Out-of-autoclave molding of carbon fiber composites pipes with interlaminar carbon nanotubes

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Abstract. Carbon fiber reinforced (CFR) composite rings with and without interlaminar carbon nanotubes (I-CNTs) were manufactured starting from high performance prepregs used in aeronautics. Nano-particles deposition was obtained by an innovative easily scalable procedure which does not affect composite processability. A CNTs-solvent solution was sonicated for an established time to reduce bulk CNTs agglomerates. The solution was poured on prepreg stripes and left at room temperature for solvent evacuation. The prepreg stripes were wrapped on steel pipe to obtain the annular configuration and manufactured by an out-of-autoclave (OOA) process. The consolidation pressure was applied through a thermo-shrinkable tube and curing occurred in oven. Stereomicroscopy and mechanical tests were performed on CFR and I-CNTs/CFR rings. A good adhesion among the plies was observed as well as the positive effects of CNTs deposition; an increase of 34%, 15% and 17% was obtained for the stiffness, the peak load and the fracture energy of the functionalized rings, respectively.

Introduction

The extensive use of carbon fiber reinforced polymer (CFRP) composites in highly-valued fields such as Automotive, Aeronautics and Aerospace is mainly due to their high structural performances and light weight if compared to alloys. Currently, the real challenge in these fields requires the development of new qualified materials and new production technologies that are more scalable at industrial level.

Generally, composite stiffness and in-plane strength are governed by reinforcing fibers, whereas matrix and matrix/fibers adhesion are responsible for creep, peeling strength and interlaminar shear strength (ILSS) resistance. Adding fillers in the polymer matrix before fiber impregnation can lead to property improvements, achieving even higher performances. For this reason, more attention must be paid to resin processability which can be negatively affected by changes in its formulation, with detrimental consequences for the final composite. Carbon nanotubes (CNTs) can interact with the matrix at a microscopic level enhancing its rigidity and strength. The CNTs insertion affects the resin mobility with a reduction in all the stages of the curing process. Consequently, the increase of the resin viscosity is responsible for lower reactivity and worse fiber impregnation during manufacturing of composites structures.

In the last decades, many researches discussed the positive effect of CNTs insertion in the resin matrix. All the studies are focused on the definition of an easily implementable and repeatable technique for spreading nanoparticles on dry or wet carbon fibers. Different solutions have been investigated. The most adopted strategies deal with the modification of the polymeric matrix before impregnation (massive mixing), using a massive interlayer between prepreg plies and the use of dispersed nano-reinforcements (interlaminar deposition).

Positive effects arising from mixing nanoparticles with the matrix before wet lamination of CFR fabrics were demonstrated by Leão et al. [1]. In particular, the positive effect was evaluated on the mechanical performances of carbon/epoxy composites with an increase of the ultimate tensile strength and the toughness of about 18% and 62%, respectively. Tefera et al. [2] demonstrated an increase in flexural strength of laminates manufactured by resin transfer molding with CNTs treated and non-treated with nitric acid to obtain carboxylic functional group. These solutions mixed with epoxy resin formed the matrix in 24 h – 96 h. Increments of about 17.4% and 15.3% for manufactured samples were measured for treated CNTs and for the lowest mixing time (24 h). Massive mixing not always ensures benefits to molded composites; in fact, matrix properties can be severely affected as well as the resin processability. For this reason, in industries other solutions are preferred, being the resin of the matrix already qualified for specific applications and changes in its properties are generally undesirable.

