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# Performance analysis of MWCNT/Epoxy composites produced by CRTM

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## ABSTRACT

In the present work, carbon fiber reinforced polymer laminates were manufactured by means of Compression Resin Transfer Molding using a commercial epoxy resin additivated with Multi Walled Carbon Nanotubes to impregnate a carbon fiber fabric. The weight loads of nanotubes investigated were equal to 0.5 and 1%. As a comparison, composite laminates were also obtained using the pristine resin. **The same process parameters were used to manufactured additivated and unadditivated composites.**

The presence of nanotube agglomerates and the filtering effect of the carbon fiber fabric during the resin flow into the mold were investigated by means of Dynamic Light Scattering and microscopic techniques. In addition, Differential Scanning Calorimetry was used to analyze the polymerization reaction and to measure both the glass transition temperature of nanoadditivated matrices and the apparent viscosity. Viscosity was measured through rheological analysis. Mechanical tests were carried out on samples obtained from additivated and unadditivated laminates. It was shown that the apparent viscosity of the additivated matrices tends to decrease as the shear rate increases, reaching values similar to those of the pristine resin at high shear rate. The polymerization reaction of the thermoset matrix is influenced by nanotubes, as well as the glass transition temperature which increases with nanotube weight load. The analysis of the laminates shows homogeneous dispersion of nanotubes, indicating that no filtering effect occurs. Finally, tensile and flexural tests show a reinforcement effect of nanotubes both on strength and stiffness of the composite.

**KEYWORDS:** Carbon nanotubes, Carbon fiber reinforced polymers, Compression resin transfer molding

## 1. INTRODUCTION

Advanced composite materials are obtained by combining a high-performance matrix system (e.g. epoxy resin) with high-strength and high stiffness fiber reinforcement (e.g. carbon fibers). These materials, called Carbon Fiber Reinforced Polymer (CFRP), have recently attracted the interest of academic and industrial communities due to their high strength-to-weight and stiffness-to-weight

ratios which allow to obtain lightness and high resistance. Holmes (2017) reported that the interest of automotive industry in realizing safe and lightweight cars is increasing the diffusion of carbon composites.

Nowadays, researchers are focusing their attention on a new class of composite materials, the so-called nanocomposites, as reported by Kumar et al. (2017) and Rafiee (2017) in their investigations on the industrial application of nanofillers. Nanocomposites are typically obtained by adding Carbon Nanotubes (CNT) or graphene to thermoset matrices, used to impregnate carbon fiber preforms, in order to improve mechanical and physical properties of CFRPs. In particular, the use of CNTs is recognized as one of the most effective methods to reinforce a polymeric matrix for composites, as reported in the book published by Marcio Loos (2015). Carbon nanotubes consist of graphite sheets (carbon atoms arranged in parallel planes) rolled up to form a cylindrical structure. Their diameter is typically ranging between 0.7 and 30 nm. The very high length-to-diameter ratio allows to consider the CNT structure as virtually one-dimensional nanostructure. Holban and Andronescu (2016) showed that nanotubes are available in form of Single-Walled Carbon Nanotube (SWCNT), consisting of a single graphite sheet wrapped around itself, and Multi-Walled Carbon Nanotube (MWCNT), consisting of several coaxial tubes. SWCNTs are characterized by a diameter ranging between 0.5 and 10 nm, with an average value of 2 nm, high length-to-diameter ratio, pure and homogeneous structure and high costs. MWCNTs have a diameter of a few tens of nanometers and are easier to produce than SWCNTs.

The improvement of nanocomposite performances is affected by the quality of CNT dispersion into the matrix. As reported by Bhattacharya et al. (2006), several methods, such as solution assisted dispersion, tip/bath sonication, three-roll milling, heat stirring, can be used in order to achieve a homogeneous dispersion of CNTs. In this framework, Chandrasekaran et al. (2010) used bath sonication and tip sonication for preparing MWCNT nanocomposites showing that the best suspension preparation can be obtained with a tip sonification 2 min long, or with a bath sonication 20 h long. Hong et al. (2015) showed that the three-roll milling process results in a solvent free and scalable method for low and high nanotube loading.

The most used methods to determine the quality of the filler dispersion are microscopic analysis and Dynamic Light Scattering (DLS). Lucas et al. (2009) performed a microscopy analysis to measure size and dispersion quality of the CNTs in a bath used for sonication. Badaire et al. (2004) measured the size of CNTs dispersed on a matrix using the DLS technique. They showed that DLS does not require sample drying contrarily to microscopy.

The enhanced properties obtained by the addition of CNTs into thermoset matrices are: i) composite strength and damping effect, ii) electrical and thermal conductivity, and iii) self-monitoring. Terenzi et al. (2017) showed that the tensile modulus and bending strength of a fiber reinforced nanocomposite containing 1% in weight of CNTs are, respectively, 20 and 30% higher than the ones of composites without nanofillers. Forcellese et al. (2019) studied the effect of carbon nanotube dispersion on the surface hardness of carbon fiber-reinforced polymers. They showed an increase in microhardness equal to about 8% by adding 0.5% in weight of MWCNTs whilst the reinforcement effect decreases by adding 1% in weight of MWCNTs due to filtering phenomena. Khan et al. (2011) showed that the damping ratio of the CFRP-CNT hybrid composite increases with the CNT content. As far as the effect of CNTs on the resin chemistry is concerned, no consistent result can be found on the glass transition temperature ( $T_g$ ) of the matrix. Allaoui and El Bounia (2009), in their review article, showed that SWCNTs may lead to a decrease in  $T_g$  whilst MWCNTs could result in an increased or unchanged  $T_g$ . They concluded that a detailed investigation on this aspect have to be carried out in order to deepen the effect of CNTs on the resin  $T_g$ .

Even though some industrial attempts to manufacture ready-to-use nano additivated prepregs have been made, the Liquid Composite Molding (LCM) is the most suitable method for producing

nanocomposites. The addition of CNTs to the liquid matrices leads to an apparent increase in viscosity. However, as they are subjected to shear stresses during mixing or injection phases, viscosity drastically decreases until reaching the typical value of the unfilled resins. The thixotropic effect of the additivated resins is addressed by some authors in literature. To this purpose, Kotsilkova et al. (2014) observed that viscosity strongly rises with the increase in CNT load; such effect is more marked at low shear rates. Furthermore, even if a very small quantity of CNTs is dispersed in the matrix, viscosity is higher than that of the pristine resin. Similarly, Rahatekar et al. (2006) performed a study on the viscosity enhancement of an epoxy resin containing MWCNTs. They carried out rheological measurement and microscopic analysis in order to investigate the correlation between shear rate and formation of MWCNT agglomerates concluding that low shear rate values promote MWCNT aggregations whilst high shear rates lead to a size reduction of aggregates. Among the LCM processes, Resin Transfer Molding (RTM), Resin Infusion (RI) and Compression Resin Transfer Molding (CRTM) are preferred owing to good processability of the nano additivated resins. Reia da Costa et al. (2012) used nanoadditivated epoxy resin to produce CFRPs by RTM. They showed a filtration effect of the preform which results in a gradient of properties, especially electrical conductivity, in the cured part. Haesch et al. (2015) used the RTM to investigate the effect of CNT dispersion on the mechanical properties of a laminate, by analyzing the resin rich zones, demonstrating that composite with CNTs in the resin rich zones presents higher strain-to-failure and lower density of transverse cracks in comparison with unadditivated composites.

Only few researches concern the use of CRTM as manufacturing process for nanocomposites. The Compression Resin Transfer Molding consists in injecting matrix into a fiber preform while the mold is partially closed. During this stage, the resistance to matrix flow is smaller than the one taking place in the RTM process since the fiber volume fraction has not yet reached the final value. The full impregnation occurs in the compression stage during which the mold is closed and resin is forced through the fiber preform. The CRTM can be a useful process to reduce mold filling time as compared to the RTM techniques, even if clamping forces are strongly increased, as confirmed by Vita et al. (2020). CRTM is used for low cycle time production of high-quality composite parts with low environmental impacts. To this purpose, Vita et al. (2019) performed a comparative LCA analysis of different RTM techniques. They concluded that CRTM can lead to a reduction of impact equal to 19 and 70% as compared with low pressure RTM and high pressure RTM, respectively. Abliz et al. (2014) used flexural tests to assess CNTs filtration effect due to the preform during the CRTM. However, owing to the low sample thickness, a very slight discrepancy between the top and bottom surfaces of the panels have been measured. Terenzi et al. (2017) used electrical tests to evaluate the filtration effect of a preform with a fiber volume fraction of 0.45. They obtained a percolation threshold at values between 0.75 and 1.0% in weight of CNTs. Wicks et al. (2010) investigated the interlaminar and intralaminar properties of CNT reinforced composites. Through Mode I interlaminar fracture test, they showed that alignment of CNTs in the thickness direction led to a strong improvement of the delamination resistance. Thus, CRTM can lead to more uniform properties than in plane impregnation and align the CNTs in the through thickness direction increasing the interlaminar properties. An aspect not yet well investigated in the manufacturing of nanoadditivated composites concerns the definition of CRTM process parameters. The advantages of the CRTM can be fully exploited only if the improvements in mechanical properties due to the presence of nanotubes are not associated to an increase in the manufacturing costs with respect to unadditivated composites. Indeed, the variations in the resin properties due to the presence of nanotubes may make changes to the process parameters and tooling necessary with respect to the pristine resin. Among them, the most important is the increase in viscosity occurring as MWCNTs are added to matrix. Such increase may require an increase in the injection pressure and flow rate to keep the flow front velocity at values minimizing the void content in the composite. Furthermore,

since MWCNTs influence the polymerization reaction, changes in the parameters of curing process may be required in order to obtain a fully cured matrix with reduced polymerization time. Finally, the tendency of MWCNTs to agglomerate, especially during the resin flow through the preform, can result in inhomogeneous mechanical properties as well as a general decrease in the reinforcing effect of the nanotubes on the composite.

