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Composite Laminates with Recycled Carbon Fibres and Carbon Nanotubes

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Abstract. *Carbon fibre reinforced composites were manufactured by using recycled carbon fibres (CF) and carbon nanotubes (CNT). Dry fabrics were impregnated by hot melting with 1 wt% CNT filled epoxy resin to produce prepregs. Subsequently, composite laminates were manufactured by vacuum bagging and autoclave moulding. Only materials and industrial equipment were used for the laminate production. Laminates with unfilled resin and virgin CFs were also manufactured for comparison. Samples were extracted for physical and mechanical measurements. Dynamic mechanical analyses and bending tests were carried out to evaluate the interaction between CNTs, resin matrix and recycled CFs.*

Keywords: *Recycled carbon fibres, Composite Laminate, CNT, Manufacturing*

1.Introduction

In Europe over 1 million tonnes of thermosetting composites are manufactured each year [1], and are destined to disposal at their end-of-life. Thermosetting matrices of these composites polymerize during the production process. A compact 3D network originates which cannot flow under heating. Management of end-of-life composites is a very well-known problem but valid technological solutions are absent for this aim. Nowadays, recycled carbon fibres (CFs) are available on the market for the production of new composite materials. Their properties are lower than virgin fibres. The aim of this study is to understand if an improvement in their performances may be achieved by integrating the use of carbon nanotubes (CNTs). In fact, CNTs can increase matrix strength and stiffness with very low amounts. However, as CNTs also increase liquid matrix viscosity and resin reactivity, they strongly affect composite manufacturing as well.

Several studies deal with the production of CF reinforced (CFR) laminates with CNTs but there is a lack of information about the use of recycled CFs in these laminates. In 2017, Leao et al. [2] evaluated the positive effect of CNTs and multi-layer graphene in carbon/epoxy composites by tensile tests. Laminates were made by wet lamination of carbon fabrics with the filled uncured matrix. The ultimate stress increased around 18%, while toughness had an improvement close to 62%. Zhou et al. [3] proposed the use of hierarchical short CFs synthesized with CNTs as interleaves to increase up to 125% the fracture energy of carbon fibre/epoxy (CF/EP) composite laminates. Zheng et al. [4] used vacuum filtration method to fabricate sandwiched CNT/polysulfone nanofiber paper as interleaf of the CFR laminates. They found that laminates with the sandwiched paper increased both mode I and mode II interlaminar toughness. Analogously, Kaynan et al. [5] developed micron-scale thin CNT reinforced adhesive nano-fibrous interleaves. They used these materials to produce interlayered CFR laminates. In 2018, Mikhalchan et al. [6] discussed that CNT assemblies such as vertical arrays and mats have the potential to provide additional interlaminar toughness for carbon fibre-reinforced laminates. However, they concluded that the achieved improvement in mechanical properties was not always been consistent so far. In their technological proposal, they introduced thin interlayers of continuous unidirectional CNT fibres for additional in-plane reinforcement and toughening of conventional autoclave-cured carbon fibre composites.

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Tensile tests on double-notched specimens with and without CNT fibre reinforcing layers showed that the introduction of relatively thin interlayers of continuous CNT fibres at local regions close to the notch tip increased the failure load and stress by 9% and the failure strain by 15% respectively, suggesting the toughening potential of CNT fibres. Abdelal et al. [7] evaluated vacuum bagging process to prepare carbon fibre/CNT composites but they found negligible improvements of the strength which were covered by data scattering. In the same year, Yourdkhani et al. [8] started with the consideration that effective dispersion of CNTs in the polymer matrix of fibre-reinforced composites is challenging due to the re-agglomeration and filtration of CNTs that occur during liquid processing. They used resin film infusion process for manufacturing composite laminates and investigating the degradation of CNT dispersion during high-temperature processing. Results showed that laminates manufactured by interleaved lay-up exhibited good compressive strength and electrical conductivity but the comparison with neat laminates was not impressive.

