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# **Influence of nanorubber toughening on the tensile deformation and tensile fatigue behaviour of a carbon fibre reinforced epoxy composite**

Nazli G Ozdemir<sup>1\*</sup>, Tao Zhang<sup>1</sup>, Homayoun Hadavinia<sup>1</sup>, Ian Aspin<sup>2</sup>, Fabrizio Scarpa<sup>3</sup>

## **Abstract**

This study investigates the effect of nano carboxylic acrylonitrile butadiene rubber (CNBR-NP) on the tensile fatigue behaviour of carbon fibre reinforced polymer composites (CFRP) with dicyandiamide-cured epoxy matrix. The stress-controlled tension-tension fatigue behaviour at a stress ratio of  $R=0.1$  and for the maximum stress ratio range of 400 to 650 MPa was investigated for the case of CFRPs with pristine and nano rubber-modified epoxy matrices with loadings of 5, 10, 15 and 20 phr. The results from the experimental tests show that the high-cycle fatigue life of the laminates with 15 phr of nanorubber modified resin matrix was increased by a factor of two compared to the pristine matrix samples. Scanning electron microscopy (SEM) images of the fracture surfaces also show an enhanced plastic deformation existing at the fibre-matrix interface and a lower extent of fibre pull-out; both contributing towards the enhancement of the fatigue performance of the carbon fibre reinforced polymer composites.

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## **Keywords**

Polymer-matrix composites, nano-particles, fatigue, tensile, nano rubber

## **Introduction**

Carbon fibre reinforced polymer composites (CFRP) experience constant and variable amplitude fatigue loads in service. Safe operation of structures made with CFRPs throughout their lifetime necessitates high fracture toughness capabilities and a good fatigue resistance. Epoxy is the main matrix material of fibre-reinforced composites. It is a highly cross-linked material with brittle characteristics that affects the overall fatigue and fracture performance of the fibre reinforced polymer structure. Fillers are often incorporated into the matrix to enhance the mechanical properties of the composites. The enhancement of the fatigue life of the composite depends on the type of toughener agent, its concentration, size of the toughening particles and their physical and chemical interactions with the matrix [1, 2, 3]. Apart from the interaction existing between the particles and the matrix, the influence of the fibre/resin interface on the overall performance of the composites is also quite significant. An enhancement in the fatigue life of advanced composite laminates can help engineers with the design and manufacturing of more durable composites with an extended lifetime.

A significant amount of work can be found in the literature about the effects of dispersing nano rubber on the mechanical properties of epoxy resin systems [4, 5, 6]. However, it is apparent that there is not a sufficient amount of activities performed on the evaluation of the mechanics of CFRPs with nano rubber-toughened epoxy matrix. The fabrication of hybrid carbon/nanorubber epoxy composites is made problematic by the viscosity build-up of the matrix with the nano rubber dispersion, which makes difficult to penetrate the resin through the dry fibres and therefore hinders the production of hybrid CFRPs with satisfactory mechanical behaviour. Hand lay-up techniques are however a viable solution for small-scale productions, because the toughened matrices are pasted on the dry fibres and the plies are stacked together. By using hand lay-up the higher viscosity of the nanorubber toughened resin matrix results in better interfacial properties between the fibres and the matrix, leading to an improvement of the mechanical properties of the composite structure.

Nanoparticles such as nanosilica, nanoclay, graphene and carbon nanotubes have shown the capability of delivering significant improvements to the mechanical properties of polymer matrices. Manjunatha et al. have studied the influence of rubber and silica nanoparticles on the fatigue behaviour of epoxy matrix. The addition of 10% of nanosilica improved the lifespan by 3-4 times [7]. Graphene nanoplatelets have also been observed to improve the bonding between the carbon fibres and the matrix, leading to an enhancement in the overall lifespan of the CFRPs [8]. Moaseri et al. have

functionalised carbon nanotubes to form covalent bonds between the epoxy matrix and the surface of the nanotubes that led to an enhancement in the fatigue life of reinforced composites [9]. Jen et al. have acid-treated carbon nanotubes and dispersed them in epoxy matrix. The fatigue strength of the resulting composites did not show a significant change [10]. Ferreira et al. have observed a 12% improvement in the fatigue strength of Kevlar composites by dispersing nanoclay in the epoxy matrix [11]. In the majority of published studies about the use of nanoparticles in composites it is apparent that the large-scale production of nanocomposites is made difficult by the high cost of the nanoparticles, the agglomeration (or clustering) of the particles and the complicated processing techniques required. In the current work, we present a hybrid CFRP composite with a carboxylic acrylonitrile-based nanorubber toughened epoxy resin matrix. The specific processing technique presented in this work could be also potentially applied to scale-up industrial manufacturing. In a previous work, we have demonstrated that by adding 20 phr of carboxylic acrylonitrile based nanorubber to the matrix, one could obtain a 250% increase in the Mode I delamination fracture toughness of CFRP composites [12]. Also, the carboxylic acrylonitrile-based nanorubber does not show any increase in the viscosity of the epoxy resin beyond its processing limits, and neither appears to affect the glass transition temperature ( $T_g$ ) of the system [13]. The current work describes how the use of this novel nanorubber toughened epoxy matrix could improve the tension-tension fatigue behaviour of the CFRP composites.

