Influence of manufacturing parameters on the mechanical properties of nano-reinforced CFRP by carbon nanofibers

P. Santos¹, a), Alberto Maceiras¹, P. N. B. Reis¹

¹ C-MAST, Depart. of Electromechanical Engineering, University of Beira Interior, 6201-100 Covilhã, Portugal

a)Corresponding author: paulo.sergio.santos@ubi.pt

Abstract. One of the most relevant problems of nano-reinforced resins is the uniform dispersion of nanoparticles. This problem is even more relevant when they are involved in the production of laminated composites. In this case, in addition to the agglomeration of nanoparticles, air bubbles are also very frequent during the manufacturing process of laminated composites with nano-reinforced resins. These air bubbles are even more frequent in the manual lay-up process. In this context, this study intends to study some manufacture parameters in order to maximize the mechanical properties. For this purpose, the mixer rotation speed, the dispersion time of the nanoparticles and the vacuum time applied to the system were analyzed in detail. It was found that the mixing time is very dependent on the rotation speed used and there is an ideal vacuum time. A short vacuum time allows air bubbles to exist in the resin, while a long time promotes a decrease in mechanical properties due to the removal of resin in the laminates and, consequently, the fibers are not fully wet.

1. Introduction

Nowadays, polymer matrix composites (PMC) are replacing, more and more, the traditional metallic materials and this trend extends to the most diverse industrial applications. This is consequence of their high specific strength and stiffness, good fatigue performance, corrosion resistance, and low processing costs [1].

The manual lay-up process, also called the wet lay-up method, is the simplest and oldest method and it is particularly suitable for large components/structures. In this process, each layer is handled manually, layer by layer, up to the desired thickness. Although brushes are often used to distribute the resin evenly onto the fibers, rollers are used to ensure complete wetting of the fibers and to remove air bubbles. However, the large amount of air bubbles that a laminate can present is the main drawback of this process. In this case, the vacuum bagging process proves to be a good alternative, because, as it is a closed mold process, it is able to manufacture components/structures with higher mechanical performance and low cost [2,3].

On the other hand, the open literature reports that the mechanical properties of nanocomposites are dependent on the content of nanoparticles, type of resin and manufacturing process. In this case, for example, in order to maximize mechanical properties, good dispersion is essential, which often involves great technical difficulties and high costs to achieve them. For example, Reis et al. [4] compared two dispersion processes, direct method (DM) and indirect method (IDM), in terms of...
mechanical properties, and they concluded that the nanocomposites obtained by the indirect method had lower mechanical properties than the neat resin due to the residual acetone.

Therefore, the present study intends to analyze the effect of some manufacturing parameters on the mechanical properties of nano-reinforced CFRP by CNFs. The influence of the rotation speed, mixing time and vacuum application time will be analyzed in detail for an epoxy resin. In fact, epoxy resins are thermosetting polymers used as matrices due to their chemical resistance, high specific strength, dimensional stability, and excellent adhesion to fillers, among others. Epoxies are two-component materials: resin and hardener, where resins are normally diglycidyl ethers of bisphenol-A and/or bisphenol-F; and hardeners are the curing agents. There are different types of hardeners, but the most commons are based on amines, and these amines when reacting with the epoxy rings are able to start the polymerization and subsequent crosslinking [5]. On the other hand, CNFs present superior mechanical and chemical properties over commonly used carbon fibers owing to their unique small-size characteristics. In addition, they have excellent electrical and high thermal conductivity. Therefore, CNFs can be considered for extending the physical and mechanical properties of conventional carbon fiber composites for lightweight structural applications.

2. Materials and Experimental Procedure

An SR 8100 epoxy resin and a SD 8822 hardener, both supplied by Sicomim, were used to produce nanocomposites and carbon/epoxy laminates reinforced with CNFs. Their average diameter is about 130 nm, length between 20 and 200 μm, and average specific surface area around 54 m²/g. The SR 8100 epoxy is composed of a mixture of bisphenol A (DGEBA), bisphenol F (DGEBF) epoxy resins, and 1,6-bis(2,3-epoxypropoxy)hexane, as diluent. The hardener SD 8822 is a mixture of amines, 2-methylpentane-1,5-diamine, m-phenylenebis(methylamine), and trimethylolpropane tris[poly(propylene glycol), amine terminated] ether [5].