Interlaminar deposition of nano-reinforcements is another possible strategy that has a small influence on the resin processability. The insertion, as interlayers of hierarchical short carbon fibers synthetized with CNTs was proposed by Zhou et al. [3] who obtained increase of 125% in the fracture energy of nano-reinforced CFR epoxy laminates. Following this approach, Zheng et al. [4] manufactured CBT/polysulfone nanofiber paper by vacuum filtration, to be used as interleaf. Enhancements in interlaminar toughness both in mode I and mode II were obtained. The former is related to pre-cracked laminate failure governed by peel forces and the latter to the crack propagation by shear stresses. Moreover, interleave thickness greatly affects the interlaminar properties. Ou et al. [5] demonstrated that the interlaminar fracture toughness in mode I increase up to 76% for an interleaf thickness of 10 μm whereas it decreases to 36% by increasing thickness interleaf up to 15 μm. On the other side, mode II fracture toughness increases continuously when increasing the interleaf thickness up to 15 μm. Another important aspect was demonstrated by Nasirmanesh et al. [6] who inserted a CNTs interleaf in the midplane of an 8-ply laminate. In this case, impact tests revealed that crack initiation and propagation is confined around the CNT interleaf whereas it spreads all over the thickness for the base laminate. Moreover, flexural tensile failure is the predominant fracture mechanism on CNTs sheet base laminates compared to interlaminar shear breakage. Static tests revealed that tensile strength is the same whereas residual tensile strength and corresponding strain to failure was higher for CNT based laminates. Superior mechanical performances can be obtained by an aligned CNT configuration over composite plies. This effect is exalted by the use of thin plies as demonstrated by Cohen et al. [7]. In particular, an increase in the ILSS up to 10% compared to traditional laminates were obtained. Kaynan et al. [8] produced thin CNT reinforced adhesive interlayers used to mold interlayered CFR laminates. On one hand, the use of massive interlayers allows to increase the composite mechanical properties, on the other it leads to a lower manufacturability. Drawbacks come from both deposition strategies. Yourdkhani et al. [9] demonstrated that re-agglomeration and filtration of CNTs during liquid processing affect CNTs dispersion in the resin matrix. At first, they evaluated the degradation of CNT dispersion and the results underlined that laminates with interlaminar nano-reinforcements exhibited values slightly greater for compressive strength and electrical conductivity than traditional neat laminates. To date, the most viable solution is integrating CNTs in composites by using functionalized interlayers even if a more complex manufacturing procedure is necesary. This trend is confirmed by Li et al. [10] who inserted CNT buckypaper in the mid-plane of glass fibre reinforced laminates.

In previous works, the authors developed an innovative procedure easily scalable on an industrial level. The process allows CNTs deposition during the lamination sequence without adding intermediate step and thus avoiding to negatively affect the processability of the matrix. Specifically, multiwalled carbon nanotubes (MWCNTs) are mixed with a solvent and sonicated for an established time to exfoliate the bulk agglomerates. After, the mixture is poured on one surface of the uncured CF prepreg plies and left at room temperature for solvent evacuation before lamination. Finally, increase in peeling and bending strength were obtained compared to neat laminates, when commercial automotive prepreg were used [11], as well as a better bending strength was achieved for aeronautical autoclave-molded prepregs [12].

In this study, MWCNTs were deposited as interlaminar reinforcements (I-CNTs) on a commercial aerospace fabric prepreg with the same procedure described above and developed by the authors. In this case, the laminated prepregs were molded in a tube shape with and without I-CNTs. Specifically, an out-of-autoclave process was used for the molding step as already done previously by authors for thermoplastic composites [13]. Observations with stereomicroscope and compression tests up to failure were carried out to evaluate both the soundness of the manufacturing process and the mechanical performances.

Materials and Methods

Tube shaped composite samples with and without 1wt% I-CNTs were manufactured by an out-of-autoclave (OOA) process. A 1 wt% of I-CNTs was chosen thanks to authors’ previous studies [10, 11] that had established a good interaction of MWCNTs with the resin matrix with this percentage. Higher percentages caused an excess of CNTs which worsen the interaction with the resin matrix. Conversely, lower percentages cause less detectability of matrix interaction effects. Commercially epoxy matrix prepregs (40%) CYCOM® 977-2 by Solvay, commonly used in aeronautics, were used in the experimentation as well as commercial MWCNTs. The whole manufacturing process is shown in Fig. 1.