In this framework, the present research aims at investigating carbon fiber nanocomposites obtained through CRTM. The main goal consists in studying the CRTM process of nanoadditivated composite using the same process parameters and tooling of unadditivated composite. To this purpose, an epoxy resin was additivated with MWCNTs at two different weight contents (0.5 and 1%). The chosen process parameters, in terms of gap thickness, resin temperature, injection pressure and flow rate, derives from the industrial practice on unadditivated composites of a large Italian enterprise, leader in the manufacturing of composite components for automotive market. The presence of nanotube agglomerates was investigated by means of the Dynamic Light Scattering and microscopic techniques whilst the polymerization reaction and the glass transition temperature of nanoadditivated matrices were assessed using Differential Scanning Calorimetry. The apparent viscosity was measured using a rheometer. Then, the pristine and additivated resins were used to produce carbon fiber nanocomposites by means of the CRTM process. Uniaxial tensile and flexural tests were carried out on samples obtained by the CRTM laminates to evaluate the improvement, in terms of mechanical strength and stiffness, resulting from the addition of MWCNTs to the matrix.

## 2. Material and experimental procedures

### 2.1. Material

The reinforcement used in the present work was a carbon fiber fabric 2x2 twill, 12K, with an areal weight of 600 g/m<sup>2</sup> (CC600, SAATI group, Tensile Strength 4900 MPa and Tensile Modulus 230 GPa), an in-plane permeability of  $2 \times 10^{-10}$  m<sup>2</sup> and a through thickness permeability equal to  $1.1 \times 10^{-12}$  m<sup>2</sup>. On the top surface of each layer, a powder thermoset binder (Hexion Epikote 06720) was dispersed to hold the dry fibers. The thermoset resin HEXION Resin TRAC 06150, suitable for RTM processes, was used as matrix (Tensile Strength 85 MPa and Tensile Modulus 2900 MPa, Flexural Strength 130 MPa and Flexural Modulus 3000 MPa). Multi walled -OH functionalized CNTs (Nanoamor) were dispersed into the matrix by a three-roll mill in two different weight contents: 0.5 and 1%. The average values of diameter and length of the MWCNTs were 20 nm and 20 μm, respectively. Carbon nanotubes dispersion was performed through a three-roll mill that has been proved to be effective in dispersing CNTs in epoxy resin (Gojny et al., 2004). The procedure described by Gojny et al. was performed, letting the suspension pass through the rolls for three times in order to obtain a more uniform dispersion. The scheme of the three-roll milling process is reported in Figure 1.

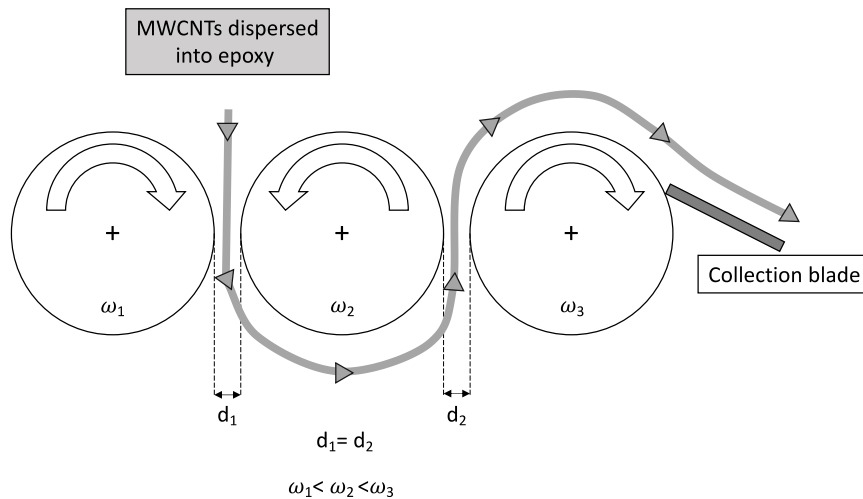


Figure 1: Scheme of the three-roll milling process

Quality of the MWCNT dispersion was evaluated by the Dynamic Light Scattering (DLS Zetasizer Nano S - Malvern Instruments Ltd) and microscopic techniques (Biological Optech microscope with 5 Mpixel camera). The DLS allows to estimate, through the hydrodynamic diameter, the average size of the CNTs that generate a suspension by measuring the intensity fluctuations of the light scattered by nanotubes. The MWCNTs dispersed into the matrix diffuse at a speed depending on their size due to the Brownian effect. In particular, the smaller particles diffuse faster than the larger ones. The measurement of the diffusion speed was performed using laser lighting device and evaluating the generated speckle pattern. A photodiode was used to detect the change of the scattering intensity which was analysed by a digital autocorrelator. The results were analysed to obtain particles size and distribution. Microscopic analysis allows to identify the MWCNT aggregates and their distribution. Images of resin loaded with both 0.5 and 1% of nanotubes were collected. For each sample, three slides were prepared and ten images per slide were acquired. Each image was analysed using an image processing software (Image J) which allows to identify the image area in calibrated square units covered by MWCNT aggregates (area tot) and the number of aggregates recognized in the image (count).

More accurate microscopic analysis was performed using FESEM Zeiss Supra 40 Scanning Electron Microscope (SEM). Two different zones of the samples were analysed: injection gate zone (IGZ) and vacuum application point (VAP) in order to evaluate the nanotube dispersion and alignment. For this reason, laminates with a thickness equal to 4.2 mm were studied. To recognize nanotubes dispersed in the epoxy matrix, a specific sample preparation procedure, consisting in polishing the resin top layer with a diamond oil impregnated cloth, was developed.

Finally, in order to evaluate the processability of the nano additivated matrices, the dynamic viscosity was evaluated as a function of shear rate by the means of Brookfield Fungilab VISCOLEAD ADV rheometer.

## 2.2. CRTM experiments

A total of 15 composite flat panels were manufactured by means of the Compression Resin Transfer Molding. Among them, 5 panels were obtained by impregnating the dry carbon fiber fabric with the unadditivated resin (batch 1, pristine resin), 5 panels with 0.5% in weight of additivated resin (batch 2), and 5 panels with 1% in weight of additivated resin (batch 3). The theoretical fiber volume

fraction was equal to 0.6. The resulting weight percentages, considering the carbon fiber fabric, are 0.498% of MWCNTs in batch 2 and 0.99% of MWCNTs in batch 3.

Contrarily to the Resin Transfer Molding, in the CRTM process the mold is not completely closed during the injection phase. The upper mold is slightly raised to obtain a gap of 0.5 mm over the dry fibers. The matrix is injected into the gap and tends to slide over the dry reinforcement, even though a small amount of resin also penetrates into it, as showed by Baskaran et al. (2017). Then, the upper mold moves downward forcing matrix into preform and causing preform compaction to the required fiber volume fraction. Finally, the mold temperature is increased and resin undergoes polymerization. A simplified scheme of the different phases of the CRTM process is shown in Figure 2.

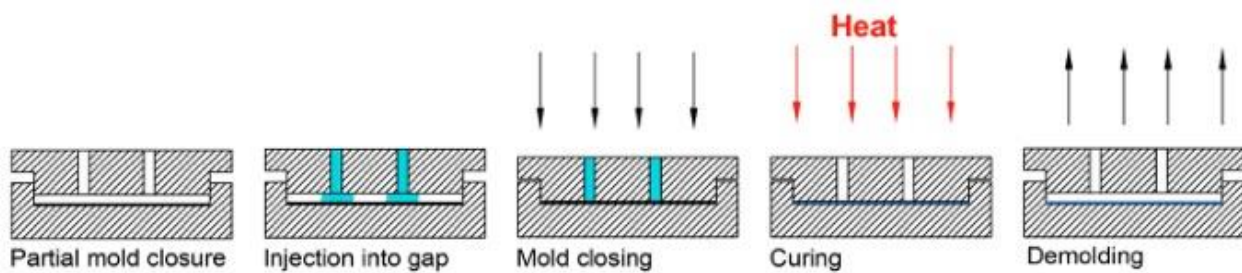


Figure 2: Main phases of the CRTM process

A rectangular shaped aluminum mold was used with cavity width and length of 282 and 382 mm, respectively. Different laminate thicknesses can be obtained by changing the internal plate to fulfil the requirements of the standards for mechanical tests of composite materials. The mold consists of two parts: mold and countermold (Figure 3). In order to maintain the countermold partially opened, an inflatable silicon seal, with a specific profile, was used. By increasing or decreasing the inflation pressure, the gap between preform and countermold was increased or decreased, respectively.