The enhancement of the fatigue life of rubber particle modified epoxies has been reported in open literature [7, 5, 14]. However, to the best of our knowledge, there is no study available about the tensile fatigue analysis of hybrid carbon fibre reinforced polymeric composites with nano rubber-toughened epoxy as the matrix. Hence, the main aim of this investigation is to address the stress-controlled constant-amplitude tension-tension fatigue behaviour of carbon fibre-reinforced polymeric composite (CFRP) with nano rubber-modified epoxy matrices. This study also presents the investigation on the quasi-static tensile strength, and the morphological characterisation of carbon fibre reinforced laminates.

### **Experimental studies**

Diglycidyl ether of Bisphenol-A, (DGEBA resin, trade name: Araldite LY1556, epoxide equivalent weight: 188) was supplied by Huntsman, UK. As a curing agent dicyandiamide (DICY, trade name: Dyhard D50EP) was used, and a difunctional urone (trade name: Dyhard UR500) was employed as accelerator. AlzChem, UK supplied both the two chemical compounds. Nano carboxylic acrylonitrile butadiene rubber (CNBR-NP) Narpow VP-501 (single particle size distribution 50-100 nm, acrylonitrile content, 26 wt%), was received in powder form from SINOPEC, Beijing Research Institute of Chemical Industry (BRICI), China. The nano carboxylic acrylonitrile butadiene rubber was prepared by the manufacturer by irradiating the corresponding rubber latex with a cobalt-source (dosage: 25 KGy and dose rate: 50 Gy/min). The irradiation was

instrumental to crosslink the nanorubber before drying with a spray dryer. A Malvern particle size analyser indicated that 90 vol. % of the particles had diameters below ~500  $\mu\text{m}$  in received, powder form.

Fumed silica (FS) from Aerosil, UK ( $D_{50} = 1 \mu\text{m}$ ) was dispersed in the pristine epoxy to modify its rheological behaviour and facilitate the fabrication of the laminates. In previous work [12] we have proved that such small amount of fumed silica does not have any significant effect on the mechanical properties of the CFRP composites. The reinforcement of the composites consisted in T300 twill carbon plies from Sigmatex Ltd. The carbon fibres had a density of 199 grams per square meter (GSM). The matrix formulations used in this research work are given in Table 1.

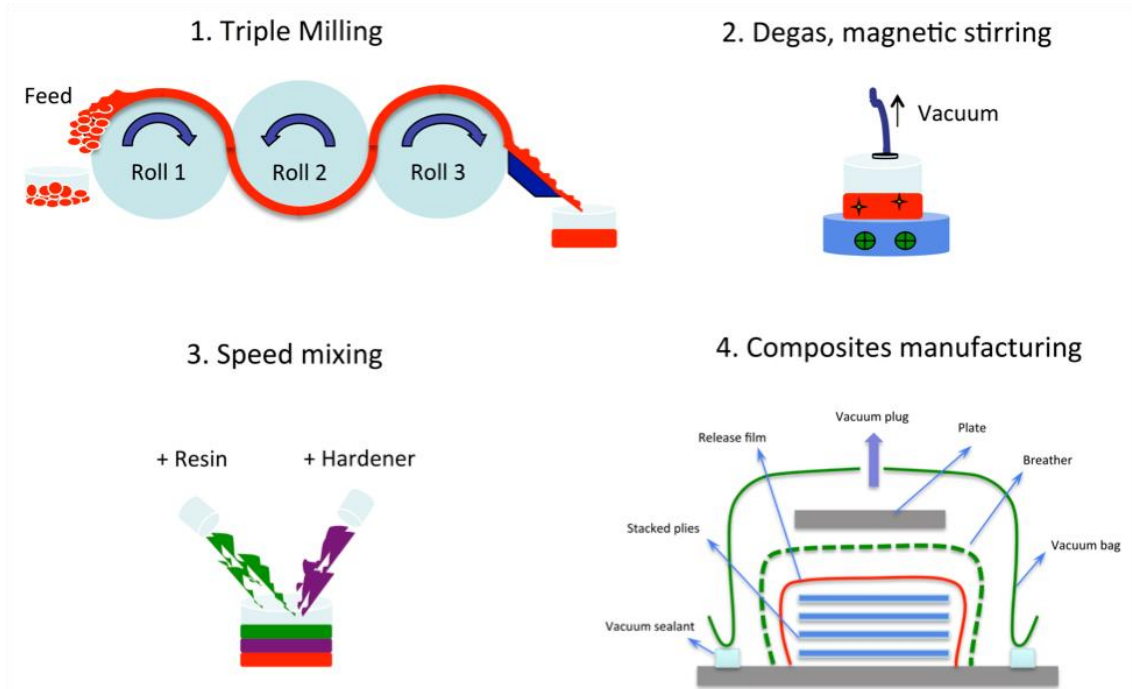
**Table 1.** Matrix formulations used in the experimental work in phr (parts per hundred of DGEBA)

<b>CODE</b>	<b>DGEBA</b>	<b>DICY</b>	<b>Diurone</b>	<b>CNBR-NP</b>	<b>Fumed Silica</b>
<b>R/ 1 FS</b>	100	14	6	-	1
<b>5 CNBR-NP/ R</b>	100	14	6	5	-
<b>10 CNBR-NP/ R</b>	100	14	6	10	-
<b>15 CNBR-NP/ R</b>	100	14	6	15	-
<b>20 CNBR-NP/ R</b>	100	14	6	20	-

