Investigation of Interlaminar Fracture properties of Out of Autoclave manufactured CFRPs having CNTs modified Carbon Fiber reinforcements

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Abstract
The present study focuses on the development of carbon fiber reinforced polymers (CFRPs) with the incorporation of carbon nanotube-enriched sizing agent. Four different kinds of CFRP laminates, one with neat matrix and three doped with various weight concentrations of Multi-walled Carbon Nanotubes (MWCNTs) using vacuum-assisted resin infusion process (VARI) were manufactured. The incorporation of CNTs is applied on the surface of carbon fabrics during the preparation of carbon fabric preform and prior of resin is infused. Experimental results showed that the Mode I fracture toughness was significantly increase up to 110% for the concentration of 1.5% wt. of MWCNTs, whereas composites with the addition of 0.5% wt. MWCNTs did not showed enhancement compared to pristine carbon fabric/epoxy composite. Mode II results were enhanced up to 36.5% with the incorporation of 2.5% wt. of MWCNTs, while the nano-modified CFRP samples with the weight content of 0.5% wt. MWCNTs showed increase up to 21%, compared to reference CFRP samples.

1. Introduction

Fiber–reinforced polymer (FRPs) composites are mainly used as structural materials in a broad range of different areas including aerospace, marine, automotive, wind energy transportation and sporting goods industries. [1]. This tendency is clearly driven by the need for usage of structural materials with excellent mechanical properties, low specific strength- to- weight ratio, notable stiffness and corrosion resistance, making them the most ideal candidates. These superior properties make them more desirable when compared to the other conventional materials such as metals. However, they are most vulnerable to the out-of-plane properties, especially delamination resistance due to the absence of through the thickness reinforcement. A weak fiber-matrix interface and the brittle nature of polymer matrix in composite laminates leads to delamination failures. More specialist through-thickness reinforcement techniques have been successfully developed to improve the interlaminar fracture toughness, such as 3-D weaving [2], stitching [3-4] or z-pinning [5], knitting, fiber hybridization, toughening the matrix resin and placing an interleaf, mainly of thermoplastic material, in the interplay regions of the laminate. These techniques are proved to be effective, but large resin rich areas are observed and the in-plane properties are degraded. Thus, it is necessary to develop an effective method to improve the through the thickness properties without degrading the in-plane properties [6-7].

In last decades, carbon nanotubes (CNTs) are thought to be primary candidates for reinforcement in CFRP composites, due to the attractive mechanical and electrical properties [8-10]. Additionally, the small size and high aspect ratio make them an ideal filler material in order to incorporate them into

resin matrix at low weight fractions. In recent years, many research works have investigated the influence of incorporating nanomaterials on the properties of FRP composites. Some studies focused on modifying the epoxy resin properties by incorporating carbon nanotubes (CNTs). However, a directly addition of CNTs into the matrix would increase the resin's viscosity, making infiltration of carbon fiber fabrics and it is impossible to implement them during the Out-of-Autoclave (OoA) processes. On the other hand, other studies focused on modifying the reinforcement' properties by grafting CNTs on the fabric surface, improving the interfacial bonding between fiber and matrix, but it causes the fiber strength degradation because of the extreme condition and is difficult to implement on an industrial scale [11-12].

As an alternate method, the spraying technique is a simple and cheap method for coating of carbon fabric surface with carbon nanotubes, obtaining significant improvement in out-of-plane properties such as interlaminar fracture toughness. For this technique, carbon nanotubes are dispersed into solvent by ultrasound probe and then an airbrush system is used to uniformly spray of CNTs onto the surface of carbon fabrics. The solvent on the fabric is removed, remaining the CNTs-deposited fabrics. This technique is easier to scale-up to the industrial sectors.

In this study, CNT-enriched sizing agent (SA) was incorporated on the surface of four carbon fabric layers at mid-plane of CFRP composite laminates using a bulk-dipping techmique. Four laminates at different contents of MWCNTs were produced by liquid resin infusion (LRI) process. Sizing agent was sonicated and applied on a carbon fabric surface at room temperature. The achievement of this study is to assess the ability of CNTs to enhance the interlaminar fracture properties of the composites. Therefore, this technique allows the integration of nanoengineered hierarchical composite systems with tailored CNT localization for improved composite performances.