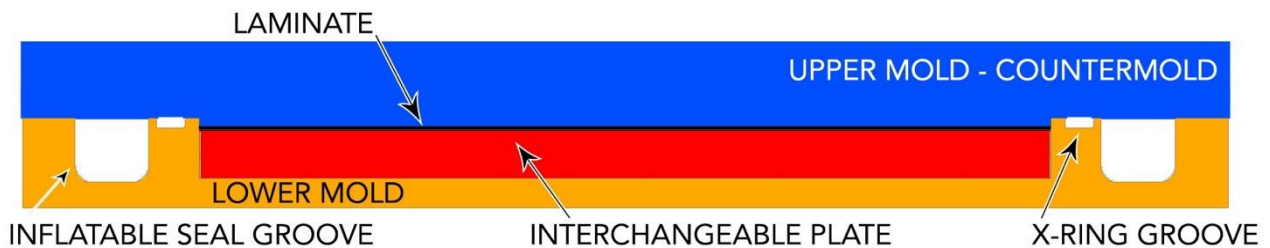


Figure 3: Schematic cross section of the mold

The mold was set in a heated platen press which was used to pre-heat and cure the thermoset matrix and to apply pressure in order to keep mold in the desired position during injection and curing phases.

The process parameters used in the CRTM experiments to realize composite panels using the unadditivated matrix are reported in Table 1. These parameters were defined and optimized at the HP Composites s.p.a. (Ascoli Piceno, Italy) by experiments and industrial practice. HP Composites is a leading company in the manufacturing of composite components for the automotive industry. Since the main goal of the work is the obtaining of additivated composite panels using the same process condition of the unadditivated material, the process parameters reported in Table 1 were also used in the production of nanoadditivated composites.

Table 1: Process parameters used in the CRTM experiments.

Gap thickness (mm)	Injection pressure (bar)	Counter mold speed (mm/s)	Injection flow (cm <sup>3</sup> /min)	Resin temperature (°C)
0.5	2	0.5	150	70

A typical panel in MWCNT/epoxy composite obtained by the CRTM process is shown in Figure .



Figure 4: A flat nanoadditivated panel produced by CRTM after demolding

### 2.3. Chemical, thermal and mechanical tests

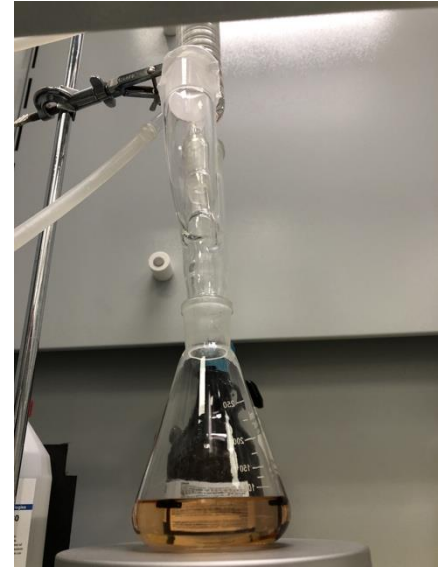
The performances of the MWCNT/Epoxy composites were evaluated by means of void quantities analysis, DSC analysis, uniaxial tensile and flexural tests.

#### 2.3.1. Void quantity analysis

The presence of voids into laminates strongly reduces the material strength. Moreover, voids affect the humidity absorption and other properties such as chemical and physical degradation of fibers. The test to detect the presence of voids in composite materials was performed following ASTM D3171 standard according to the procedure B “matrix digestion using sulfuric acid/hydrogen peroxide”. The matrix digestion test allows the determination of the resin and void contents. Three specimens were taken in different zones of each panel in order to evaluate the occurrence of inhomogeneities in the impregnation phase. Figure a shows the dry fibers after the resin digestion and Figure 5b the equipment used in the experiments.



a)



b)

Figure 5: a) dry fibers after resin digestion and b) equipment used for the void quantity analysis.

### 2.3.2. DSC analysis

DSC analysis allows to evaluate the kinetics of reaction taking place during the cross-linking phase as well as the influence of MWCNTs on the  $T_g$  of thermoset resin. Tests were performed using Mettler Toledo scanner, characterized by a precision of  $\pm 0.1^\circ\text{C}$ , with a sampling rate equal to 10 Hz. Samples were obtained by mixing, at room temperature, both the unadditivated and additivated (with a weight content of MWCNTs of 0.5 and 1%) liquid resins with the amount of hardener suggested by the resin manufacturer. Then, a quantity of about 25 mg, taken from each sample, was poured in a dedicated aluminum pan and heated with a ramp of  $10^\circ\text{K}/\text{min}$  in the DSC scanner, using air as reference. Once polymerization occurs, samples were cooled to room temperature and then re-heated with a ramp of  $20^\circ\text{K}/\text{min}$  to determine the  $T_g$  of matrix.

### 2.3.3. Mechanical tests

Uniaxial tensile and flexural tests were performed on samples obtained from composite panels, obtained by impregnating the carbon fiber fabric with both pristine resin and additivated resins with a weight load of MWCNTs equal to 0.5 and 1%, with thicknesses of 2.5 and 4 mm.

The uniaxial tensile tests are very effective in order to study adhesion at the fiber-matrix interface and to evaluate the load capability of matrix. They were performed according to the ASTM D3039 standard. From each panel, 5 samples, with length, width and thickness equal to 250 mm, 25 mm and 2.5 mm, respectively, were obtained by water jet cutting. Unacceptable failures were avoided by bonding glass fiber end tabs to samples. A multipurpose servohydraulic testing system (MTS 810), characterized by a load capacity of 250 KN, was used. The movable head velocity was equal to 2 mm/min. An extensometer was used to measure strain along the loading direction (Figure a).

Flexural tests allow to evaluate the ability of a laminate in transferring interlaminar loads. As the bending force is applied to the composite material, shear stress occurs among layers and useful information about the mechanical behaviour in terms of tensile, compressive and shear properties can be obtained. Five samples for each panel, 77 mm in length, 15 mm in width and 4 mm in thickness (span-to-thickness ratio of 16:1), were tested according to the standard ASTM D790 using

procedure A (three-point loading system utilizing center loading on a simply supported beam). Figure b shows the tooling used in the flexural tests.

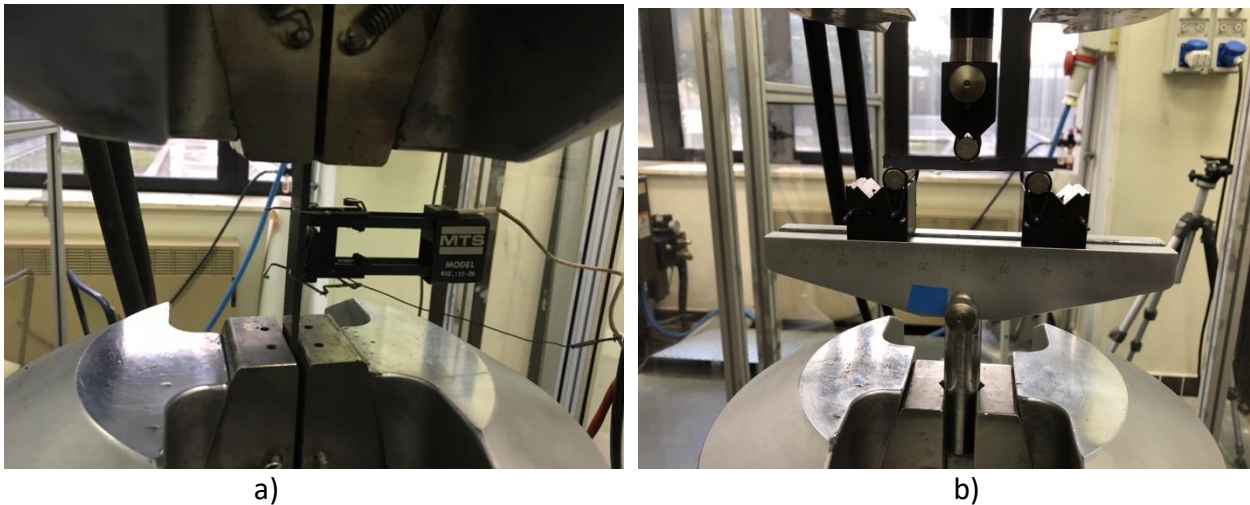


Figure 6: a) Tensile test and b) flexural test performed in the universal servohydraulic testing machine MTS 810