\*FS: fumed silica, DGEBA: diglycidyl ether of Bisphenol-A resin, DICY: dicyandiamide hardener, CNBR-NP: carboxylic acrylonitrile butadiene nanorubber

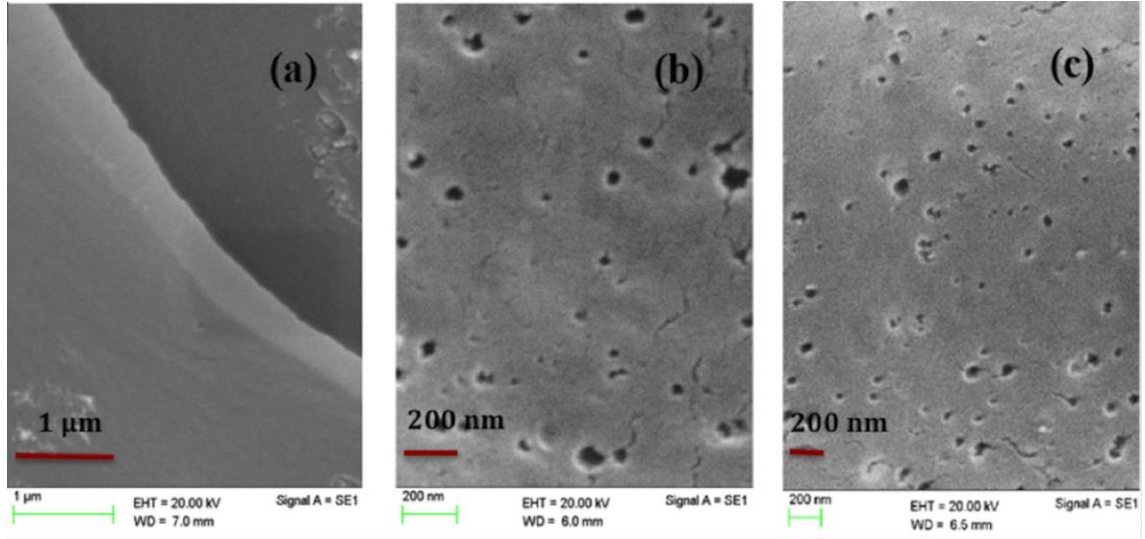
The nano rubber was dried overnight in a vacuum oven at 80 °C and dispersed in a diglycidyl ether of Bisphenol-A (DGEBA resin) matrix. The blend was mixed in a speed mixer, and later 1 phr of fumed silica was added to the pristine epoxy to increase the viscosity of the samples. The blend was triple-milled at room temperature (RT=23 °C) for six times. After the mixing, the solution was magnetically stirred and degassed under vacuum. The curing agent and the accelerator were added and the final mixture was then speed mixed. Further details on the processing techniques adopted in this study can also be found in reference [13]. A hand lay-up technique was used to produce the CFRP laminates for the quasi-static and fatigue tests, each laminate consisting of 12 layers of bi-directional dry carbon plies. The composite panels were heated at 120 °C at a rate of 0.5 °C/min, held for one hour at the final temperature before being cooled down to room temperature at the same rate. The CFRP samples destined to the mechanical testing were cut from the cured panels using a high-pressure water jet. Figure 1 gives an overview of the manufacturing process used in this study.





**Figure 1.** Manufacturing techniques used in this work

Figure 2 shows a scanning electron microscope (SEM) image related to a toughened resin sample (X CNBR-NP/ R). The SEM analysis carried out on the different CFRP panels showed that the nanorubber was uniformly distributed within the various matrix configurations developed in this work.



**Figure 2.** Scanning electron microscope (SEM) images of the fracture surfaces of (a) R sample, (b) 5 CNBR-NP/ R sample, (c) 20 CNBR-NP/ R sample

The volume fraction of the dry fibres in the CFRP-composites was estimated using the following equation:

$$\%V_f = \frac{100W_{FAW}N_p}{Br_F} \quad (1)$$

In (1),  $W_{FAW}$  is the fibre surface weight,  $N_p$  the number of plies,  $B$  the thickness of the CFRP panels and  $\rho_F$  is the density of the carbon fibre. The value of  $W_{FAW}$  is quoted from the manufacturer's datasheet of the carbon fabrics (199 g/m<sup>2</sup>). The density of the carbon fibre is 1.76 g/cm<sup>3</sup>. The mean values of the thicknesses of the CFRP panels measured using a digital micrometre and the carbon fibre volume fractions are shown in

Table 2. The CFRP panels with the highest nano rubber concentrations (15 CNBR-NP/R and 20 CNBR-NP/R matrices) have the lowest carbon fibre volume fraction. The volume fraction also differs significantly (8%) due to the differences in the viscosity of the nano rubber-modified formulations and the pristine matrix. The unmodified resin has a considerably lower viscosity, and leaks from the vacuum bag under high pressures and temperatures in the autoclave. It is therefore expected that the laminates with the pristine matrix and also with lower concentrations of nano rubber have the highest carbon fibre volume fractions (Table 2).

The tensile properties of the specimens, including the ultimate tensile strength (UTS) and the modulus  $E_1$  have been determined following the ASTM D3039 standard by using three replicates (Table 2). The dimensions of the tensile test samples were  $250 \times (25 \pm 0.2) \times (3 \pm 0.4)$  mm.