2. Experimental Procedure

2.1. Materials

For the purposes of the present study, TR30S carbon fiber twill weave 2 x 2 fabric was selected as the base material. The fabric was supplied by Fibermax Composites (Greece) with a filament count of 3K, fibre areal weight of 194 g/m^2 and a dry ply thickness of approximately 0.35mm. The resin system was purchased by Resoltech Advanced Technology Resins (France) and consists of the thermosetting epoxy resin Resolcoat 1400, the hardener Resolcoat 1407 and the accelerator AC140 in ratios of 100:90:0.5 by weight. A CNT-enriched liquid sizing agent used was SIZICYL XC R2G (Nanocyl SA, Belgium) containing 6.2% solid content of multiwalled CNTs. The sizing agent can be used to size fibers before further impregnation by the resin matrix and is compatible with glass and carbon fibers.

2.2. CFRP laminate preparation

Four carbon fiber composite (CFRP) plates 200 x 300 mm^2 were manufactured by Vacuum Assisted Resin Infusion (VARI) process. The CFRP laminates consisted of sixteen carbon fabric plies which were stacked on a tool. The nano-doped laminates were produced by varying the amount of CNTs and sizing agent. Three MWCNTs contents were used, including 0.5, 1.5 and 2.5 %wt. to the weight of epoxy resin.

Table 1. Amounts of materials used to produce the carbon fiber composite laminates

Material	MWCNTs (theoretical) (%wt.)	MWCNTs (%wt.)[1]	SIZICYL XC R2G mixture (g)[2]	SIZICYL XC R2G (g)
Reference	0	0	0	0
Plate 1	0.5	0.63	53	9
Plate 2	1.5	1.42	53	23
Plate 3	2.43	2.43	53	48

[1]Concentration of MWCNTs in the epoxy
[2]Amount of Sizing Agent with distilled water for treatment of four CF plies

The sizing agent mixture was prepared as follows: first, a suitable amount of sizing agent was diluted into a suitable amount of distilled water and then the obtained mixture was sonicated for 2h in an ultrasonic probe (Bandelin), operated at an output power of 60W. The quality control of mixture was performed using optical microscopy, placing one drop of sizing agent mixture between two glass plates in order to secure the absence of the agglomerates. After that, the mixture was degassed in a vacuum chamber for 5 min and the amount of 53 g was applied on the four plies of carbon fabric surface using a squeegee and a paintbrush. It is remarkable to mention that for each nano-doped laminate, different ratios of mixtures (sizing agent with water) were prepared in order to obtain the effective MWCNTs concentration, as it can be seen in Table 1.

In the case of nano-doped laminates, four nano-modified layers were treated with the mixture of sizing agent, as described above, and placed in the middle of the laminates. Furthermore, a polytetrafluoroethylene (PTFE) film of 70 mm wide, 250 mm long and 13 μm in thickness was introduced in the mid-plane (between 8th and 9th ply) of each composite laminate, acts as the initial crack during the Mode I test. The layers were left to dry for 1h at 150 ºC using a heating plate. Then, carbon fabrics of each laminate were covered by consumables layers (peel ply and a layer of a highly permeable medium) and sealed with a vacuum bag. The epoxy resin was infused under vacuum through the fabrics. The temperature of the resin and the preform was kept to approximately 40ºC during infusion process, according to manufacturer guidelines. The laminates were cured in a conventional oven for 4h at 80 ºC followed by post curing for 4h at 140 ºC. Regarding the production of an unmodified CFRP reference laminate, the same procedure was followed without the application of sizing agent at four central layers of laminate. The final thickness and the V_f calculated values of each plate were: 3.06 ± 0.02 mm and 58% for reference, 3.13 ± 0.03 mm and 57% for 0.5%wt., 3.07 ± 0.03 mm and 58% for 1.5%wt., 3.37 ± 0.02 mm and 54% for 2.5%wt. for nano-doped plates respectively.

2.3. Interlaminar Fracture Toughness

Interlaminar fracture toughness experiments were performed using double cantilever beam (DCB) and three point end-notched flexure (3ENF) according to Airbus Standard for both reference and CNT modified specimens on a hydraulic universal testing machine (Instron 8872) to evaluate the mechanical toughening effect introduced by the CNTs. Five samples were tested for each kind of produced laminate and for each type of experiment. The cured CFRP laminates were cut by a diamond saw machine into specimens with dimensions of 250mm in length and 25mm in width.