### 3. Results and discussion

#### 3.1. Viscosity, DLS and microscopic analysis

Figure 7 shows dynamic viscosity of pristine matrix and nanofilled matrices vs. shear rate. The experiments were performed starting from a shear rate of  $1 \text{ s}^{-1}$  and ending at  $50 \text{ s}^{-1}$  after each curve have reached its plateau. The pristine resin exhibits a Newtonian behavior with a viscosity of about  $10 \text{ Pa}\cdot\text{s}$  at  $25^\circ\text{C}$ . This value is in excellent agreement with that given by the matrix manufacturer. Resin filled with 0.5% in weight of MWCNTs shows a shear thinning behavior, consisting in a decrease in viscosity with increasing shear rate. Furthermore, viscosity at low shear rates is higher than the pristine resin one ( $15.5 \text{ Pa}\cdot\text{s}$  against  $10 \text{ Pa}\cdot\text{s}$  at  $1 \text{ s}^{-1}$ ) can be seen. However, viscosity of the additivated resin decreases with rising shear rate and at about  $50 \text{ s}^{-1}$ , a very similar value to that of the pristine resin is obtained. As far as the weight content of MWCNTs is equal to 1%, the nanofilled matrix shows a more marked reduction in viscosity with growing shear rate due to the alignment of MWCNTs in the direction of deformation. In particular, viscosity at  $1 \text{ s}^{-1}$  is equal to about  $30.5 \text{ Pa}\cdot\text{s}$ , and, irrespective of shear rate, it is always higher than the ones of both pristine and nanoadditivated matrix filled with 0.5% of MWCNT ( $13.3 \text{ Pa}\cdot\text{s}$  against  $10 \text{ Pa}\cdot\text{s}$  at  $50 \text{ s}^{-1}$ ). The results are very similar to those achieved by Kotsilkova et al. (2014) which found that, at low shear rates, the apparent viscosity of matrix filled with a weight content of MWCNTs equal to 0.5 and 1% is higher than the one of pristine resin; as shear rate increases, viscosity strongly decreases and becomes almost independent of the presence of nanotubes.

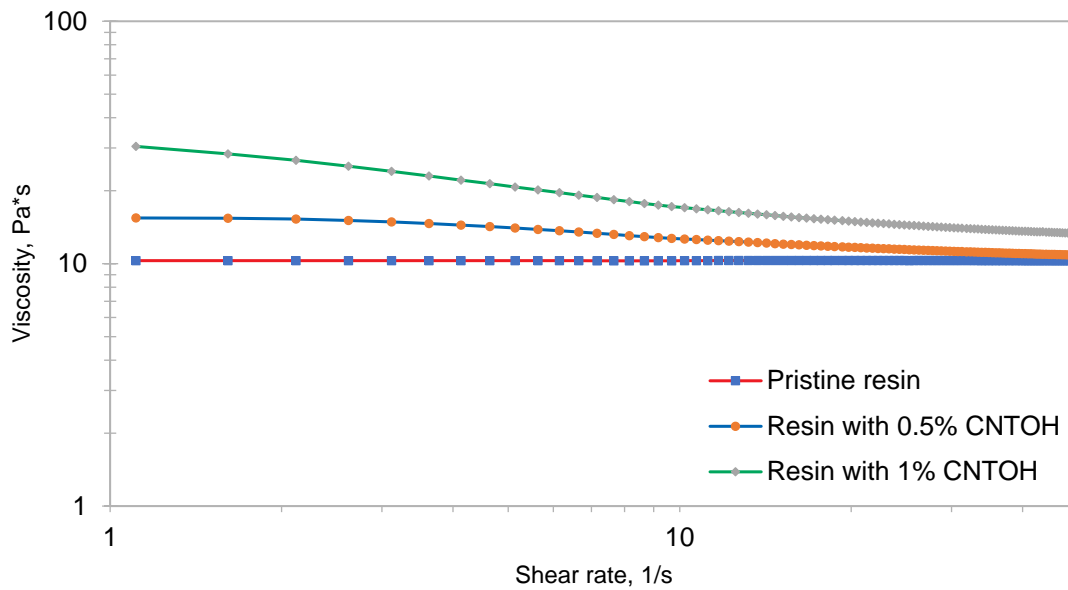


Figure 7: Viscosity profile at 25°C vs. shear rate

The results of DLS measurements are shown in Figures 8 and 9. Six curves are reported for each batch. Each curve was given by the average of several measures (called runs) taken automatically by the DLS and depending on the stability of sample. The time span between two measurements was about 10 min. The abscissa of the plots represents the hydrodynamic diameter distribution of the nanotubes whilst the ordinate is proportional to the quantity of MWCNTs included in the specific dimension class. As can be seen, the peak values are very similar each other which means a very good measurement repeatability. Furthermore, each curve presents only one peak, demonstrating that nanotubes belong to the same dimension class and that sedimentation and flocculation phenomena do not occur.

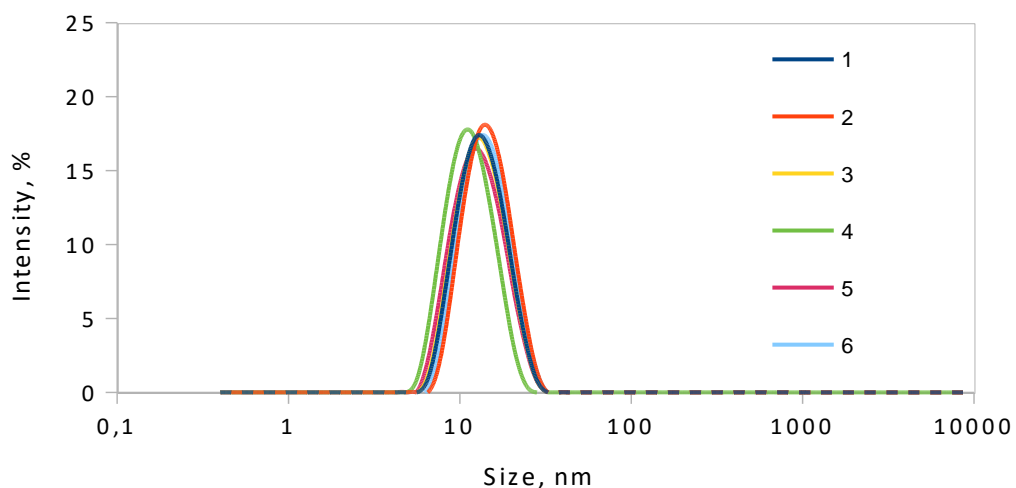


Figure 8: Results of the DLS analysis performed on resin with 0.5% MWCNTs.

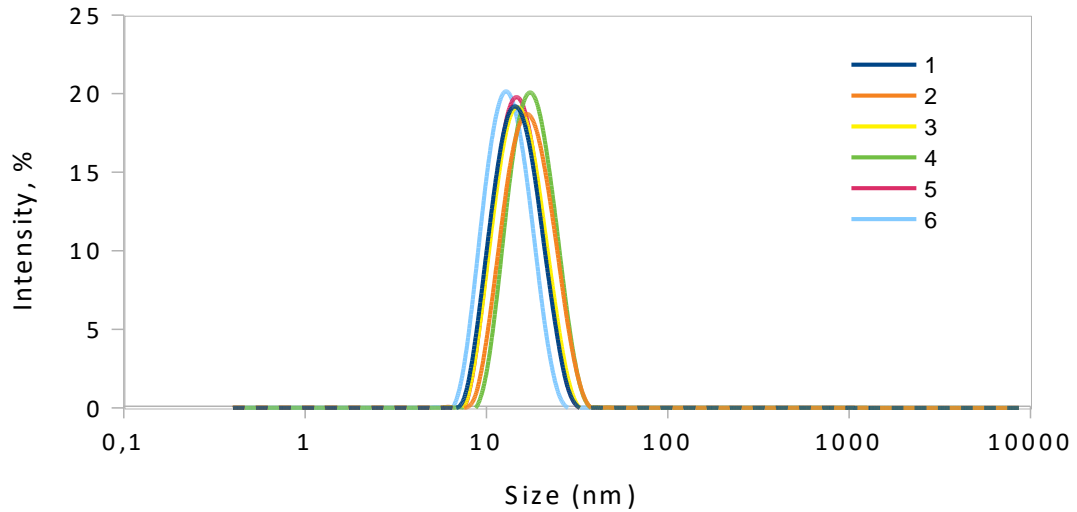


Figure 9: Results of the DLS analysis performed on resin with 1% MWCNTs.