In terms of nanocomposites three different manufacturing processes were adopted, which are shown in Table 1

| Manuf. Process | Detail used during the manufacturing process                                                                 |
|----------------|--------------------------------------------------------------------------------------------------------------|
| 1              | Resin and hardener mixed manually.                                                                           |
| 2              | Resin and hardener mixed manually, followed by vacuum for 10 minutes. The resin mixture with 0.5 wt.% CNFs was conducted at 1000 rpm for 3 h and, at same time, submitted to an ultrasonic bath (frequency of 40 kHz). The hardener was subsequently added at 150 rpm for 10 minutes and, finally, the mixture was degassed for 10 minutes in a vacuum chamber. |
| 3              |                                                                                                              |

After the manufacture process reported in Table 1, the mixture is carefully poured into a cardboard mold with dimensions of 100×130×3±0.09 mm³ and cured at room temperature for 24 hours. Finally, a post-cure at 40°C was applied for 24 hours.

In terms of composite laminates, eight ply laminates of woven bi-directional carbon 195-1000P (195 g/m²), all in the same direction, were prepared by hand lay-up and the overall dimensions of the plates were 150×150×1.5±0.18 mm³. The resin used was prepared by process 2. The system was placed inside a vacuum bag and a load of 2.5 kN was applied during 24 h in order to maintain a constant fiber volume fraction and uniform laminate thickness. The bag remained attached to a vacuum pump to eliminate any air bubbles existing in the composite, and the vacuum time of 5 s, 1 min, 2 min, 3 min, 5 min and 10 min was analyzed. Finally, the post-cure was followed according to manufacturer datasheet (epoxy resin) in an oven at 40 °C during 24 h.
Finally, similar composites laminates were produced, but the epoxy resin was, in this case, enhanced by 0.5 wt.% of CNFs. Nine different manufacturing processes were studied, which are summarized in Table 2. In all conditions, the manufacturing process is completed with a post-cure in an oven at 40 °C for 24 h.

Three-point bending (3PB) static tests were performed at room temperature and using specimens cut nominally to 60×10×3 mm³ and 60×10×2 mm³ from those plates, respectively, for resin and composite laminates as shown in Figure 1. The specimens were tested with a span of 50 mm and 40 mm, respectively, for resin and composite laminates, according to the European Standard EN ISO 178:2003. An Autograph AGS-X universal testing machine, from Shimadzu, with a 10 kN load cell and a displacement rate of 2 mm/min was used to test six different samples for each configuration.

Table 2. Manufacturing process of composite laminates.