MWCNTs had a length of 10-30 μm, minimum outer diameter of 8 nm, purity higher than 95 wt%, ash lower than 1.5 wt%. Exfoliation of MWCNTs occurred in order to minimize the presence of bulk aggregates, and subsequently interlaminar deposition was performed. A MWCNTs-isopropanol solution was mechanically mixed through a magnetic stirrer for 1h and sonicated for 1h. In this way, a good level of nanoparticles exfoliation was achieved and agglomerates were not visible at naked eye. The solution was poured on prepreg stripes 960 mm in length and left at room temperature for 1 day to allow solvent evacuation. From now on, neat samples have been named CFR while the ones with interlaminar carbon nanotubes have been called I-CNTs/CFR. Prepreg stripes were wrapped around a steel pipe, being the mold, of 50 mm as nominal outer diameter and of 220 mm in height, and about 6 windings were obtained. The assembly was placed inside a thermo-shrinkable tube made of crosslinked polyethylene (PEX) by ELCON. A release film of fluorinated-ethylene-propylene (FEP) was placed on the rings-mold and at rings-PEX interfaces to favor the tube extraction. When heated, the thermo-shrinkable tube reduces its initial non-equilibrium diameter (85 mm) to a smaller equilibrium-diameter (25 mm), exerting a circumferential pressure on the tube surface. Curing was carried out in oven (by Nabertherm) at 180 °C for 1 h, and after cooling at room temperature, the workpieces were extracted. Four rings with and without I-CNTs were produced.

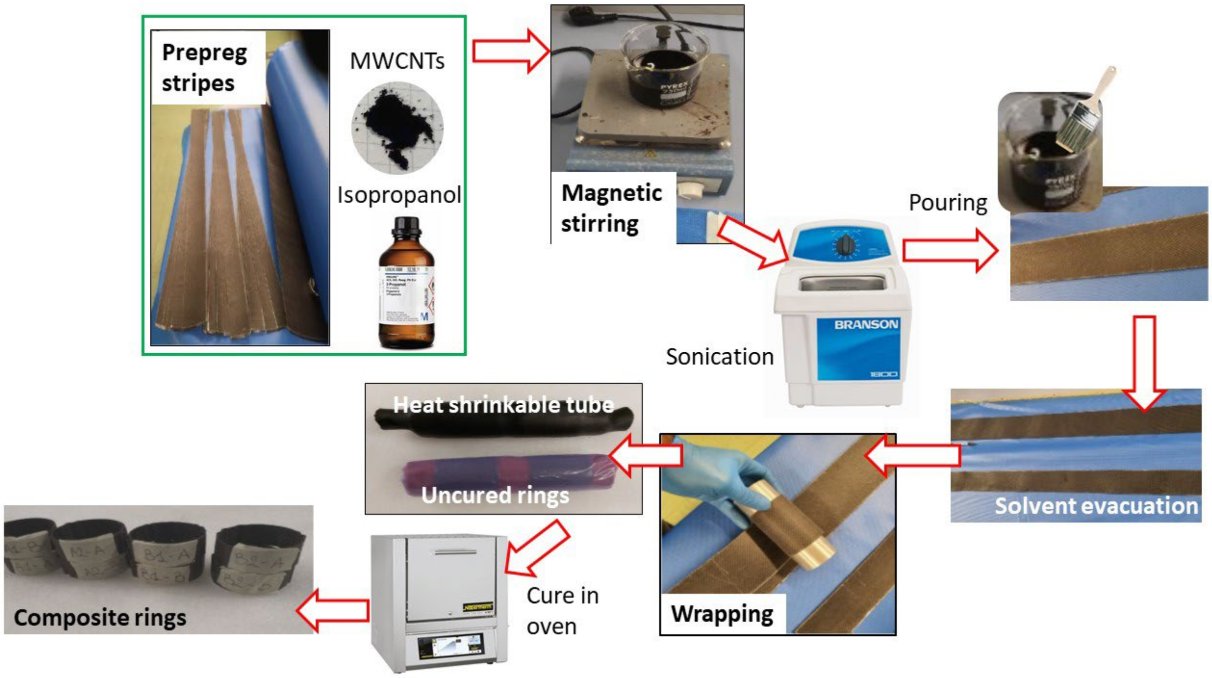

Fig. 1. Procedure of I-CNTs deposition and rings molding by the out-of-autoclave process.

