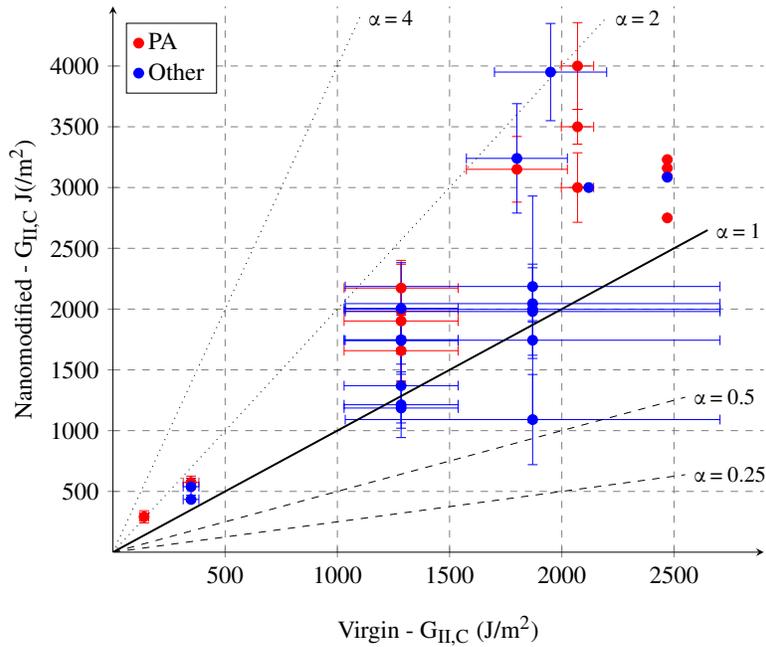
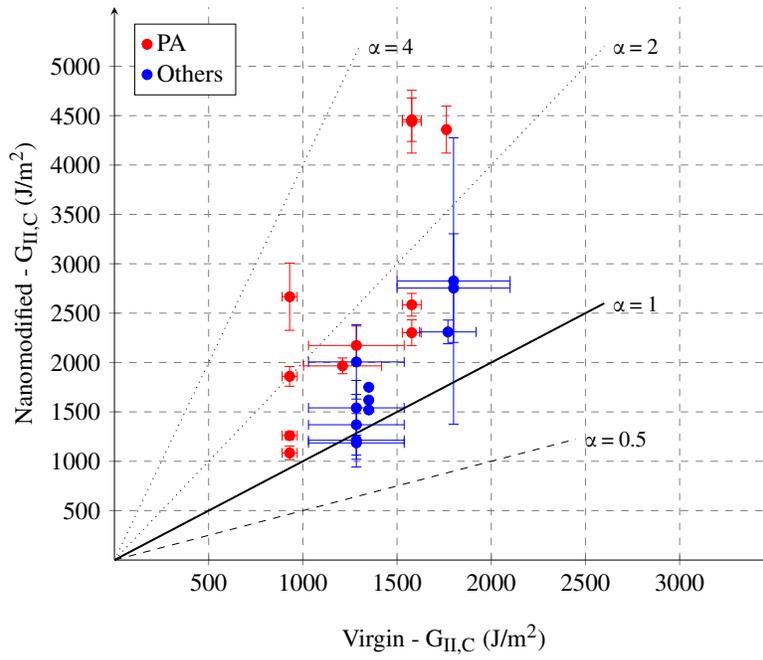


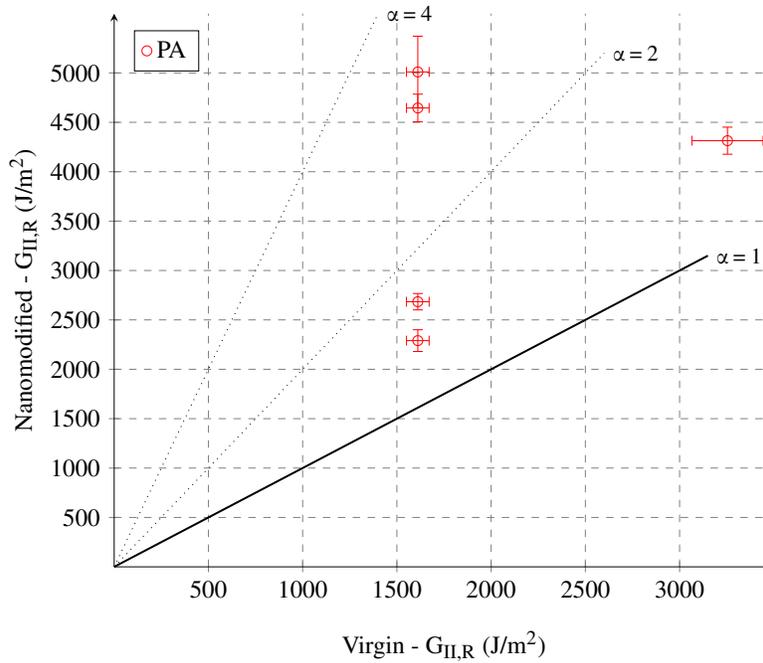
Figure 8: Mode II energy release rates for GFRP. $\alpha = \frac{G_{Nanomodified}}{G_{Virgin}}$