**Table 2.** Thickness B and fibre volume fraction  $V_f$  of the CFRP-composites with pristine and X CNBR-NP/ R matrices (SD = Standard deviation)

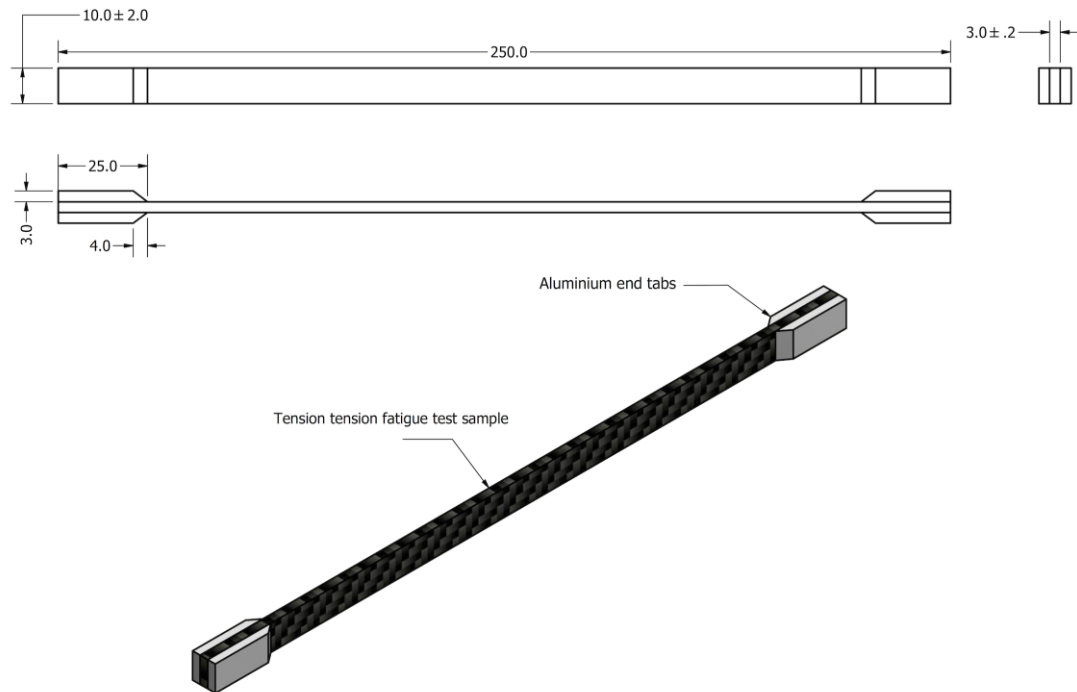
<b>X</b>	<b>Specimen thickness, B (mm)</b>	<b><math>V_f</math></b>	<b>UTS (MPa)</b>		<b><math>E_1</math> (GPa)</b>	
			<b>Mean</b>	<b>SD</b>	<b>Mean</b>	<b>SD</b>
<b>R/ 1FS</b>	2.7 ( $\pm 0.10$ )	0.50	661	24	58.2	4.2
<b>5</b>	2.6 ( $\pm 0.15$ )	0.52	696	20	58	5.1
<b>10</b>	2.6 ( $\pm 0.18$ )	0.53	645	18	55.9	3.2
<b>15</b>	2.8 ( $\pm 0.14$ )	0.48	561	22	53.1	4.3
<b>20</b>	3.0 ( $\pm 0.30$ )	0.45	531	32	53.9	5.3

Force-controlled tension-tension fatigue tests of the CFRP specimens were performed at room temperature (23°C) with a servo-hydraulic Zwick Roell test machine having a load cell of 25 kN, and using a sinusoidal wave load. The maximum stress ratio range for the tension-tension fatigue tests was 400 to 650 MPa, based on the ultimate tensile strengths of the specimens, as reported in Table 2. The ratio between the minimum to maximum stress (R-ratio) was 0.1. A cyclic frequency of 5 Hz was used to avoid the overheating of the samples during testing. The dimensions of the samples for the tension-tension fatigue tests were  $250 \times (10 \pm 2) \times (3 \pm 0.2)$  mm (Figure 3). Aluminium end tabs were used to reduce possible stress concentration resulting from the presence of high gripping pressure. For each matrix formulation and stress level three tests were

performed. During the tests the number of cycles to failure and the maximum and minimum displacements of the specimens were recorded. The results were then analysed in terms of stress versus the number of cycles to failure ( $S-N$  Wohler curves).

The loads versus displacements for one complete fatigue cycle were analysed at regular intervals during the fatigue test, and the sample stiffness was calculated [15]. Fifty points of load/displacement data were used for this analysis. The normalised stiffness of the samples was taken as the ratio of the measured stiffness at any given fatigue cycle to the initial stiffness in the first cycle.