Physical dimensions were measured and densities were evaluated through a hydrostatic scale to reduce the effects of manufacturing defects. Optical observations through a stereomicroscope Leica S9i were made to investigate plies adhesion and compaction. Compression tests up to failure were performed on an MTS Alliance RT/50 Universal testing machine to investigate the effect of I-CNTs on the macroscopic behavior of the composite rings. Transverse compression setup configuration, where the axis of-the movable machine crosshead is perpendicular to the longitudinal axis of the rings was used. A test speed of 1 mm/min and an acquisition frequency of 10 Hz were set.

Results and Discussions

Reduction of the molecular mobility in composites laminates is the key factor to understand the positive effect of the nanoparticles with the polymer matrix. The strongest effect is obtained when interpenetrating structures are placed in the interlaminar region. Also, the resin processability in thermosetting-based composites should be affected as little as possible, and molecular mobility is the main parameter to take into account. Fiber impregnation and diffusion, responsible of high polymerization degrees, are enhanced by low resin viscosity. In light of this, the positive effect of CNTs integration is a compromise between the improvements in the structural behavior and the minimum influences on the resin processability. This aspect represents the main goal of all the new developed technologies.

The proposed manufacturing procedure of interlaminar nanoparticles deposition does not alter the resin composition, minimally affecting its processability. Moreover, the use of additional layers either in the form of interleaves or adhesives is avoided. This procedure only adds a technological step consisting in sonicating the resultant isopropanol-MWCNTs solution to debundle and exfoliate CNTs and to reduce the presence of bulk agglomerates. Also, the solvent is used only to obtain a uniform distribution over the prepreg surfaces and its ease of evacuation allows to leave only the interlaminar nanoparticles. The use of commercially available prepreg, already optimized for industrial applications, requires a good experimental setup for interlaminar nano-reinforcements deposition, in order to enhance the structural behavior of functionalized laminates.

The proposed out-of-autoclave molding process guarantees good compaction among composite layers, after winding. The stereoscope observations, shown in Fig. 2, clearly highlight the six windings obtained after wrapping. Bleeding occurred during curing and a good level of adhesion was reached; fibers interpenetration among the layers was not observed. Defects related to the manufacturing procedure were observed in some areas since the mold was not optimized at this stage of the experimentation. The external surfaces un-homogeneities are due to asperities of the inner surfaces of the PEX tube and these irregularities can be easily overcome optimizing the molding assembly. However, the main objective in the study is to verify the feasibility of the process and this has been confirmed.