Similar results can be found in Figure 9 on carbon fibers' samples: nanofibers improved the energy release rate at delamination initiation in 18 cases out of 21 (85.7%), and in 3 cases (14.3%) results were unclear. No clear detrimental results have been found.

By comparing Mode I and Mode II results it appears that nanofibers are more effective in the latter case.



(a) $G_{II,C}$



(b) $G_{II,R}$

Figure 9: Mode II energy release rates for CFRP. $\alpha = \frac{G_{\text{Nanomodified}}}{G_{\text{Virgin}}}$

In Mode II fracture mechanic tests, the delamination grows between two interfaces sliding one over the other in opposite directions. Nanofibers are placed at least into the delaminated interfaces, and it has been widely recognised that they bring a strong positive effect into the laminates. Authors' results showed the same reinforcing mechanism already presented for Mode I:

- crack path modification, detected in [19, 29, 31, 37, 48, 49, 68];
- nanofiber bridging, in [29, 31, 38, 46, 49];
- matrix reinforcing, in [23, 37, 53].

3.1.3. Fracture mechanics under fatigue loads

Only 5 papers have been found on fatigue tests of nanomodified composites: one testing GFRP under Mode II, and 4 testing CFRP under Mode I, as shown in Table 4.

(a) Glass fibers - Papers on Fatigue Mode II

Ref #	Pol	Solution	NF _{diam}	NF _{amount}	Man	Layup	Results
[31]	PCL PA6 PA6,9	NA% in 1:1 FA:AA	650±150 195±35 250±30	14±0.5g/m ²	VARTM	[0] ₈	CCP: PCL best results ENF: Growth rate: -15 times

(b) Carbon fibers - Papers on Fatigue Mode I

Ref #	Pol	Solution	NF _{diam}	NF _{amount}	Man	Layup	Results
[22]	nPVA	16, 18, 20, 22% in H ₂ O	40-80	mixed into epoxy	VARTM	[0/90] ₇	at 0.1 % nPVA: Fatigue life: 10-30 times longer
[36]	PA6,6	12% in 3:1 FA:AA	75-250	1.6-2.0g/m ²	PrP	[0] ₂₀	Delamination onset life: improved Fatigue G _{I,C} : +66%
[39]	PA	20% in 1:1 FA:CLF	400-650	40µm (1.8g/m ²)	PrP	[0/90] ₁₄	G _{I,threshold} : +90%
[45]	PA6,6	20% in 1:1 FA:CLF	520±100	18g/m ²	PrP	[0/90] ₁₄	Fatigue life: +96%.

Table 4: Papers on Mode I/II Fatigue tests

Fatigue tests have been performed by cyclically loading samples according to the mode at a lower loading compared to that supposed to initiate delamination. All the fatigue tests reported in literature present a significant positive effect of the nanofibers on delamination grow rate, fatigue life, and delamination onset. Polymeric nanofibers are made of soft materials, compared with both the epoxy resin and the carbon/glass reinforcement, and when interleaved in low-stress samples like those under cyclic loads, can have an even higher impact compared to when interleaved in high-stressed

static tested samples. An accurate and deep analysis of the micro- and nano-mechanics inside an interleaved laminate during fatigue tests is presented in [31]. The three reinforce mechanisms mentioned above for the static tests can take place during a cyclic solicitation, together with some specific mechanisms, and in particular three regions with different behaviour have been observed. Interlaminar crossing is the behaviour observed in region 1, at the early stage of the test, and the delamination propagates slower than in non-interleaved material. In the next region 2, during fracture propagation the interlaminar crossings gradually fades away, to eventually disappear in the region 3, where the delamination growth rate equals that of the non-interleaved material. Regions 2 and 3 are separated by a transition zone in which the interlaminar crossings combine and disappear.

3.2. Tension

The most straightforward characterisation test for the vast majority of materials is the tensile test: a beam-like sample is pulled apart from the two ends; the stress-strain behaviour recorded during the test provides a number of fundamental parameters: ultimate and yielding stresses and strains, Young's modulus, elastic field, and etc. . Composites do not make exception and papers have been found reporting results of tensile tests on nanomodified samples.