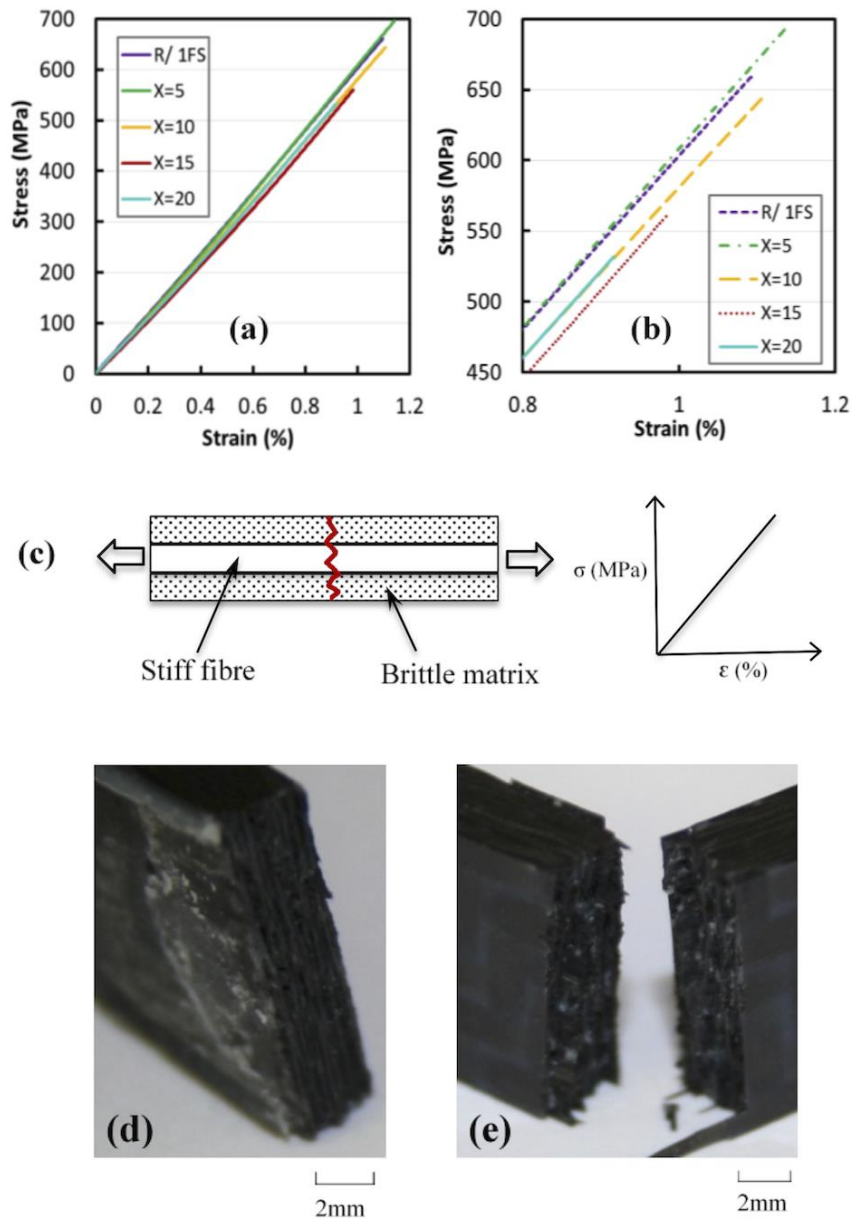
The fracture surfaces of the fatigue test specimens were observed using scanning electron microscopy (SEM) at secondary electron mode. The samples were vacuum coated with gold, and the images taken using an accelerating voltage of 20-25 keV with a magnification between 90 times and 2000 times.



**Figure 3.** Tension- tension fatigue test specimens used in this study

## Results and discussions

Figures 4 (a) and (b) show the tensile stress-strain curves of the CFRP panels. All specimens failed immediately after the tensile stress reached the maximum value. This type of premature failure indicates a damage mechanism that is observed in panels that consist of a brittle matrix and high modulus carbon fibre (Figure 4 (c)). In such type of laminates the strain cannot be efficiently transferred from the high modulus fibres to the low modulus matrix, resulting in a brittle failure as can be observed in Figure 4 (d) and (e) [16, 17]. The specimens mostly failed in ‘LAT’ mode, detailed in ASTM D3039.



**Figure 4.** (a), (b) Tensile stress-strain curves of the composite panels with X CNBR-NP/ R matrices, (c) Damage mechanism resulting in a premature failure [17], (d) tensile fatigue fracture surface of the laminate with R/ 1FS matrix ( $\sigma_{\max} = 563$  MPa), and (e) 20 CNBR-NP/ R matrix ( $\sigma_{\max} = 530$  MPa)

The stress-controlled, cyclic-fatigue test results at constant amplitude for the CFRP panels are shown in Figure 5. The figure clearly shows that the fatigue life of the composite with the pristine epoxy matrix was extended by 55% by adding 5 phr of nanorubber. However, further increases of the nano loading shortened the fatigue life of the composites at every stress ratio. This behaviour is mainly attributed to the reduction in the tensile strength of the nano-modified CFRP panels consequent to any further integration of the nano rubber into the matrix (Table 2). The presence of the nanorubber results in a build-up of the viscosity of the resins, and the formulations with the higher loadings show indeed an improved tackiness. The unwanted leakage of the resin from the vacuum bag at high pressures is prevented to some extent, resulting in a lower fibre volume percentage (Table 2). It is well known that in composite structures properties such as the tensile strength and fatigue behaviour are fibre-dominated [18, 19]. In practice, as the nanorubber loading increases the tensile strength of the composite decreases because of the lower fibre volume fraction. This phenomenon is clear and evident in this study.