Results given by optical microscopy show good repeatability of the measurements (Figures 10 and 11). The two plotted parameters (area tot and count) provide information about the quality of nanotube dispersion. The boxplots related to the three slides for each sample are in the range of 4%. Therefore, such value is always included into the standard deviation of the other measurements demonstrating the homogeneity of resin distribution in the entire volume.

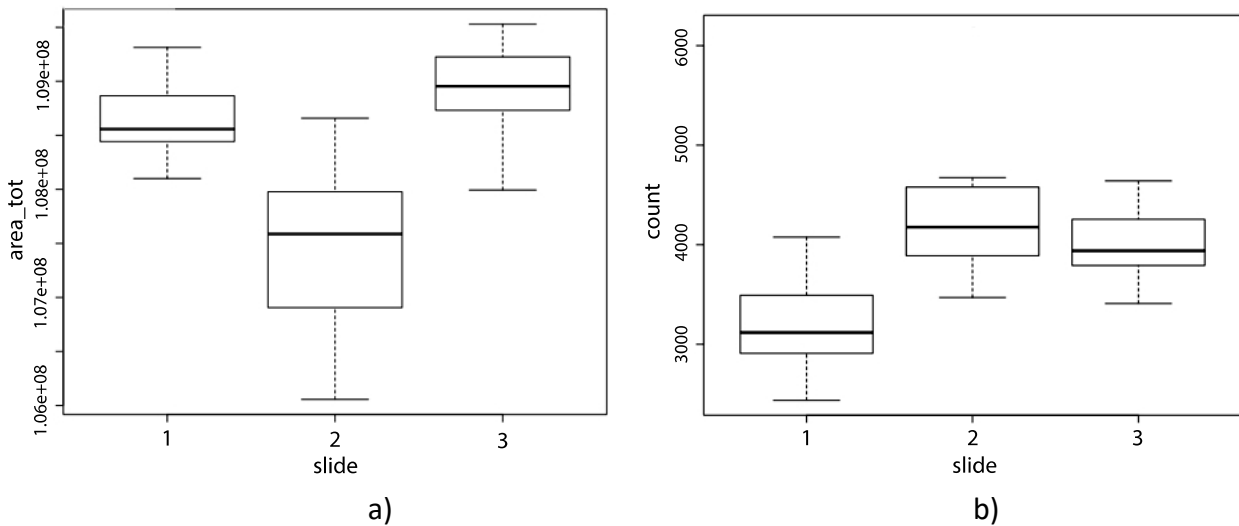


Figure 10: Measurement of a) image area covered by the aggregates (area\_tot); b) aggregate numbers (count) of 0.5% MWCNTs resin and comparison of three different samples.

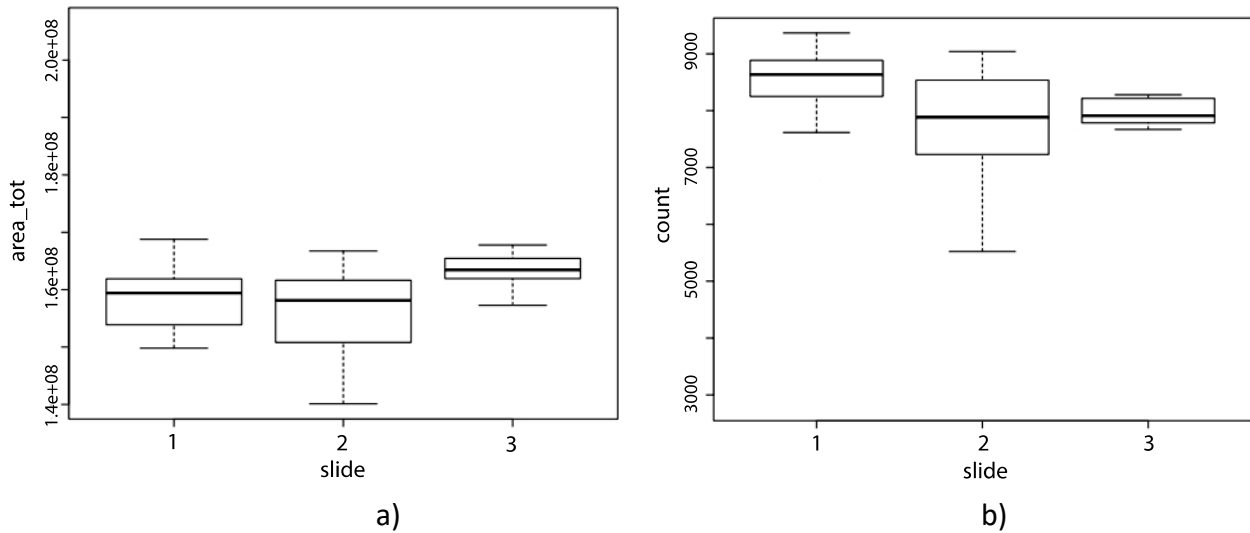


Figure 11: Measurement of a) image area covered by aggregates (area\_tot); b) aggregate numbers (count) of 1% MWCNTs resin and comparison of three different samples.

Figures 12 and 13 show SEM images of nanotube distribution in the injection gate zone and vacuum application point of resins loaded with 0.5 and 1% of MWCNTs, respectively. Irrespective of the weight load, it appears that the nanotube distribution is homogeneous in both zones investigated (IGZ and VAP) indicating that no agglomeration takes place during the matrix flow into the mold from injection to extraction gate.

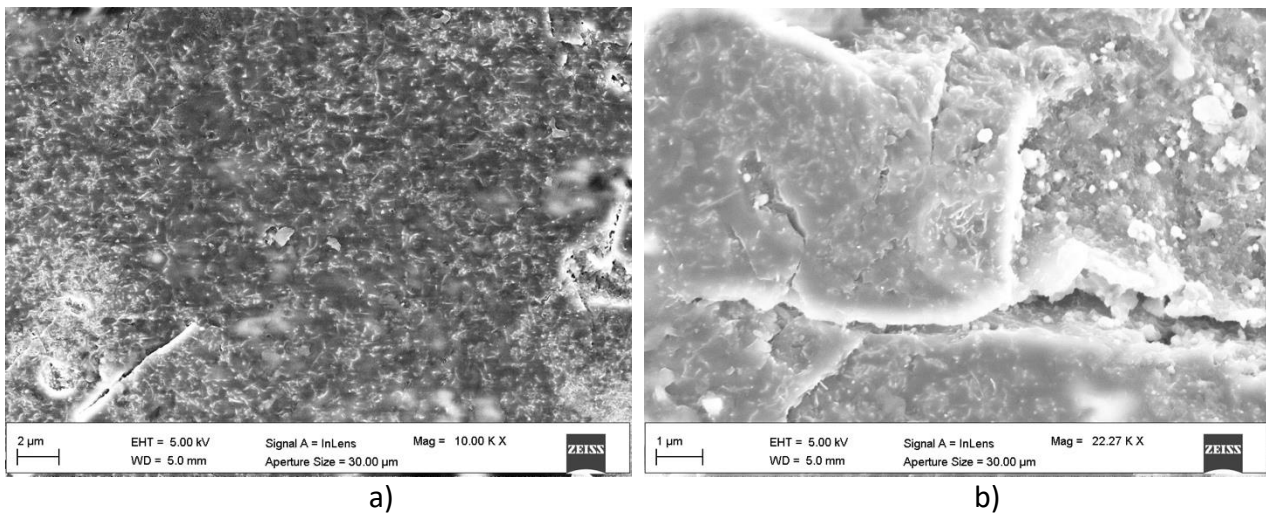


Figure 12: SEM images of 0.5% MWCNT filled resin in a) IGZ and b) VAP.

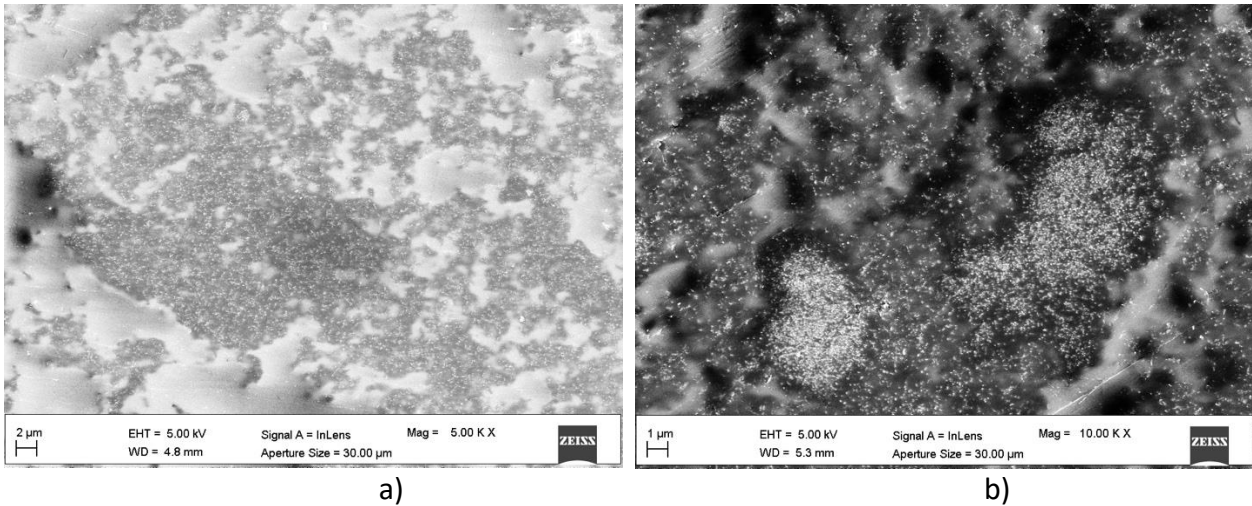


Figure 13: SEM images of 1% MWCNT filled resin in a) IGZ and b) VAP.