| Manuf. Process | Detail used during the manufacturing process |
|----------------|---------------------------------------------|
| 1              | Control samples obtained by: Resin and hardener mixed manually, followed by vacuum for 10 minutes. The bag remained attached to a vacuum pump for 2 min. Composite laminates were manufactured based on process 3, reported in Table 1, but conducted at 400 rpm for 3 h. Thereafter, the system was placed in a vacuum bag, a 2.5 kN load was applied for 24 h and vacuum for 2 min. |
| 2              | Composite laminates were manufactured based on process 3, reported in Table 1, but conducted at 400 rpm for 3 h. Thereafter, the system was placed in a vacuum bag, a 2.5 kN load was applied for 24 h and vacuum for 2 min. |
| 3              | Composite laminates were manufactured based on process 3, reported in Table 1, but conducted at 700 rpm for 3 h. Thereafter, the system was placed in a vacuum bag, a 2.5 kN load was applied for 24 h and vacuum for 2 min. |
| 4              | Composite laminates were manufactured based on process 3, reported in Table 1, but conducted at 700 rpm for 4 h. Thereafter, the system was placed in a vacuum bag, a 2.5 kN load was applied for 24 h and vacuum for 2 min. |
| 5              | Composite laminates were manufactured based on process 3, reported in Table 1, but conducted at 700 rpm for 5 h. Thereafter, the system was placed in a vacuum bag, a 2.5 kN load was applied for 24 h and vacuum for 2 min. |
| 6              | Composite laminates were manufactured based on process 3, reported in Table 1, but conducted at 1000 rpm for 3 h. Thereafter, the system was placed in a vacuum bag, a 2.5 kN load was applied for 24 h and vacuum for 2 min. |
| 7              | Composite laminates were manufactured based on process 3, reported in Table 1, but conducted at 1000 rpm for 4 h. Thereafter, the system was placed in a vacuum bag, a 2.5 kN load was applied for 24 h and vacuum for 2 min. |
| 8              | Composite laminates were manufactured based on process 3, reported in Table 1, but conducted at 1000 rpm for 5 h. Thereafter, the system was placed in a vacuum bag, a 2.5 kN load was applied for 24 h and vacuum for 2 min. |
| 9              | Composite laminates were manufactured based on process 3, reported in Table 1, but conducted at 1000 rpm for 3 h. The system, after 2 min in a vacuum chamber, was subsequently placed in a vacuum bag and a 2.5 kN load was applied for 24 h. Finally, the bag remained attached to a vacuum pump for another 2 minutes. |

The flexural strength was calculated as the nominal stress in the middle span section obtained using maximum value of the load (equation (1)), while the bending stiffness modulus was obtained by linear regression of the load-displacement curves considering the interval in the linear segment with a correlation factor greater than 95% according with equation (2) [6]. Finally, the bending strain is obtained according with equation (3):
where $P$ is the load, $L$ the span length, $b$ the width, $h$ the thickness of the specimen, $I$ the moment of inertia of the cross-section, $\Delta P$ and $\Delta u$ are, respectively, the load range and flexural displacement range in the middle span for an interval in the linear region of the load versus displacement plot and $S$ is the deflexion.

\[
\sigma = \frac{3PL}{2bh^2} \quad (1)
\]
\[
E = \frac{\Delta P L^3}{48 \Delta u I} \quad (2)
\]
\[
\epsilon_f = \frac{6Sh}{L^2} \quad (3)
\]

**Figure 1.** a) Specimens geometry; b) Schematic view of the three-point bending apparatus.

### 3. Results and Discussion

Flexural static tests were performed to obtain the effect of some manufacture parameters on the mechanical performance. In this context, Figure 2 shows the stress-strain curves and the results obtained for the procedures described in Table 1.

From Fig. 2a), it is possible to observe a linear increase of the bending stress with the bending strain, followed by a non-linear behaviour in which the maximum load is reached. It is also noticed that, when the resin is enhanced by CNFs, higher bending stress and modulus are achieved, while the bending strain decreases. After the peak load is reached, the bending stress decreases, arising the impending failure of the specimen. Figures 2b) to 2d) show the main bending properties in terms of average values (marks), and the bands represent, respectively, the maximum and minimum values for each condition. In terms of bending stress, Fig. 2b, it is noticed that the highest value was obtained with the resin enhanced by CNFs (114 MPa), reaching values around 12.6% higher than with the neat resin obtained without vacuum (process 1). However, when compared to the neat resin that involved vacuum, this improvement was only around 7.9%. Similar behaviour was observed for the bending modulus with values around 20.9% and 5.6%, respectively. Finally, the effect on the bending strain is not so evident due to the dispersion of the values observed. However, a small downward trend is observed for nano-enhanced resin. These results are in line with the open literature, because nanomaterials have a large surface area per volume unit compared to macro level materials and, in addition to their unique surface effects, increased chemical activity and particular physical properties, they promote synergy between constituents (polymer and CNFs) [6–8]. Simultaneously, the benefit of the vacuum is evident, where improvements in bending stress around 4.3% are obtained compared to the procedure that did not involve vacuum (process 1). Regardless of the resin/hardener mixture being made manually, and with particular care to avoid air bubbles, this process is not free from defects that need to be removed. In this context, the vacuum proved to be a viable technique for this purpose [2,3].
Figure 2. a) Representative bending stress-strain curves; b) Bending stress vs manufacture process; c) Bending modulus vs manufacture process; d) Bending strain vs manufacture process.