When a composite laminate is subjected to a tensile load, its components work in parallel: resin, fiber, and, when present, nanofibers, all act as parallel spring; consequently, fibers bear most of the load, as they are the stiffest and strongest component. Within this frame, polymeric, randomly oriented nanofibers would not be expected to give significant contribution; however several authors found otherwise, and their results are summarised in Table 5.

The most used polymer is the PVA, and tests on carbon fibers present a very close range of results: [22] (PW laminates), [59] (UD laminates), and [60] (PW CF/VE composites), where 12, 9, and 11% improvement in tensile strength have been reported, respectively. In [66] similar (UD and woven specimens, P(St-co-GMA) nanofibers) but only minor improvements have been found: their open holed specimens' tensile strength registered a tensile strength 5% higher than that of the control sample.

In [22] and [60], samples are tested under tensile-tensile fatigue loads, and present very similar improvements: nanomodified samples had 10 to 30 and 3 to 50 times longer lives, respectively.

(a) Glass fibers - Papers on Static Tensile tests

Ref #	Pol	Solution	NF _{diam}	NF _{amount}	Man	Layup	Results
[30]	PA6	16% in 1:1 FA:AA	150±19 230±26	5g/m ² 10g/m ²	VARTM	[0,90] _{2s}	Stress at failure: +6% Stress at failure: +11%
[32]	PA6,6	10% in 75:25 FA:CLF	110 nm	0.525-1.05 g/m ²	VARTM	[0] ₄	Modulus/Strength: none/-10%
[50]	PCL	14% in 1:1 FA:AA	400±100	30-176µm single layer 17-89µm double layer	VARTM	[0] ₈ [0,90] _{2s}	Results not affected
[69]	Silk	13% in FA	50-100	0, 3, 5, 10% _{cc} resin content	VARTM	[0/90] ₁₀	Strength: +5% at 0.05% wt.

(b) Carbon fibers - Papers on Fatigue Tensile tests

Ref #	Pol	Solution	NF _{diam}	NF _{amount}	Man	Layup	Results
[22]	PVA	16, 18, 20, 22% in H ₂ O	40-80	mixed into epoxy	PrP	NA	Strength: +5%
[59]	PVA	15% in H ₂ O	329±58	7.10±0.70g/m ²	VARTM	[0] ₄	Strength: +12%
[60]	PVA	20% in H ₂ O	80-100	0.05-0.1 wt.%	VARTM	[0] ₈	Strength: +11% Young's modulus reduced Strain at failure increased
[66]	P(St-co-GMA)	30% in DMF	300-600	5 interlayers	PrP	[0] ₆ [0/90] ₆	Strength: +12% Strength: +9-18%

(c) Carbon fibers - Papers on Static Tensile tests

Ref #	Pol	Solution	NF _{diam}	NF _{amount}	Man	Layup	Results
[22]	PVA	16, 18, 20, 22% in H ₂ O	40-80	mixed into epoxy	PrP	NA	Life: +10-30 times
[60]	PVA	20% in H ₂ O	80-100	0.05-0.1 wt.%	VARTM	[0] ₈	Life: +3-50 times

Table 5: Papers on Tensile tests

Three works in literature have been found dealing with tensile properties of nanomodified GFRP laminates, and they do not show the same agreement registered for carbon fibers. In [50] it is showed that tensile properties of UD GFRP laminates are not affected by the presence of PCL nanofiber; in [30], it is shown that PA6 nanofibers caused an increase of stress at failure of the composite of about 6% and 11% when the nanofibers were added during lay-up and when directly deposited onto the fabric, respectively. A unique use of Silk has been presented in [69], showing a 5% improved tensile strength. The main evidence of the reinforcing mechanisms of a nanointerleave in tensile tested specimens is provided in [113]. In particular it has been observed that Poisson's ratio mismatches and edge effects have a significant role on the delamination resistance of composite laminates subjected to static and fatigue tensile loads, and it is the field of action of the nanofibers. In [30] it is suggested that nanofibers prevent or minimize the formation of delamination cracks between two fiber plies, and also demonstrated that the nanofibers facilitate the load transfer from the resin to the glass fibers. They also agree with results showed in [60], on the fact that the nanolayers create a matrix-enriched interlayer, which extensive deformation and slower growth

of damage improve the tensile properties of the laminate.

3.3. *Pure bending*

Interleaving a nanofibrous layer in between plies of a sample subjected to bending, follows the same base idea that has been presented in Section §3.1 on Mode II fracture mechanics. The only difference here is that the tested samples are not pre-cracked, and therefore the interply that will delaminate is not known a priori. In fact it is not even known if the sample fails for delamination or for matrix/fiber breakage.