The through thickness nanotube distribution is shown in Figure 14 which is referred to the most severe condition corresponding to the highest weight load investigated (1% in weight of MWCNTs). The SEM images were captured in the bottom part of the panel. It can be clearly distinguished carbon fibers and resin. In the areas in which resin is polished, nanotubes appear with a homogenous distribution. This indicates that no filtering effect of MWCNTs occurs as the resin flows from the top face of the panel to the bottom one.

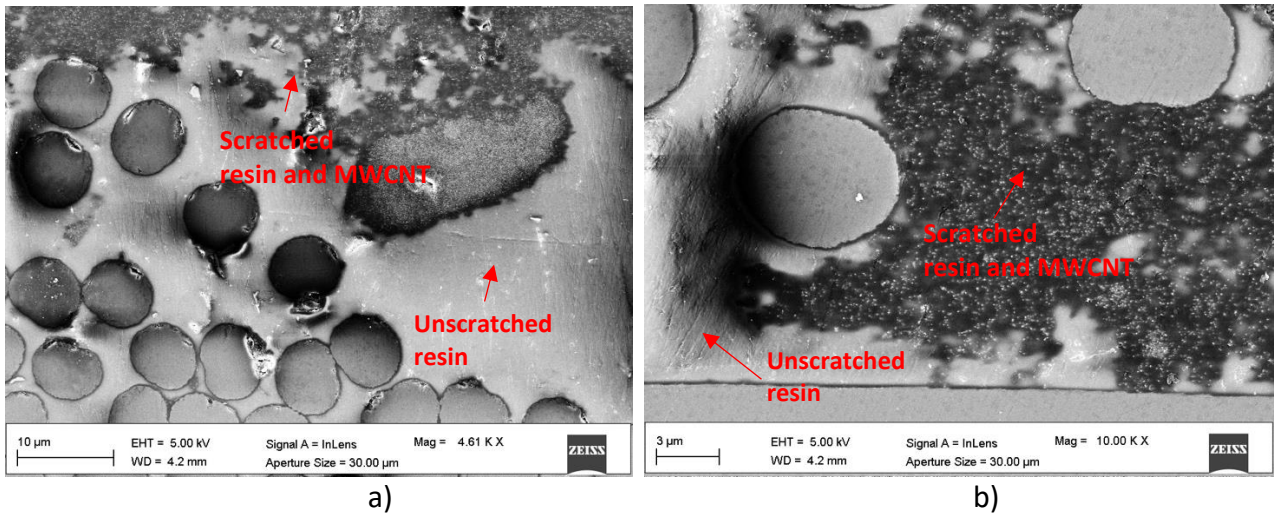


Figure 14: SEM images of 1% MWCNTs filled resin along the thickness of the sample at a) 4.61 K X and b) 10.00 K X.

### 3.2. Void quantity analysis

The results of the void quantity analysis are reported in Table . No appreciable discrepancy can be found among laminates obtained using unadditivated and nanoadditivated resins, demonstrating that the MWCNTs have no remarkable effect on the void volume fraction. The very low values ( $\leq 1.2\%$ ) can be attributed to the high pressure applied during the compaction stage of the Compression Resin Transfer Molding. Indeed, in this closed mold process, pressure values up to 20 bar were achieved. Finally, since during the compaction phase an excess of resin equal to about 10% was squeezed out from the vacuum gate, air entrapped between fibers was evacuated efficiently.

Table 2: Results of the void quantity analysis.

SAMPLE	PRISTINE RESIN			MWCNT 0.5 %			MWCNT 1 %		
	Void fraction specimen 1 (%)	Void fraction specimen 2 (%)	Void fraction specimen 3 (%)	Void fraction specimen 1 (%)	Void fraction specimen 2 (%)	Void fraction specimen 3 (%)	Void fraction specimen 1 (%)	Void fraction specimen 2 (%)	Void fraction specimen 3 (%)
1	0.8	1.1	1.0	0.8	1.0	0.9	1.0	1.0	0.8
2	0.7	1.0	0.9	0.9	0.8	0.8	0.7	1.1	0.7
3	1.0	0.8	0.9	1.1	0.8	1.0	0.8	0.8	0.9
4	1.0	0.9	1.0	1.0	0.8	1.0	0.7	1.0	0.8
5	1.0	0.9	0.9	0.7	1.1	0.9	1.1	0.9	0.8
Average value	0.90	0.94	0.94	0.90	0.90	0.92	0.86	0.96	0.80
Standard deviation	0.14	0.11	0.05	0.16	0.14	0.08	0.18	0.11	0.07

### 3.3. DSC analysis

The glass transition and polymerization temperatures of pristine and additivated resins, and the heat produced during their polymerization are shown Table . The presence of MWCNTs leads to a significant growth in Tg of matrix; furthermore, an almost negligible influence of the MWCNT weight content can be observed. Finally, the MWCNTs tend to promote the polymerization reaction even if heat generated is lower than the one of the pristine resin and decreases with rising the nanotube weight content. Such results are in excellent agreement with those given by Allaoui and El Bounia (2009) which showed both an increase in Tg, ranging from 16 to 24°C as resin was additivated with MWCNTs and, depending on the nanotubes typology, a promotion of the polymerization reaction.

Table 3: Results of the DSC analysis

	Glass Transition Temperature		Polymerization reaction			
	Midpoint [°C]	Onset [°C]	Onset Temperature [°C]	Peak Temperature [°C]	Endset Temperature [°C]	Heat produced [J/g]
Pristine resin	122.0	114.8	75.0	105.5	134.5	415.0
MWCNT/Epoxy 0.5%	141.5	135.6	69.8	105.0	141.4	397.0
MWCNT/Epoxy 1%	140.4	131.6	65.4	101.0	140.5	359.0

The heat flow/temperature curves provided by the DSC are shown in Figures 15-17. It can be clearly seen that the rise in the filler load results in the shift of the polymerization curve (black line) to the left (initiation of polymerization) and its flattening (reduction of heat production). In addition, the curve indicating the glass transition temperature (red line) shows a marked increase in Tg as the pristine resin is loaded with 0.5% in volume of MWCNTs, whilst a very small variation in Tg takes place as the weight content of nanotubes is equal to 1%.

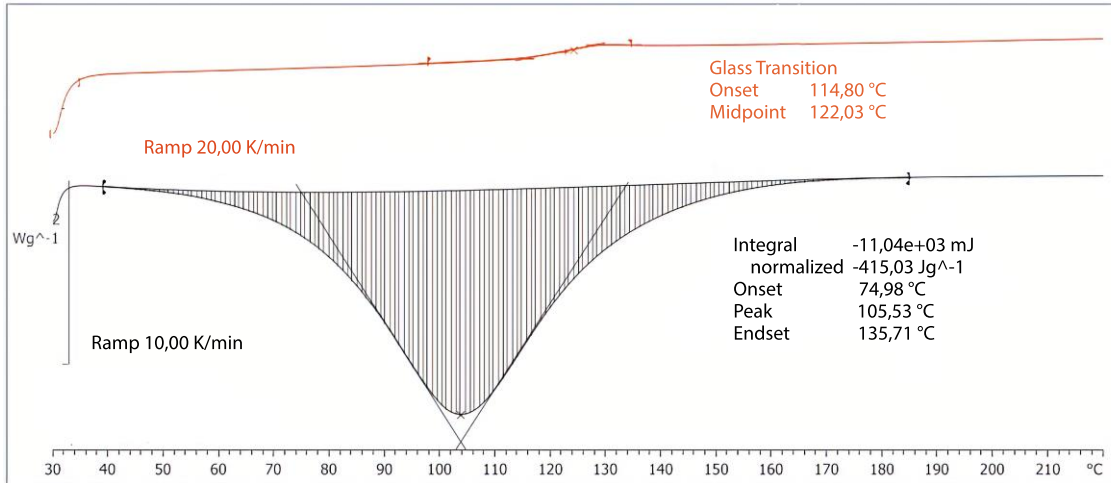


Figure 15: DSC curves of the pristine resin.