Figure 3 shows the fracture surface, showing a typical behaviour of brittle polymers with low resistance to crack propagation. On the other hand, the absence of air bubbles and a good dispersion of CNFs are also evident, confirming the benefits previously reported with the nanoparticles used. In fact, according to the open literature, agglomerations/aggregations are responsible for stress concentrations in nanocomposites and reduce the interfacial area between the polymeric matrix and nanoparticles [8–11]. On the other hand, only a few polymer molecules are able to penetrate between the nanoparticles, which promotes an increase in viscosity [12].

Figure 3. SEM image of the fracture surface.
In terms of composite laminates, Figure 4 shows the effect of the vacuum time on the bending properties. This study involved only laminates produced with neat resin obtained according to process 2 in Table 1. Therefore, the vacuum time is studied after the lamination of the composites. In fact, one of the most common defects of epoxy resins is the formation of air bubbles, so it is crucial to analyse the time for removing air by applying vacuum.

Fig. 4a) shows that all curves present a nearly fragile behaviour with a linear region up to the maximum load, followed by a significant drop after this value. Fibres breakage in compression side is the main damage mechanism observed, which is in line with the open literature [13,14]. According to Giancaspro et al. [14], carbon fibre composites fail mainly on the compression side, because this damage mechanism is consequence of the high compressive stress concentration in the pin load contact region associated to the low compressive strength of the carbon fibres [13,14].

![Figure 4. Effect of vacuum time on the: a) Bending stress-strain curves; b) Bending stress vs vacuum time; c) Bending modulus vs vacuum time; d) Bending strain vs vacuum time.](image)

From the other figures, Fig 4b) to 4d), it is possible to observe that the bending properties increase up to a vacuum time of 2 min, reaching their maximum values, after which they start to decrease. For
example, compared to the values obtained for a vacuum time of 5 s, the bending stress increases around 14.1%, the bending modulus about 11% and the bending strain around 10.1%. On the other hand, the same comparison for the vacuum time of 10 min promotes decreases of 26.8% and 25.7%, respectively, for bending stress and bending strain, while the bending modulus remains very similar (comparisons in relation to the vacuum time of 5 s).

In order to explain this phenomenon, Fig. 5 illustrates typical cross sections of specimens produced with vacuum times of 1 min and 2 min. As shown in Fig. 5a), it is possible to observe some voids, corresponding to air bubbles, in laminates that were produced with 1 min of vacuum, while for laminates subject to 2 min of vacuum, the absence of these voids is notorious (Fig. 5b)). Therefore, the increase in the mechanical properties previously reported up to 2 min of vacuum is a consequence of the decrease in voids. On the other hand, for higher vacuum times, the mechanical properties no longer decrease due to voids, but as a consequence of the lower amount of resin in the laminate. Vacuum suction was carried out at the end of the bag and, in this case, the resin was sucked into the absorbent fabric that delimits the laminates. In this case, with the increase in the vacuum time, more resin is removed from the laminate and, consequently, the remaining resin is not enough to completely wet the fibers. Because the load transfer between fibers is not effective, due to the lack of resin, the mechanical properties of the laminates decrease. This can be justified by the lower thickness of the laminates that is observed with the increase in the vacuum time, because they were all subject to the same 2.5 kN load during the manufacturing process. For example, average thicknesses around 1.47 mm, 1.45 and 1.36 mm were measured for laminates subjected to vacuum times of 3 min, 5 min and 10 min, respectively, which is a clear evidence of the lower resin content. In this context, the vacuum time of 2 min proved to be the ideal.