3. Results and discussion

3.1. Quality Assessment

Ultrasonic Testing (C-Scan) was carried out for the quality control of all produced CFRP plates. The equipment consists of a MISTRAS Group AD-IPR 1210-PCI card and a VUB2000 tank. The transducer was a Krautkramer single element probe at 5MHz, non-focal. The C-Scan runs for reference and nano-doped laminates showed acceptable quality without major defects (delamination, porosity and thickness variations), as shown in Figure 1. The color bar indicates the signal response from the weakest (green) to the strongest (red).

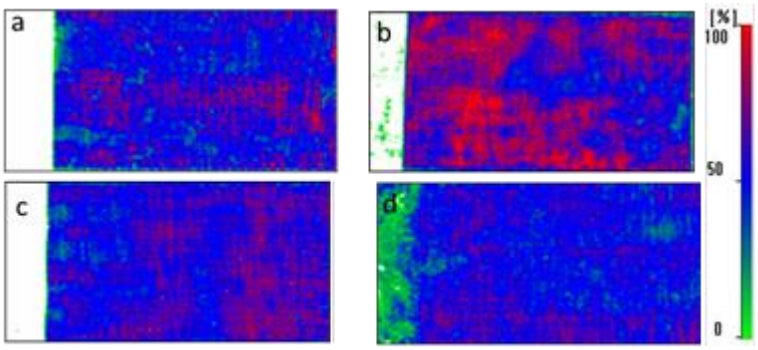

Figure 1. C-Scan inspection for produced composite laminates a) Reference composite plate, b) laminate with 0.63%wt. MWCNTs, c) laminate with 1.5%wt. MWCNTs and d) laminate with 2.43%wt. MWCNTs

3.2. Mode I DCB tests

As it can be seen, the G_{IC} values of nano-doped CFRP specimens are significantly higher than that of reference material. The higher propagation G_{IC} value, the more energy is required to propagate the crack, which should result in a greater resistance to delaminations. It is observed that an increase of about 110% is achieved with the incorporation of 1.5% wt. MWCNTs compared to the reference CFRP samples. Also, the addition of 0.5%wt. MWCNTs did not showed significant improvement in G_{IC} value, without the observation of knock-down effect, compared to baseline specimens, as shown in Table 2. Finally, it is worth to conclude that further increase of the weight content of MWCNTs of CFRP samples did not lead to further enhancement of G_{IC}, as it was observed in the case of nano-modified CFRP composites with the incorporation of 2.5%wt. MWCNTs.

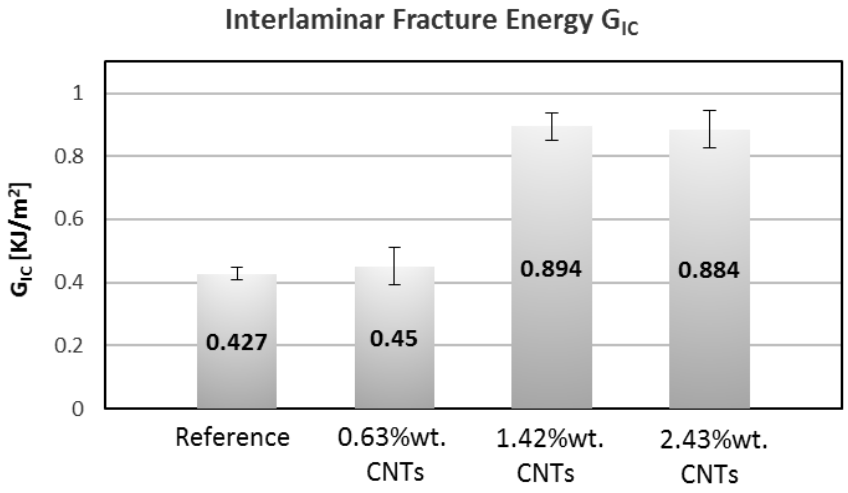

Figure 2. Interlaminar fracture energy under Mode I of carbon fiber/epoxy composites with different concentrations of carbon nanotubes (CNTs)

Table 2. Summary of G_{IC} fracture toughness increase compared to the reference material