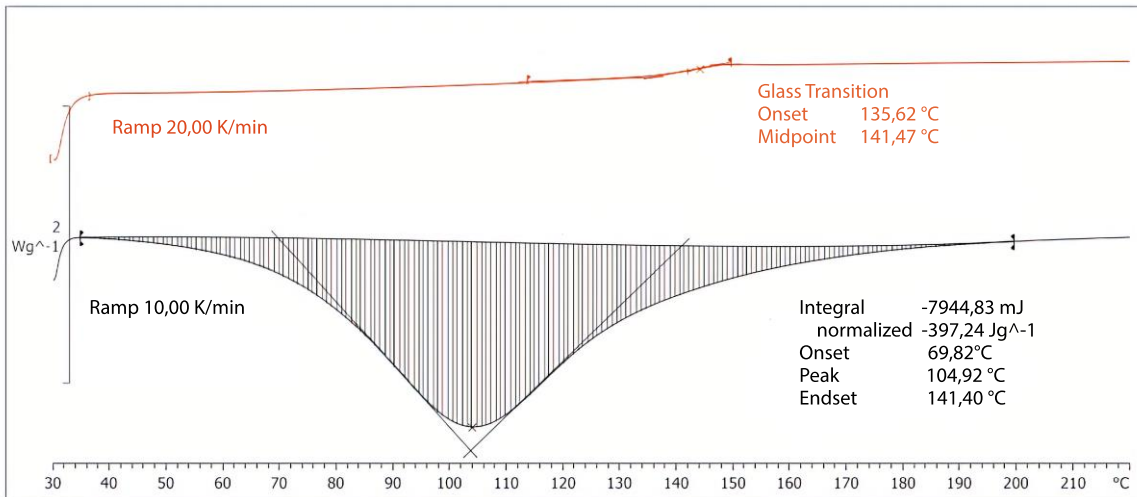


Figure 16: DSC curves of the resin additivated with 0.5% in weight of MWCNTs.

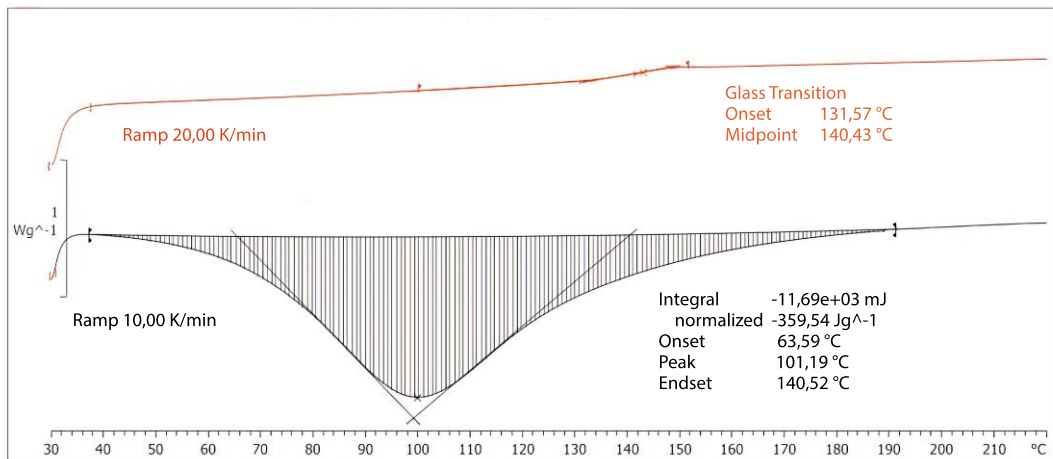


Figure 17: DSC curves of the resin additivated with 1% in weight of MWCNTs.

### 3.4. Mechanical tests

The stress-strain curves resulting from uniaxial tensile tests carried out on samples obtained from laminated panels produced by the CRTM process are shown in Figure 18. The average values of

ultimate tensile strength (UTS), elastic modulus (E) and ultimate elongation (UE) are summarized in Table .

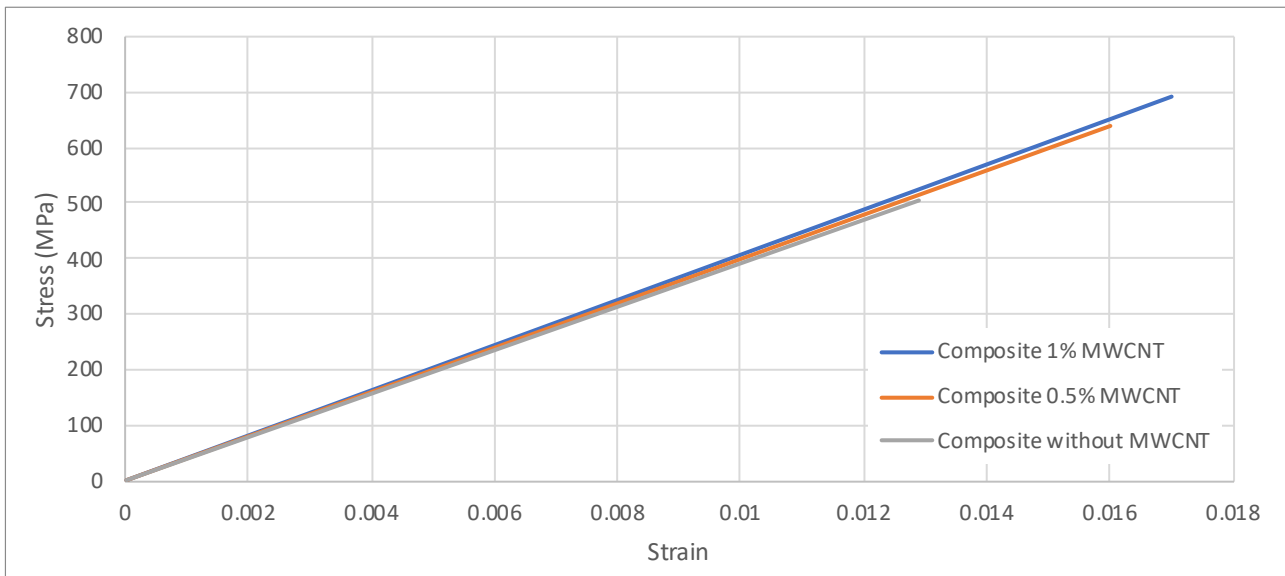


Figure 18: Stress-strain curves obtained by tensile tests.

Table 4: Average values of UTS, E and UE and their standard deviations, as a function of the weight content of MWCNTs, obtained by analyzing the stress-strain curves.

MWCNT weight content [%]	UTS [MPa]	E [GPa]	UE [%]
0	505 ± 28	56 ± 2	1.29 ± 0.13
0.5	640 ± 31	58 ± 3	1.60 ± 0.19
1	691 ± 40	60 ± 4	1.70 ± 0.14

It appears that UTS, E and UE values increase as MWCNTs are added to the pristine resin; such growth tends to be less marked as the weight content of nanotubes increases from 0.5 to 1%. This means that the addition of a small amount of MWCNTs (0.5%) to epoxy resin significantly improves the load bearing capability and the strain-to-failure of the composite material. As the weight content rises to 1%, both UTS and UE further increase but with a lower growth rate. This behaviour can be attributed to the improvement of the load transfer capability of the additivated matrices which are able to distribute the stress between the fibers more efficiently than the pristine resin. Table 4 also shows that the growth rate of the elastic modulus with the quantity of nanotubes in the matrices almost constant in the range investigated. Indeed, the elastic modulus of composite materials is strongly influenced by the modulus of fibres and weakly affected by the one of matrix.

The results obtained by the flexural tests are shown in Figure 19, whilst Table 5 reports the ultimate flexural strength (UFS) and bending modulus (BE) of composites obtained using unadditivated and nanoadditivated resins. The presence of MWCNTs into the resin leads to an increase in the UFS and BE values denoting an improvement of the interlaminar properties. **However, the failure of flexural samples occurs due to compression on the top surface, which is scarcely affected by the presence of MWCNTs, as reported in Jia et al. (2015) and Randjbaran et al. (2017).** This enhancement is less sensitive to the MWCNT weight content with respect to the output of the tensile tests. Indeed, the UFS and the BE values exhibit a constant growth rate as the quantity of MWCNTs increases from 0 to 0.5% and from 0.5 to 1%. The very small increase in modulus with weight content of MWCNTs

obtained with flexural test confirms the reduced contribution of matrix to the stiffness of MWCNT/epoxy laminate.

Table 5: Average values of UFS and BE and their standard deviations, as a function of the weight content of MWCNTs, obtained by analyzing the results of flexural tests.