Similar experiments, such as 3PB or 4PB [21, 24, 27, 28, 32, 33, 57, 59, 71, 72], ILSS [24, 32, 53, 77], and SBSH [21, 33, 78] have been performed to investigate behaviour of nanomodified composites under bending loads. Areas of interest are the flexural properties of the laminates and the shear stresses occurring between two laminae. Pure bending stress, like that generated with 4PB tests, usually breaks fibers on the tensile side of the specimens before inducing delamination; in ILSS and SBSH tests, instead, the load is applied to a very short beam to generate dominant shear stresses on the interlaminar region where the nanofibers are laid, increasing the chances of delamination. Three papers have been found testing glass fibers, and eight carbon fibers; results are shown in Table 6.

Despite few works presenting negative results under certain conditions [21, 24, 28], experiments generally show the positive effects that the interleave has on the composite laminates.

The reasons for such improvements are related to aspects discussed in Section 3.1.2, in particular to the matrix reinforcing effect. In [28] it is mentioned that nanofibers have the effect of reinforcing regions with localised stress concentrations, reducing stress concentration effects. In [27] it is claimed that nanofibers cause a delay in in-plane bending damage and thus delamination. An interesting point of view is presented in [24], where the beneficial effects of the nanofibers are attributed to their energy-absorption behaviour and to the fact that they transfer load toward the carbon fibers, again reducing stress concentrations.

3.4. *Impact*

In those applications where laminates are employed on outer sides of structures (e.g. airplanes, cars, etc.), impacts are a main concern, and the delamination behaviour of laminates subjected to impulsive loads has been

(a) Glass fibers - Papers on Bending tests

Ref #	Pol	Solution	NF _{diam}	NF _{amount}	Man	Layup	Results
[21]	PA6 Epoxy 609 TPU	10% in 3:7 FA:TFE 29% in 3:1 MEK:PGME 10% in 1:1 DMF:THF	150-500 350-1200 300-600	20-150 μ m all interfaces interleaved	PrP	[0] ₈	Strength: -30% Modulus: +16/-40% ILSS: +18/-50%
[71]	TEOS	<i>see reference</i>	200	6 μ m (2.5g/m ²) all interfaces interleaved	VARTM	[0/90] ₆	Strength: +65% Modulus: +33% ILSS: +105%
[72]	TEOS	<i>see reference</i>	250-450	1-2% half interfaces interleaved	VARTM	[0/90] ₈	Strength: +14% Modulus: +8% Energy absorption: +93%
[77]	TEOS	<i>From Sol-Gel</i>	250-300	0.2-0.8% wt.	VARTM	[0/90] ₄	Strength: +15%
[78]	TEOS	<i>From Sol-Gel</i>	250-300	NA	PrP	[0] ₁₂ [0, 90, 90, 0, 0, 90] ₈ [0, 60, -60, -60, 60, 0] ₈ [(+45, -45) ₃] ₈	Energy absorbed: +16% +7% +20% +4%

(b) Carbon fibers - Papers on Bending tests

Ref #	Pol	Solution	NF _{diam}	NF _{amount}	Man	Layup	Results
[24]	PAN	11% in DMF	195 \pm 46	27 \pm 5 μ m all interfaces interleaved	HLu	[0] ₆ [0/90] ₄ [0] ₃ [0/90] ₄	3PB: Strength/Modulus: +21/+54% 3PB: Strength/Modulus: -12/+13% ILSS: +11% ILSS: +7%
[27]	PAN	5% in DMF	150	all interfaces interleaved	PrP	[0/90] ₈	Modulus: +21% Strength: +56%
[28]	PCL PVDF PAN	12-15-20% in 1:1 DMF:CHL 16% in 1:1 DMF:AC 13% in DMF	103-125-210 542 607	0.2%	VARTM	[0/90] ₄	Modulus: -19%
[32]	PA6.6	10% in 75:25 FA:CLF	110 nm	0.525-1.05 g/m ²	VARTM	[0] ₄	Modulus/Strength: +16%/+13% ILSS: +10%
[33]	PA6.6	14 % in 1:1 FA:CLF	170 \pm 30	30 μ m 1 and 9 interlayers	PrP	[0] ₁₀	3PB: Modulus not affected ILSS: +32%
[42]	PA6.6	14% in 1:1 FA:CLF	150 \pm 20	25 \pm 8 μ m 2 interfaces per side, symmetric 3 interfaces, bottom side	PrP	[0/90] ₁₀	Stiff before impact: -12% Stiff after impact: +7%
[53]	Phenoxy	30% in 3:7 DMF:THF	909 \pm 126	70 μ m - all interfaces interleaved	PrP	[0/90] ₈	ILSS unchanged
[57]	PSF	25% in 9:1 DMAC:AC	230	1%, 3%, 5% of resin matrix	PrP	[0] ₂₄	Strength: +5% Modulus unchanged
[59]	PVA	15% in H ₂ O	329 \pm 58	7.10 \pm 0.70g/m ²	VARTM	[0] ₄	Modulus: +21% Strength: +16%