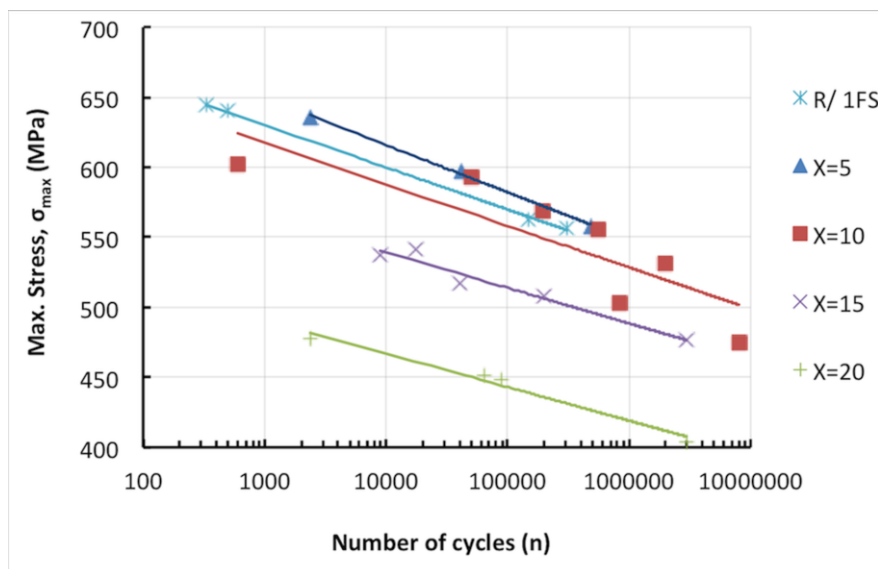
The stress versus number of cycles to failure for the CFRP panels was fitted with Basquin's law [20]:

$$S = S_f(N_f)^b \quad (2)$$



Where  $S_f$  is the fatigue strength coefficient (FSC), and  $b$  is the fatigue strength exponent (FSE). The values of the FSC and FSE determined for the CFRP with pristine and nanoparticle-modified matrices are given in Table 3. The dispersion of 5 phr of nanorubber into the matrix contributed to an increase in the fatigue strength coefficient and decreased the fatigue strength exponent by 4% and 15%, respectively. This means that the panel with 5 phr of nanorubber loading in its matrix exhibited the highest fatigue performance. However, the general fatigue properties did not show a significant variation amongst the various matrix formulations. A relatively large scatter in the laminate with 10 phr of nanorubber loading (10 CNBR-NP/ R) in its matrix was observed, which may be attributed to the unstable dispersion quality of the nanorubber in this particular laminate. In Table 3, the equations for the characteristic fatigue curves of the composite samples are listed. A consistent decrease in the slope of the nano rubber-modified samples is noticeable above 5 phr of nanorubber loading, which indicates that the composites with the nano rubber-modified matrices endure more cycles at lower stresses. This effect may be explained by the nature of the failure mechanisms in carbon fibre composites subjected to cyclic loading. Fatigue life of carbon fibre composites is related to the nucleation and growth of damage in the polymer matrix [11, 3]. At high cyclic stress levels, a significant amount of damage in the matrix is generated within few cycles. On the contrary, at low cyclic stress levels the damage in the matrix is small and with continued cycling isolated cracks propagate

slowly until failure occurs. Nanoparticles in general tend to suppress the matrix cracking and lead to a decrease in the crack growth rate of the system. However, nanoparticles tend to be effective only at high cycle fatigue combined with low stress levels [21]. The improvement in the tensile strength and the fatigue performance is also often explained by the higher matrix strength and the fibre/matrix interface strength. In this work it is apparent that the main reason behind the difference in the quasi-static tensile and fatigue properties of the CFRP panels is the carbon fibre volume fraction of the panels (Table 2). A volume fraction of 0.52 was the second highest for the CFRP panel with 5 phr of nanorubber in its matrix, and resulted in a slight increase in the tensile strength and a relatively higher number of cycles till failure.