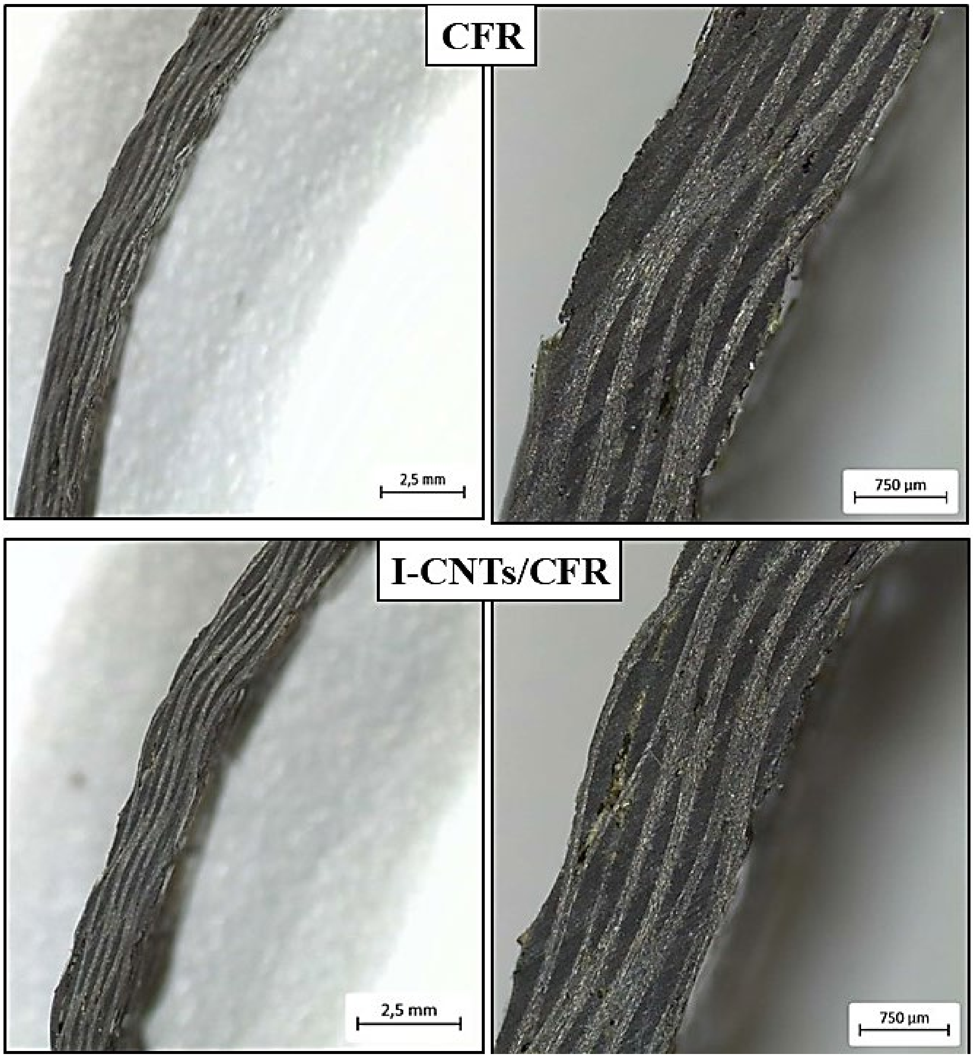

Fig. 2. Stereoscope images of CFR and I-CNTs/CFR ring samples.

CFR and I-CNTs/CFR rings had similar thickness of 2.1±0.2 mm and 2.0±0.3 mm respectively, nearly 0.3 mm for each ply. In Fig. 3 the evolution of thickness for rings with and without CNTs is shown in polar coordinates, that is, ring thickness was measured at a different angular position. Densities of CFR and I-CNTs/CFR rings were 1.37 g/cm^3 and 1.34 g/cm^3 on average. They were measured through a hydrostatic scale because of the irregularities on the rings surface. Lower densities of functionalized composites are due to the presence of interlaminar reinforcements which slightly increase the distance among prepreg plies.

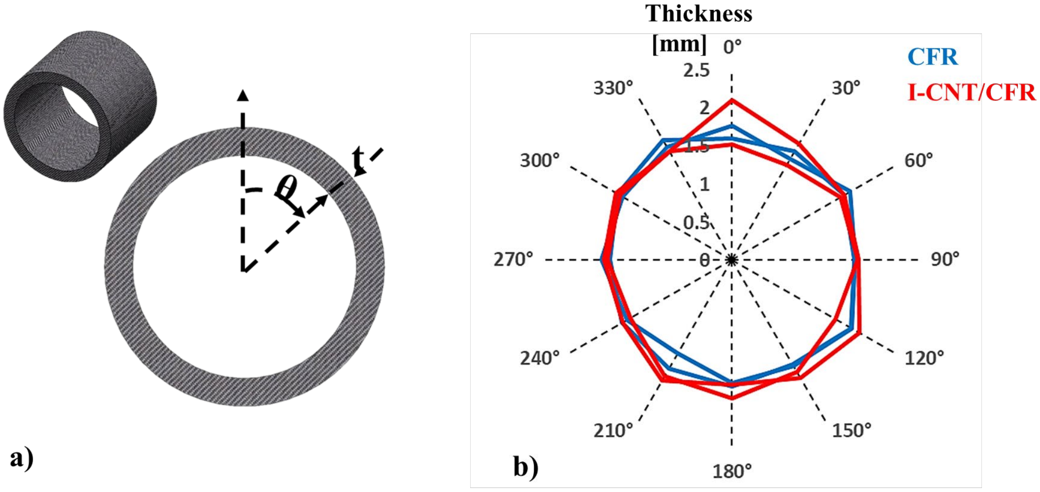

Fig. 3. Evolution of thickness for CFR rings and I-CNTs/CFR rings in polar coordinates.