Table 6: Papers on Bending tests

widely investigated. Impacts on composite structures may induce delamination cones through the thickness, irreversibly damaging the structure [114]. Depending on the severity of the impact, such cone can develop from top to the bottom of the laminate (∇ shape), or from the bottom to the top (\wedge shape). Interleaving nanofibers into specimens subjected to impacts has the purpose of hindering the formation and the development of such cone. Table 7 summarise the literature on this specific type of load.

(a) Glass fibers - Papers on Impact tests

Ref #	Pol	Solution	NF _{diam}	NF _{amount}	Man	Layup	Results
[29]	PCL	12% in 9:1 FA:AA	343±150	5-15g/m ²	VARTM	[0/90] _{2s}	Damaged area: -50%
	PA6	16% in 1:1 FA:AA	195±35	4-20g/m ² - all interfaces interleaved			
[49]	PA6.9	20% in 1:1 FA:AA	457±53 random 464±110 aligned	11±0.5g/m ² 1 interlayer	PrP	[0] ₁₂	Mode II IFT: +50-100%
[51]	PCL	12% in 3:2 FA:AA	300	30µm all interfaces interleaved	PrP	[0, 90, 0, 90] _s	Damaged area: -26%
[64]	PVDF	15% in 3:7 DMSO:AC	300-700	39, 64µm - all interfaces interleaved	PrP	[0, 90, 0, 90] _s	Absorbed energy: +10-13%
[71]	TEOS	<i>see reference</i>	200	6 with 2.5 g/m ² - all interfaces interleaved	VARTM	[0/90] ₆	Absorbed energy: +37%
[75]	TEOS	<i>From Sol-Gel</i>		8.2g/m ² - all interfaces interleaved	PrP	[0/90] ₁₀	Damaged area: +9%

(b) Carbon fibers - Papers on Impact tests

Ref #	Pol	Solution	NF _{diam}	NF _{amount}	Man	Layup	Results
[24]	PAN	11% in DMF	195±46	27±5µm all interfaces interleaved	HLu	[0] ₆ [0/90] ₄ [0/90] ₄	Absorbed energy: +64% Increase in initiation/total breaking energies
[32]	PA6.6	10% in 75:25 FA:CLF	110 nm	0.525-1.05 g/m ²	PrP	[0] ₄	Strength: +18%
[34, 36]	PA6.6	12% in 3:1 FA:AA	75-250	1.7g/m ² all interfaces interleaved	PrP	[-45, 90, 45, 0] _{2s}	Damage: -33% Threshold force: +60% Damage growth rate: -50%
[40]	PA6.6	10% in 3:1 FA:AA	65-120	0.7g/m ² all interfaces interleaved	PrP	[-45, 90, 45, 0] _{3s}	Delamination on-set force: +7% Threshold energy +33%
[42]	PA6.6	14% in 1:1 FA:CFL	150±20	25±8µm 2 interfaces per side, symmetric 3 interfaces, bottom side	PrP	[0/90] ₁₀	Peak force: -8% Energy absorption: -14%
[59]	PVA	15% in H ₂ O	329±58	7.10±0.70g/m ² all interfaces interleaved	VARTM	[0] ₄	Fracture energy: +11%
[67]*	P(St-co-GMA)	30% in DMTF	400	0.1% wt.	PrP	[0/90] _{25s}	Energy dissipation +80% in-plane, +40% through thickness

* Compressive Split-Hopkinson pressure bar test

Table 7: Papers on Impact tests

The effects of nanointerleave on CFRP subjected to LVI have been mainly investigated using PA6,6 nanofibers as reinforce [34, 36, 40, 42]. In [34, 36, 40] UD samples interleaved at each interface have been tested, while [42] tested woven laminates with nanofibers only in selected interlayers. An important parameter in impacts is the sample's thickness: in [34, 36] nanofibers increased sample's thickness of 1-2%, while in [40, 42] pristine and nanomodified samples had the same thickness, due o a lower number of interleaves. The most common impact test is the LVI test, where a spherical object is dropped falling from a certain height to the specimens [34, 36, 40, 42]. These papers all present very positive results in terms of improved impact threshold force (+64%), damaged area (-50%), damage resistance (3 times), delamination on-set force (+7%), threshold energy (+33%), peak force (-8%) and energy absorbed during the event (-14%) in nanomodified laminates compared to virgin ones.