![Figure 5](image.png)

**Figure 5.** a) Laminates with defects: air bubbles 1 min; b) Laminates without defects 2 min.

Finally, the effect of rotation speed and mixing time was analyzed to obtain the best dispersion of CNFs in the resin and, consequently, in the composite laminates. For this purpose, nine different manufacturing processes were studied, which are summarized in Table 2, and the results obtained shown in Fig. 6.

From Fig. 6a) it is possible to observe a typical profile to those obtained in Fig. 4a), where all curves present a nearly fragile behaviour with a linear region up to the maximum load, followed by a significant drop after this value. Only three curves are illustrated, but they are representative of all the
others. As reported previously, fibres breakage in compression side is also the main damage mechanism observed.

In terms of bending stresses, it is noticed that composite laminates produced according to process 5, reported in Table 2, show improvements about 11.3% higher than the value obtained for the control samples (resin and hardener mixed manually, followed by vacuum for 10 minutes, the bag remained connected to a vacuum pump for 2 min and a load of 2.5 kN was applied). This is clear evidence of the benefits obtained with CNFs, which were described in detail earlier when only the resin was analysed. In this context, CNFs have a large surface area per unit of volume, good physical and mechanical properties and promote synergy with the matrix [6–8]. However, the bending strength can be further improved by degassing the system (resin and fibers) after mixing with CNFs (beyond 2 min in the vacuum bag). In this case, for process 9, the bending stress is around 16.5% higher when compared to the control laminates (808.5 MPa). This benefit is related to the effect of the vacuum on the mechanical properties, as previously discussed [2,3]. It is worth mentioning that another vacuum step performed after mixing the resin with CNFs, in addition to the vacuum in curing, increased the flexural strength by about 4.7%.

![Figure 6](image_url)

**Figure 6.** Effect of the manufacture parameters on: a) Typical bending stress-strain curves; b) Bending stress; c) Bending modulus; d) Bending strain.

In terms of bending modulus, the same tendency was observed. In this case, the benefits obtained with CNFs, compared to the composites with neat resin, were around 15.6% higher, and the extra step
of vacuum promoted improvements of 16.6%. In this example, comparing only the extra step of vacuum, it promoted an improvement around 6.4%. On the other hand, from Fig. 6d), it is possible to observe that the bending strain is not as affected as the bending stress and bending modulus, because the values are much more uniform. However, the processes that promoted higher bending stress and bending modulus were those that, as expected, presented lower values of bending strain. For example, compared to the control samples (1.57 %), the bending strain decreased between 1.3% and 1.9%.

Conclusions
CNFs were used to improve the mechanical properties of a commercial epoxy resin and a laminate composed by eight layers of bi-directional carbon woven prepared by hand lay-up process.

It was possible to conclude that the rotation speed of the mixer, dispersion time of the CNFs and vacuum time applied, both in the resin after its preparation and in the laminate after its manufacture, influence the mechanical properties of these materials.

In terms of resin, the best mechanical properties were obtained when 0.5 wt.% of CNFs were mixed at 1000 rpm for 3 h, simultaneously using an ultrasound bath, followed by degassing for 10 minutes in a vacuum chamber. For example, the resin enhanced by CNFs reached values around 12.6% higher than the bending stress obtained for neat resin produced without vacuum. Finally, in relation to laminated composites, it was found that the manufacturing process that promoted the best mechanical properties involved two vacuum stages. In this case, resin and CNFs were mixed at 1000 rpm for 3 h followed by 2 min in a vacuum chamber. The system composed of fibres and nano-enhanced resin was, subsequently, placed in a vacuum bag and a 2.5 kN load was applied for 24 h. Finally, the bag remained attached to a vacuum pump for another 2 minutes. The benefits obtained with CNFs, compared to the composites with neat resin, were around 15.6% higher, and the extra step of vacuum promoted improvements of 16.6%.

Acknowledgements
This work was supported by the project Centro-01-0145-FEDER-000017 - EMaDeS - Energy, Materials and Sustainable Development, co-financed by the Portugal 2020 Program (PT 2020), within the Regional Operational Program of the Center (CENTRO 2020) and the European Union through the European Regional Development Fund (ERDF).

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