Improvements by the addition of MWCNTs can be seen at room temperature as a consequence of the molecular mobility reduction mechanism. Compression tests were performed in transverse configuration and results are shown in Fig. 4 as load-displacement curves.

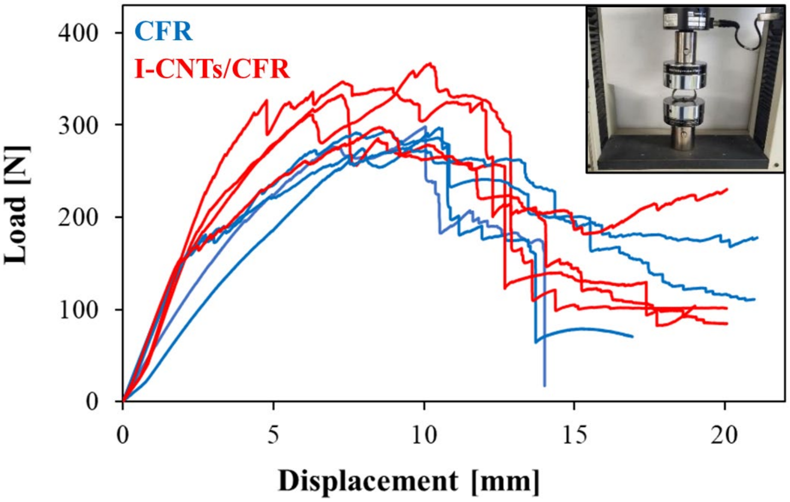

Fig. 4. Compression curves of composite rings.

Table 1. Stiffness, load peak and fracture energy values calculated from the curves.

	Stiffness	Peak Load	Fracture Energy
	N/mm	N	J
CFR	65 ± 20	291 ± 11	3.5 ± 0.7
I-CNT/CFR	86 ± 7	336 ± 34	4.1 ± 0.6

The non-homogeneous nature of the composite rings is responsible for some oscillations in the load-displacement curve, which do not affect the interpretation of the interlaminar CNTs effect. Stiffness, peak load and fracture energy are summarized in Table 1. Despite the lab scale OOA procedure, stiffness, peak load and fracture energy increase of 32%, 15% and 17%, respectively, for I-CNTs composites compared to traditional ones. In particular, also considering only the better responses for CFR without I-CNTs (e.g. 83 N/mm for stiffness, 283 N for peak load and 4.1 J for fracture energy), the ameliorative effect of the CNTs would be in any case confirmed. The manufacturing process does not affect the positive role of CNTs at all. This preliminary experimentation, aims to highlight the effectiveness of interlaminar CNTs on the global mechanical behavior of I-CNTs composites. The increased structural performances aimed by CNTs insertion confirms what found also by literature review about this topic [9,10].

Summary

The use of commercial materials is the best solution for high-valued engineering applications in which material qualification and certification has strict restrictions. Commercial material innovation is strictly related to the improvement of already high performances which should be enhanced through simple and easily scalable processes. In this light, any proposed improvements in laminate manufacturing should minimally affect the initial structure and composition of the materials. This, in order to avoid the re-designing of the structure or the change of the processing strategies. All these needs have been matched by the proposed manufacturing procedure consisting of interlaminar deposition of CNTs on CFR prepregs by CNTs-solvent solution dispersion. In particular, the proposed additional step for composite functionalization does not alter the commercial material processability. CFR and I-CNTs/CFR composite rings were manufactured by a non-conventional out-of-autoclave process which guarantees plies compaction and repeatable structure quality even if further optimization in the molding setup are needed. The effects of CNTs deposition were demonstrated by the slight density reduction of I-CNTs composite rings with an increase of distance between the plies. Moreover, the compression tests showed a positive effect with an increase in the stiffness and in the peak load of I-CNTs/CFR composite rings. Further analysis could be performed to understand the effects of CNTs insertion on molecular mobility at higher temperature. Moreover, the ideal CNTs' content as function of the adopted manufacturing process is another big issue as well as the investigation on delamination mechanisms.

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