All these studies show that is difficult to obtain high improvements by integrating virgin CFs with CNTs. There is the doubt that better interactions could be obtained in the case of recycled CFs. In this study, recycled CF fabrics were used to produce laminates with CNT filled epoxy matrix. Laminates with unfilled matrix and other two types of virgin CF fabrics were also manufactured for comparison. Mechanical performances were measured by dynamic mechanical analyses and bending tests.

2.Materials and methods

For the experimentation three types of dry CF fabrics (virgin T200, recycled T300, and virgin T630) and two types of epoxy resins (with and without CNTs) were acquired. T200, T300 and T630 typically refer to the grade of carbon fibre, usually using tensile strength as a measurement index. For example, in T300 carbon fibre, the tensile strength is up to 3.5 GPa. This grade is not related to the tissue structure. In the present study, virgin T200 and T630 were both 0/90 fabrics whereas recycled T300 was a mat of short fibres.

The commercial CNT filled resin was Nano-Force E200 by Nano-Tech SpA with a nominal CNT content lower than 1 wt%. Technical details of used CNTs were not provided in the material datasheet. Prepregs were produced with the hot melting method by Microtex Composites Srl (Prato, Italy). Each single CF fabric was impregnated both with the filled and the unfilled epoxy resin.

After impregnation, 2-ply CFR laminates were manufactured with all the 6 prepregs with the technology of vacuum bagging and autoclave moulding by Carbon Dream S.p.A. (Florence, Italy). Up to 8 samples (120x20 mm^2) were cut from each single laminate for testing, 6 of which used for bending. The appearance of these samples is shown in Figure 1. All the samples had comparable surface quality.

Bending tests were performed to evaluate mechanical performances of CFR samples. Many preliminary tests were carried out to find best conditions to have a comparison between the different typologies of laminates. It was necessary to reach failure for all the samples but the small stiffness of such of them forced to reduce strongly the applied span. In the end, tests (by Alliance Insight 5 by MTS) were carried out at the rate of 1 mm/min with the span of 25 mm.

Burning tests were also made in oven at 500°C for 1 h to measure the CF content. In the end DMA tests (by Netzsch DMA 242C) were performed on 10x60 mm^2 which were cut from the original 120x20 mm^2 samples. DMA tests were made from room temperature to 200°C at 5°C/min with the frequency of 5 Hz.

3.Results and discussions

Thickness and density values of composite samples are reported in Table 1 in terms of average values and standard deviation σ. The ratio between σ and the mean value is also reported to have an evaluation of property dispersion. Thickness values were comparable for samples with and without CNT whereas CNT filled samples had higher densities. The dispersion is low for the density and generally acceptable for the thickness with a higher increase for the samples with recycled CFs. In fact, ratios between standard deviations and mean values are always lower than 2% for the density, and close to 3% for the thickness apart from T300 samples which reach 7%.

Samples after burning tests are shown in Figure 2. The difference between the regularity of the virgin fabrics (T200 and T630) and the recycled T300 mat is evident.

Figure 1. Manufacturing procedure for I-CNT/CFR samples

Table 1. Thickness and density values of CFR laminates

Laminate	Average thickness t (mm)	σ	σ/t	Average density ρ (g/cm^3)	σ	σ/ρ
Virgin T200	0.58	± 0.02	3.1%	1.21	± 0.01	0.5%
Virgin T200 + CNT	0.69	± 0.02	2.6%	1.22	± 0.01	0.6%
Recycled T300	1.47	± 0.11	7.4%	0.78	± 0.01	1.5%
Recycled T300 + CNT	1.42	± 0.09	6.1%	0.83	± 0.01	1.7%
Virgin T630	1.42	± 0.03	2.4%	1.39	± 0.02	1.2%
Virgin T630 + CNT	1.40	± 0.03	2.3%	1.40	± 0.01	1.0%