MWCNT weight content [%]	UFS [MPa]	BE [GPa]
0	670 ± 22	39 ± 4
0.5	705 ± 30	40 ± 4
1	750 ± 41	41 ± 5

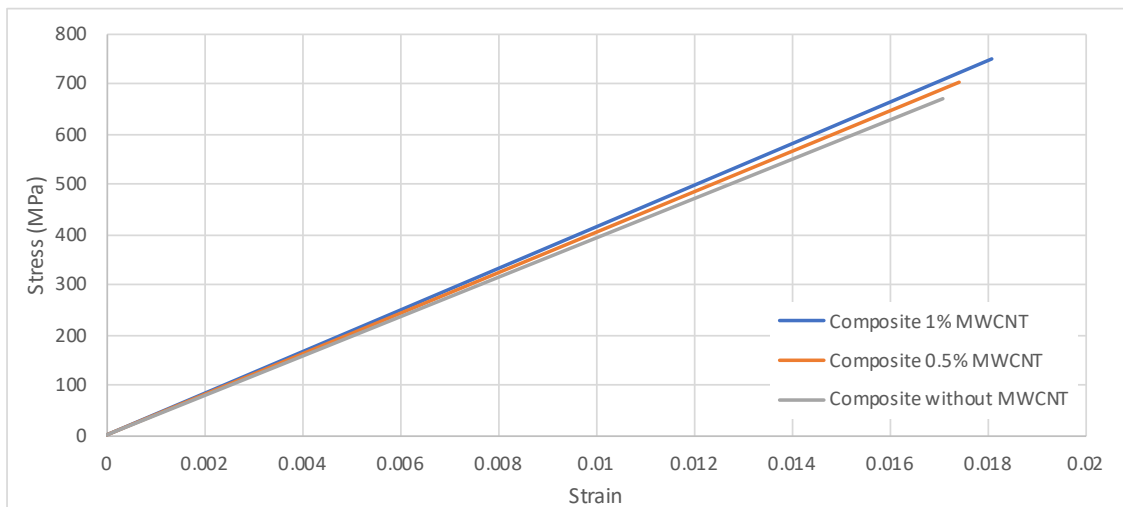


Figure 19: Typical stress-strain curves obtained by the flexural tests.

Finally, Figure 20 shows the SEM images of fracture surfaces of nanofilled composite samples subjected to bending tests.

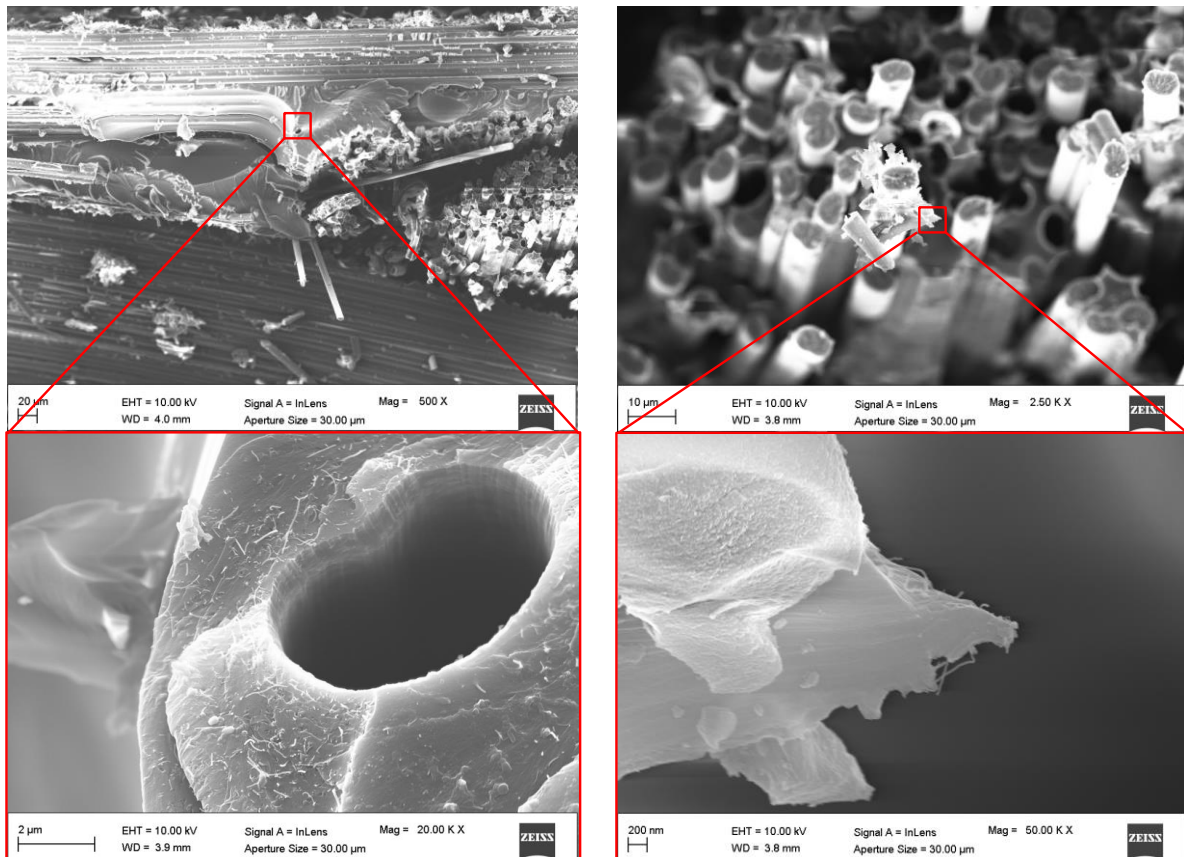


Figure 20: SEM images of fracture surface of a) 0.5% loaded composite and b) 1% loaded composite

It clearly appears that, irrespective of their weight content, the MWCNTs can be also observed in the region close to the fibers, thus indicating that the no filtering effect occurs into the tows. Furthermore, it can be seen that the main failure mechanism of the samples is the fiber pull-out.

#### 4. Conclusions

In the present work, panels in carbon fiber nanocomposites were manufactured by Compression Resin Transfer Molding using a commercial epoxy resin additivated with Multi Walled Carbon Nanotubes. Two different weight loads of MWCNTs (0.5 and 1%) were investigated; furthermore, as a comparison, composite laminates were also obtained using the unadditivated resin. The effect of MWCNTs dispersed in the matrix on chemical, thermal and mechanical properties of the composites was evaluated. The main results can be summarized as follows:

- the dispersion of MWCNTs in the resin by three-roll milling process does not lead to the formation of agglomerates, also at the highest weight content (1%), as shown by the results provided by DLS and microscopic analyses;
- no appreciable filtering effect of the carbon fiber fabric on nanotubes occurs, as shown by the SEM analysis, **owing to the shear forces generated during the compression stage and the low values of countermold speed (0.5 mm/s) and resin viscosity;**
- the increase in viscosity, resulting from the addition of MWCNTs to resin, is only apparent. Indeed, at shear rates **higher than  $50 \text{ s}^{-1}$** , viscosity of the nanoadditivated matrices, **irrespective to the weight content of nanotubes**, is very similar to that of the pristine resin ( $10 \text{ Pa}\cdot\text{s}$ );
- **the glass transition temperature is almost independent of the weight content of nanotubes. As a matter of fact, resins additivated with MWCNT weight contents of 0.5 and 1% are characterized by very similar glass transition temperatures equal to  $141.4^\circ\text{C}$  and  $140.5^\circ\text{C}$ ,**

respectively. They are higher than the T<sub>g</sub> of the pristine resin (122.0°C). Nanofillers promote polymerization reaction of the matrix by decreasing the onset temperature from 75.0°C (pristine resin) to 69.8°C (0.5% of MWCNTs), and to 65.4 °C (1% of MWCNTs) even though the heat generated decreases from 415.0 J/g (pristine resin) to 397.0 J/g (0.5% of MWCNTs), and to 359 J/g (1% of MWCNTs);

- chemical analysis shows that the CRTM process leads to a very low void content ( $\leq 1.2\%$ ) in the composite panels and there is no appreciable difference between nanoadditivated matrices and the pristine one;
- both uniaxial tensile and flexural tests show an increase in strength as the MWCNT weight content increases, even though this enhancement is more marked in the tensile behaviour than in the flexural one. In particular, the mean value of ultimate tensile strength increases from 505 MPa (pristine resin) to 640 MPa (0.5% of MWCNTs), and to 691 MPa (1% of MWCNTs) whilst the mean value of ultimate flexural strength increases from 670 MPa (pristine resin) to 705 MPa (0.5% of MWCNTs), and to 750 MPa (1% of MWCNTs)
- results demonstrate that the increase in stiffness, for both mechanical tests investigated, with the weight content of nanofillers is very low, confirming the reduced contribution of matrix to the stiffness of MWCNT/epoxy composite.

Finally, the abovementioned results prove that the CRTM process can be successfully performed on nanoadditivated composites without any modify of process parameters and tooling with respect to the same process carried out on pristine resin.

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