A different type of impact is given in the Charpy test, used in [24] and [59]. Those tests have been conducted at different energy levels: the Charpy pendulum had speed of 2.9 and 3.46m/s, and energy of 2 and 15J in [24]

and [59], respectively. Results show a reduction of the effectiveness of the nanoreinforce at high values of energy: nanofibers are still effective after a 15J impact, but the improvement falls from 64% to 11%, moving from 2J impacts. Similar conclusions have been drawn in [42], where specimens are tested under LVI protocol.

Glass fibers received even more attention than carbon, and among the papers here considered, only one showed negative results [75].

In [64] and [51], plain and curved glass-fiber specimens have been tested, respectively, showing positive results in terms of absorbed energy (+9,5% and +13,4%, depending on the thickness of the nanomat) and damaged area (-27%).

In [29, 49], the same authors present interesting studies using different types of nanofibers and different nanofiber orientation. In [29] authors used PCL and PA: PA showed negligible effect, while PCL nanofibers reduced the damaged area down to 50%. It is also observed that when nanofibers are oriented parallel to the crack growth direction, the main reinforce mechanism is the matrix strengthening; laminates interleaved with nanofibers oriented transversely to the crack growth direction showed nanofiber bridging, making this orientation more effective than the other. Laminates interleaved with a random deposition of nanofibers resulted in the largest increase in Mode II IFT, due to the contribution of both types of reinforcement.

An interesting work has been presented in [71], where electrospun glass fibers are used to manufacture a multi-scale three-phase composite laminate with 37% higher impact energy compared to the control sample.

The SEM images shown in [42], revealed that after impacts several nanofibers still link the two layers they are inserted in between, suggesting a strong fiber bridging effect. The best insights on reinforcing mechanisms are presented in [29, 49], where two types of failure have been identified: interlaminar failure and intralaminar crossing. The authors assessed that depending on their orientation, nanofibers act independently on the two types of failures. Their multiscale investigation confirms the nanofibers bridging mechanism as main reinforcing effect during impacts.

3.5. Compression after Impact

As mentioned before, nanofibers interleaved in specimens subjected to impacts aims to be beneficial by reducing the formation of the delamination cone; at the same time, due the smaller delamination cone, and the presence of intact nanofibers, result in better sample's residual properties..

Literature presents only two papers on the residual compression properties of composites after impacts, and the results are summarised in Table 8.

(a) Glass fibers - Papers on CAI tests

Ref #	Pol	Solution	NF _{diam}	NF _{amount}	Man	Layup	Results
[76]	TEOS	TEOS:ethanol:H ₂ O:HCl 1:2:2:0.01	NA	all interfaces interleaved	PrP	NA	Residual strength: -29%

(b) Carbon fibers - Papers on CAI tests

Ref #	Pol	Solution	NF _{diam}	NF _{amount}	Man	Layup	Results
[40]	PA6,6	10% in 3:1 FA:AA	65-120	0.7 g/m ² - all interfaces interleaved	PrP	[-45, 90, 45, 0] _{3s}	Strength: +10%

Table 8: Papers on CAI tests

In [40] PA6,6 nanofibers are interleaved into laminates, and it is found that the compression strength after impact increased of about 10%. Similarly to what found in [42], authors observed that the compression residual strength ratio between the nanomodified and the virgin samples decreases at increasing impact energy.

The negative results reported in [76] will be discussed in § 4.

3.6. Vibration

The study of vibrational behaviour of composites is of great importance, especially for delamination evaluation and non-destructive structural health monitoring techniques [115–117]. Despite the literature presents a large number of papers studying vibrations of composites, Table 9 shows that only two papers investigated vibrations of nanomodified laminates.

Ref #	Pol	Solution	NF _{diam}	NF _{amount}	Man	Layup	Results
[42]	PA6,6	14% in 1:1 FA:CLF	150±20	25±8µm 4 interfaces, symmetric 3 interfaces, bottom side	PrP	[0/90] ₁₀	Damping: +250% 1 st harmonic: -17%
[47]	PA6,6	14% in 1:1 FA:CLF	150-250	28.5 g/m ²	PrP	[0, 90, 0, 90, 0] _s	Damping: +36%

Table 9: Papers on Vibration tests

In [42] bump tests are performed on carbon fiber specimens before and after three different energy level impacts; authors measured harmonic frequencies and damping of the samples before and after the event. Damping behaves as expected, with nanomodified samples showing higher damping due to resin-nanofiber friction during vibration, with the effect of the nanointerleave fading away as the impact energy increases. Harmonic frequencies instead showed an unexpected behaviour: the nanomodified specimens exhibit a self-strengthening effect after impacts. Pre-impact results show that

nanomodified specimens are more compliant than their virgin counterparts due to the presence of ductile interlayers; once the matrix is broken, the nanofibers act as a bridge between the two plies, self-strengthening and self-repairing the laminates.