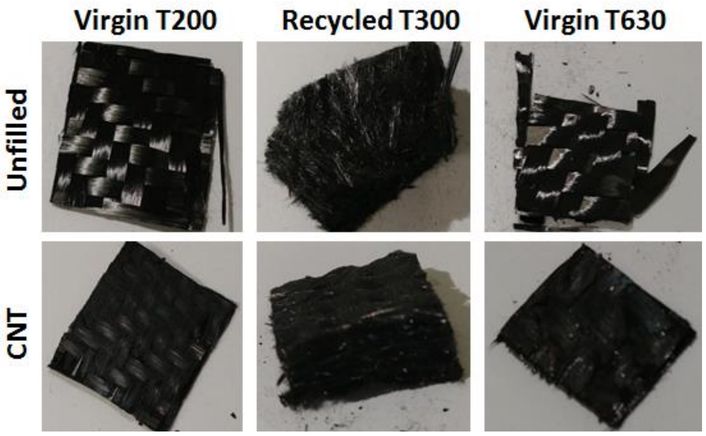

Figure 2. Samples after burning tests

Resulting fibre contents are shown in Table 2 as residuals from burning tests. It is not possible to recognize the effect of CNTs on the filling content. Lower fibre content was found for the Virgin T200 laminate in comparison with the laminate having the same CF fabric and CNTs. It can be expected that CNTs result in higher filling ratios but the difference (6.4%) is too much higher than the CNT content (less than 1 wt% of the resin matrix). For the other two fabrics, lower filling contents were found in the case of CNT functionalization. Probably the presence of CNTs affected resin fluidity during impregnation. Making a comparison between fabrics, the highest values of fibre contents were found for the CF recycled laminates. Also in this case, the difficulty of impregnating the CF mat of Figure 2 can be the reason.

DMA results are shown in Figure3 in terms of storage modulus (E') and loss factor (tgδ) curves. The curve of E' is characterized by an inflection point, the temperature of which is the glass transition temperature T_g of the resin matrix. The curve of tgδ is characterized by a peak, the temperature of which is T_g as well.

Table 2. Weight residuals from burning tests

Laminate	**Residual**
Virgin T200	42.5%
Virgin T200 + CNT	48.9%
Recycled T300	54.3%
Recycled T300 + CNT	50.0%
Virgin T630	36.6%
Virgin T630 + CNT	34.2%

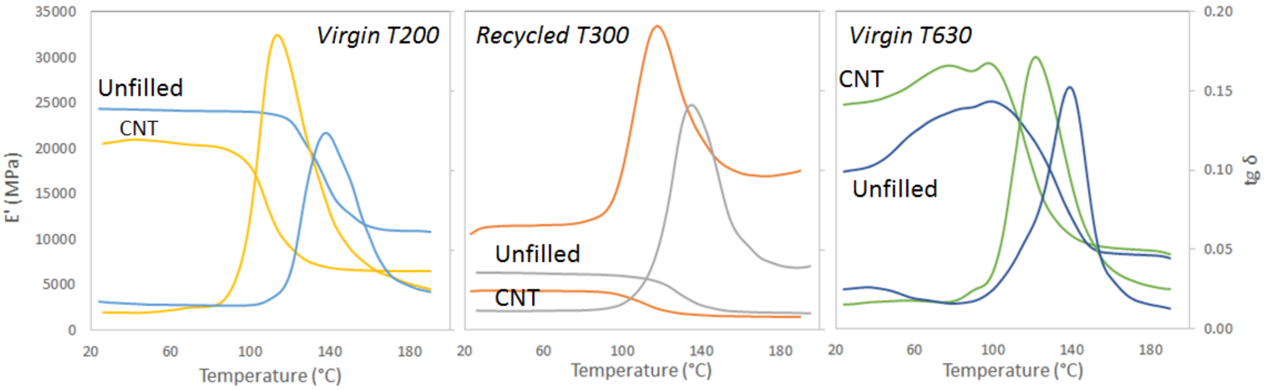

Fig. 3 DMA curves for CFR samples

Table 3. Glass transition temperature of CFR laminates

Laminate	**T_g from E' (°C)**	**T_g from tgδ (°C)**
Virgin T200	136.7	137.6
Virgin T200 + CNT	107.9	113.4
Difference	**-21.1%**	**-17.6%**
Recycled T300	128.2	137.6
Recycled T300 + CNT	111.6	117.5
Difference	**-12.9%**	**-14.6%**
Virgin T630	133.7	139
Virgin T630 + CNT	115.2	121.6
Difference	**-13.8%**	**-12.5%**