Material	MWCNTs content (%wt.)	G_{IC} Mean (kJ/m^2)	G_{IC} Stdev (kJ/m^2)	G_{IC} increase compared to Reference
Reference	0	0.427	0.02	-
Plate 1	0.63	0.45	0.059	5.4%
Plate 2	1.42	0.894	0.043	110%
Plate 3	2.43	0.884	0.059	107%

3.3. Mode II ENF tests

The Mode II fracture toughness for all manufactured CFRP is presented in Figure 3. It is clearly seen that all the nano-modified samples showed significant enhancement in Mode II (G_{IIC}) fracture toughness compared to baseline samples. Although the nano-doped samples with concentration of 0.5%wt. of MWCNTs specimens did not showed further improvement of Mode I fracture energy compared to reference material, an increase of about 21.2% is achieved in G_{IIC} value. More precisely, it can be seen that the highest improvement of 36.5% in G_{IIC} achieved in the case of 2.5%wt. MWCNTs/composite samples, without presenting much difference in corresponding value of the addition of 1.5%wt. MWCNTs, as depicted in Table 3. Thus, as in the case of Mode I tests, further increase of the concentration of MWCNTs (above 1.5%wt.) of CFRP samples did not lead to further improvement of G_{IIC}.

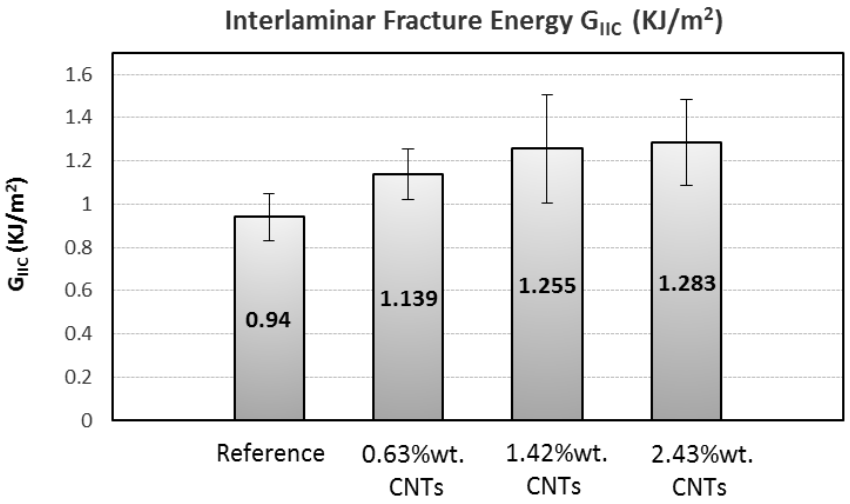

Figure 3. Interlaminar Fracture Toughness under Mode II of carbon fiber/epoxy composites with different concentrations of carbon nanotubes (CNTs)

Table 3. Summary of G_{IIC} fracture toughness increase compared to the reference material

Material	MWCNTs content (%wt.)	G_{IIC} Mean (kJ/m²)	G_{IIC} Stdev (kJ/m²)	G_{IIC} increase compared to Reference
Reference	0	0.94	0.1	-
Plate 1	0.63	1.139	0.118	21.2%
Plate 2	1.42	1.255	0.248	33.5%
Plate 3	2.43	1.283	0.198	36.5%

4. Conclusions

In the present investigation, a bulk-dipping technique was utilized for the development of multi-scale composites depositing MWCNTs on the carbon fabric surface assisted with coating of CNT-enriched sizing agent. The effects of CNTs on the mechanical properties of composite laminates manufactured by VARI process were investigated. Specifically, CFRP laminates with various concentrations (0.5, 1.5 & 2.5%wt.) of MWCNTs and reference material were produced. The presence of CNTs within inter-ply regions leads to great reinforcing efficiencies as presented by the increase in interlaminar fracture toughness of 110% and 33.5% at the concentration of 1.5% wt. MWCNTs, under Mode I and Mode II remote loading respectively, whereas further increase of weight content above 1.5% wt. MWCNTs did not exhibited further improvement of G_{IC} and G_{IIC} values. Finally, it is worth mentioning that the incorporation of 0.5%wt. CNTs onto the reinforcement did not report significant improvement both for G_{IC} and G_{IIC} values, compared to the reference material.

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