Authors in [47] tested curved glass specimens with similar bump test, and found agreement with the other paper, showing an increased damping ratio.

3.7. Nanofibers doped with CNT

A selection of works testing polymeric electrospun nanofibers doped with carbon nanostructures such as CNT or CNF is here presented. CNF/CNT are added into the polymeric solutions and electrospun together with the nanofibers, after a dedicated sonication process with the purpose of homogenising the solution. An interesting reading on how these are produced and employed can be found in [118–120].

CNT is the structure that has been the most employed in a range of different electrospun nanofibers. In [121] the effect of adding MWCNT has been assessed performed testing P(St-co-GMA) copolymer and P(St-co-GMA)/MWCNT nanofibrous mats interleaved into carbon fiber prepregs, and comparing the results. The authors performed flexural, ENF and Charpy-impact tests to determine the effect of adding MWCNT to the P(St-co-GMA) nanofibers. The improvements that the carbon nanoaddition provides to the laminate is impressive, compared to its amount: flexural strength and stiffness increase up to 25 and 29%, respectively, $G_{II,C}$ up to 70%, impact energy absorbance up to 20% and transverse tensile strength up to 27%. The weight of the interleaved was 0.2% of that of the total laminate, and the MWCNT accounted for only 1% of it. Authors analysed cross sectional fracture surfaces, and attributed as the reason for such improvements to the high compatibility of the interlayers with the surrounding matrix. Double-digit improvements have been registered by almost any experimental studies performed on carbon-doped nanofibers. In [122, 123] CNTs are added into PU nanofibers, and interleaved into epoxy-basal composite, registering 13% increase in tensile and 17.3% in flexural strength compared to neat material, addressing the improvements to an enhanced fiber-resin adhesion. In [124] CNTs are added into PA nanofibers and embedded into pure resin: resin with 3% of MWCNT-PA nanofibers (in which the CNT accounted for the 1% in mass) led to improvements of modulus of elasticity, elongation at break and tensile strength of 690, 51 and 239%, respectively. Authors addressed the improvements to the uniform distribution, alignment states and well interfacial

adhesion between the nanofibers, the MWNTs and the epoxy matrix, the PA6 serves as an intermediate layer and alleviates the modulus mismatch between the stiff MWNTs and the softer epoxy matrix. In [125], 5% and 10% CNTs/PSF interlayer has been interleaved into CFRP to investigate the mode I and mode II interlaminar toughness. $G_{I,C}$ improved 41 and 53% with 5% and 10% CNTs/PSF content, respectively, due to the intense deformation of the epoxy matrix promoted by the PSF micro-particles and pull-out of CNTs; similarly, $G_{II,C}$ increased 25 and 34%, respectively, due to better compatibility between epoxy and PSF. Flexural properties also improved: with 10% CNTs/PSF interleafs, flexural strength and flexural modulus improved of 27 and 29% compared to the control samples, respectively, owing to the reinforcing effect of the CNTs, simultaneously improving the interlaminar toughness and in-plane properties of the composite laminates.

4. Reduced properties

As shown in the previous sections, it is a general agreement that the nanofibers, under most conditions, are a powerful and effective reinforcement against delamination. However, few papers show a reduction of laminate's properties, and the aim of this section is to speculate what the causes might be:

- in [20, 21, 23, 44] it is shown that mechanical properties of nanomodified samples drop when the nanolayer reaches a certain thickness. It is observed that there is a threshold value on the amount of nanoreinforce after which the compliance of a randomly aligned polymeric nanofibrous mat overcomes the strengthening effect of the same;
- in [28], PAN, PCL and PVDF are used to produce nanofibers, and only PCL provided good results. Authors highlighted the need for a correct polymerisation-induced phase separation. The high viscosity of the polymer may retain the diffusion of the matrix through the nanofibers during the curing process, making the choice of the polymer a critical aspect with regard of the resin. The importance of the nanofibers-composite interaction is also presented in [35], where significantly different results have been found when interleaving the same nanofibers into different laminates;