Only in the case of virgin T630 fabric, the CNT filled laminate showed higher storage modulus at low temperatures than the unfilled. In the other cases, the effect of CNTs on the material rigidity was negative. That is particularly evident for the virgin T200 fabric despite of the high fibre filling content measured in burning tests. Recycled T300 fabrics generally show very poor performances in comparison with virgin fabrics but this occurrence could depend on the presence of short fibres in the CF mat. The most important result from DMA analyses is that the glass transition temperature always decreased for all the laminates with CNTs. Extracted values for T_g are reported in Table 3 both in terms of the inflection point temperature of E’ and the peak temperature of tgδ. The difference refers to the relative increment of the filled sample in comparison with the unfilled sample. In the best case, the temperature decrease is never lower than 12%. As CNTs reduce resin mobility, resin cure is affected and lower polymerization degrees are reached with the consequence of a lower T_g. That is a typical occurrence in nano-filled resins but it is also a big drawback in composite manufacturing.

Therefore, CNTs may affect prepreg impregnation and resin matrix cure, and very poor performances are given to the laminates. Nevertheless, there are some conditions when CNTs provide a positive contribution as in the case of the virgin T630 fabric. This improvement is found only at low temperatures but it could be useful for such applications in automotive and aeronautics.

Table 4. Bending strength of CFR laminates

Laminate	**Average bending strength σ_R (MPa)**	**σ**	**σ/σ_R**
Virgin T200	544	± 49	9.0%
Virgin T200 + CNT	543	± 47	8.7%
Difference	-0.3%		
Recycled T300	124	± 35	28.2%
Recycled T300 + CNT	111	± 15	13.5%
Difference	-10.9%		
Virgin T630	666	± 13	2.0%
Virgin T630 + CNT	697	± 32	4.6%
Difference	4.7%		

In order to confirm the positive contribution of CNTs in the case of virgin T630 fabric, 6 bending tests were performed for each laminate. Results are reported in Table 4 in terms of average bending strength and related standard deviation σ. According to DMA results, a light improvement was found in the bending strength of the virgin T630 fabric with CNTs (+5%). Also dispersion was limited for this typology of CNT functionalized laminate. In the other two laminates, CNTs produced negative or no effects for the recycled T300 and the virgin T200 fabric, respectively.

4.Conclusions

The use of CNTs in CFR composite manufacturing is critical because of the negative impact of the nano-fillers on the fiber impregnation and laminate curing. Lower performances may be achieved by the integration of CNTs in the epoxy matrix despite of the costs and the increase in process complexity. The strategy of using CNTs to improve low performances of composites with recycled CFs seems to be not valid as CNTs may amplify problems arising from processing recycled CF mats. Nevertheless, there are some laminate configurations which may have advantages from using CNTs in the epoxy matrix as in the case of 2-ply laminates with T630 virgin fabric. In this study, a small increase of the bending strength has been obtained (about 5%) but that is a good result by considering that less than 1 wt% of CNT content was present in the resin matrix. Further material investigation is necessary to fully understand the CNT contribution in the composite performances and to tailor final composite performances. Nevertheless, commercial materials and processes have been used in the experimentation, and this choice resulted in the difficulty of changing material parameters (such as CNT filling content). As an advantage, the real impact of CNTs in the industrial sector of composite manufacturing has been evaluated. Other performances, such as electrical and EM shielding, has to be evaluated.

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