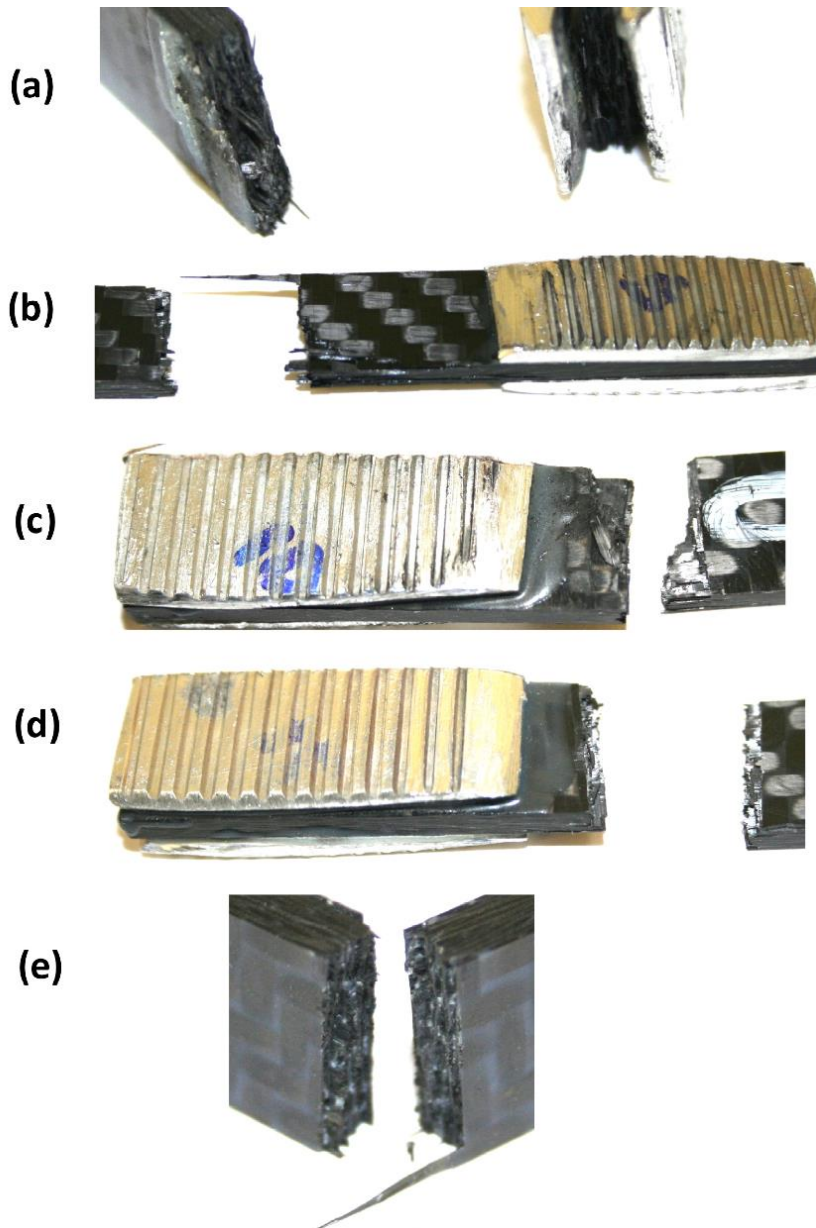


**Figure 5.** Stress versus lifetime (*S-N*) curves of the CFRP panels with R/ 1FS and X CNBR-NP/ R matrix

**Table 3.** Fatigue properties of the CFRP panels with R/ 1FS and X CNBR-NP/ R matrices, FSC: Fatigue strength coefficient, FSE: Fatigue strength exponent

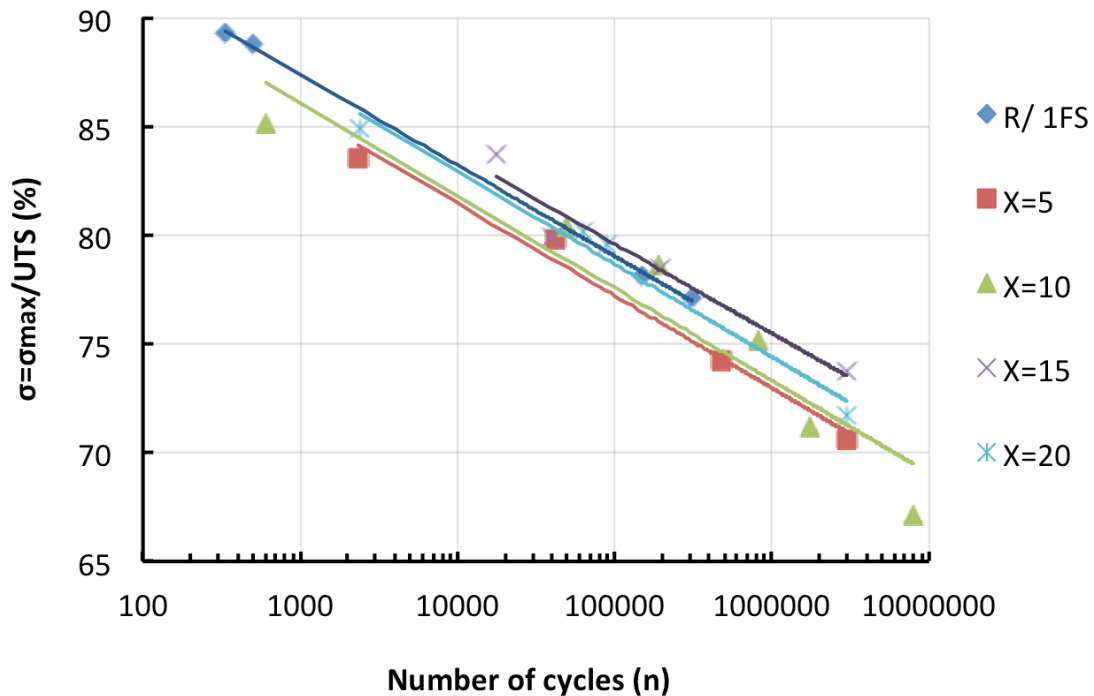
<b>X</b>	<b>Equation</b>	<b>Fatigue properties</b>	
		<b>FSC (MPa)</b>	<b>FSE</b>
<b>R/ 1FS</b>	$\sigma = 721(N_f)^{-0.020}$	721	-0.020
<b>5</b>	$\sigma = 751(N_f)^{-0.023}$	751	-0.023
<b>10</b>	$\sigma = 706(N_f)^{-0.018}$	706	-0.018
<b>15</b>	$\sigma = 641(N_f)^{-0.018}$	641	-0.018
<b>20</b>	$\sigma = 563(N_f)^{-0.019}$	563	-0.019

Figure 6 shows the fracture surfaces of the tensile fatigue specimens failed in the maximum stress range of 530 to 560 MPa. It may be argued that the extent of fibre-matrix delamination decreases with an increase in the nanorubber loading. The premature failure is very noticeable in the specimens, indicating clearly the limited stress transfer between the high modulus fibres and the low modulus matrix. Extracted/pulled-out carbon fibres on the fracture surface of the pristine resin matrix specimen are clear signs of a weak fibre-matrix (Figure 6 (a)).