- in [38], it is shown that also the load plays an important role when addressing the effectiveness of the nanoreinforce. Authors registered a significant slower crack propagation under Mode II loading than under Mode I due to the fiber direction. It is demonstrated that under Mode I, the loading of the nanofibers is less optimal and dependent on both the fabric architecture of the primary reinforcement, and on the presence of a carbon fiber bridging zone. Similar results have been found in [59, 61, 73] where different outcomes have been registered between Mode I and Mode II tests on the same samples. ENF nanomodified specimens registered improved properties compared to the neat configuration, while DCB specimens did the opposite. In [73], it is speculated that it may be attributed to improper wetting compaction;
- in [75, 76] it is shown that TEOS-nanomodified impacted specimens have larger delamination than the pristine ones, with lower strength after impact. It can be noted that other works using the same nanofibers [71–73] registered improvements when a comparable amount of nanofiber is interleaved. The detriment found in [75, 76] may be attributed to the fact that these last authors manufactured composites in autoclave, using prepreg, while those that registered improved properties manufactured samples using VARTM moulding. It is a subject that would require a deeper investigation, but these results lead to the idea that VARTM process may result in better resin penetration through the nanofibers, while the prepreg is more prone to create voids that weaken the interface if the nanomat is not porous enough;
- in [93] the propagation fracture energy has been found to be slightly lower in the interleaved samples compared to the non-interleaved ones. This has been attributed to the fact that woven fabrics introduces several in-homogeneities at the meso-scale that may favour the onset of a stick-slip propagation behaviour and the formation of thick carbon fiber bridges in the wake of the delamination.

5. Lack of research

The research on electrospun nanofibers for reinforcing purposes started several years ago, a large number of papers has been published, and a solid knowledge has been built on the topic since then. Nevertheless, the path for a full understanding of the mechanisms that rule the behaviour of the

nanoreinforce has still to be completed. Despite nanofibers have already found application in various fields, their wide introduction in laminates for reinforcing purposes has still a long way to go. Among the issues that still need to be solved (costs, dangerous chemicals, low production rate, strong dependence from environment, slow lay-up, full compatibility with the resin, low repeatability of the interleaved composite, ...), this section focuses on the gaps that still need to be filled from a research point of view, in terms of understanding the behaviour of nanomodified composite.

As shown in the tables presented in Section 3, fracture mechanics is largely the most common approach for investigating nanomodified composites, due to the interest in evaluating the fracture propagation, related to the delamination behaviour of the laminates, and thus to their most common failure mode. However, this review shows that there are still few poorly investigated aspects:

- Mode I testing has covered almost all the main aspects; however, fatigue behaviour and fracture propagation under static load in GFRP still need to be fully addressed and investigated;
- Mode II testing, instead, has still several gaps mainly due to the difficult task of addressing crack propagation in the sliding mode. For this reason, data on fatigue behaviour and $G_{II,R}$ for both GFRP and CFRP is almost absent.

Research on impact behaviour of nanomodified samples is affected by the large number of variables that has to be taken into account (thickness, lay-up, energy and speed of the impactor, number of nanolayers, ...), and it is still far to be completed. From the outcome of this review, there is still very little known about an optimal strategy to effectively interleave a laminate and strengthen its resistance to impacts. Samples for impact tests are usually larger than those used for the other tests, and require a significantly greater amount of nanofibers (i.e. for Mode I and Mode II samples only the delaminated interface is interleaved), because several (if not all) interfaces are nanomodified, making the research expensive in terms of resources and time.

The field of research that is still at its beginning is that on vibrations: only two papers have been found investigating vibrational behaviour of nanomodified composites. A very important aspect is the effect of the nanointerleave

on the damping of the structure it is interleaved in, which will have important application and implication for those structures which free vibration are source of problems. If nanofibers are proved to be able to reduce, or tune, reliably, the free vibration response of a structure, it will give a significant impulse to their application in industry.

One of the main bottleneck to a greater diffusion of nanofibers in industry is its slow production rate [16, 126]. Despite several companies around the world are producing machines for electrospinning, the technology is not mature enough to be introduced in a production line, at least for the vast majority of the manufacturer. A research effort on improving manufacturing techniques, focusing on reducing the time, would significantly benefit and encourage the use of nanofibers in a larger number of applications.

6. Conclusions

In this review the state-of-the art of composite laminates interleaved with electrospun nanofibers for reinforcing purposes has been introduced and analysed.

The papers found in literature have been presented with a mechanical approach, focusing on the main types of load an object can be solicited with. Case by case, the effect of the nanofibers and their working mechanism has been deeply investigated by many researchers, and this review has summarised the main and most significant outcomes. The vast majority of the results shows that a nanofibrous interlayer between plies of a laminate can bring significant benefits from structural and load bearing points of view. Nanofibers' impact on a laminate is minimum, if not negligible, in terms of increase of weight and sizes, but the interleaved laminate's mechanical properties are significantly improved compared with that of the base material.

The research on this topic is certainly not over, as there are several issues still to be addressed, but nanofibers have the potential that makes the investigation worthwhile. When the technology will improve the few weak points still to be addressed, it is believed that nanomodified composites will have massive diffusion in the industry and in a wide range of products and application.

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