**Figure 6.** Tensile fatigue fracture surfaces of the laminate with **(a)** R/ 1FS matrix ( $\sigma_{\max} = 563$  MPa), **(b)** 5 CNBR-NP/ R matrix ( $\sigma_{\max} = 558$  MPa), **(c)** 10 CNBR-NP/ R matrix ( $\sigma_{\max} = 555$  MPa), **(d)** 15 CNBR-NP/ R matrix ( $\sigma_{\max} = 541$  MPa), **(e)** 20 CNBR-NP/ R matrix ( $\sigma_{\max} = 530$  MPa)

The carbon fibre volume fractions of the samples produced in this study show a significant nominal deviation (8%) that clearly impacted on the ultimate strength of the laminates because of the fibre-dominated nature of the tensile strength property (Table 2). The normalised fatigue characteristics were therefore evaluated to eliminate the influence of the ultimate tensile strength on the fatigue behaviour of the panels. The normalised  $S-N$  curves for the pristine and the CNBR-NP modified CFRP panels are shown in Figure 7. It is possible in this case to observe a similarity between the  $S-N$  curves of the CFRP panel with the unmodified resin, and the CFRP panels with the nano rubber modified matrices. The normalised  $S-N$  curves therefore suggest that under tension–tension fatigue loading the nano rubber dispersions do not significantly affect the performance of the composites, due to the particular damage mechanism observed in these laminates consisting of a high modulus fibre and a low modulus matrix. From observing the tensile stress-strain curves of Figure 4 (a), it is possible to argue that the strain in the carbon fibres is not efficiently transferred to the matrix, therefore limiting the contribution of the matrix to the fatigue behaviour of the panels.



**Figure 7.** Normalised *S-N* curves for the CFRP panels with neat and X CNBR-NP/ R matrices

It is also worth noticing that the samples with the matrices R/ 1FS, 15CNBR-NP/ R and 20CNBR-NP/ R had a similar performance. Compared to the composites with the pristine resin, the fatigue life was extended by 32% in the CFRP panels with 15 phr of nanorubber loading at 80% normalised cyclic stress. Table 4 gives the complete lists of the normalised experimental data. It is interesting to observe that the samples with the 15 CNBR-NP/ R matrix perform very similarly to the other specimens at the applied maximum stresses of 80 and 85% UTS. However, the fatigue life of the panels with 15

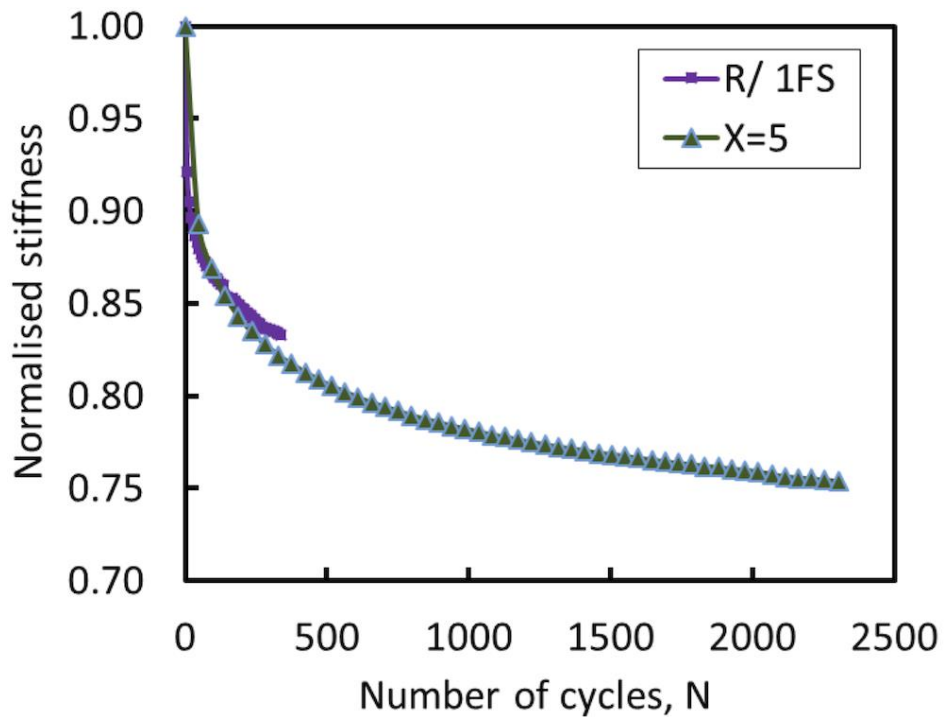
phr of nanorubber loading was extended by almost a factor of 2 at the maximum applied stress of 75% UTS.

**Table 4.** UTS (ultimate tensile strength) normalised experimental data for the CFRP with neat and X CNBR-NP/ R matrices

Maximum cyclic stress, %UTS	Number of cycles to failure, CFRP with X CNBR-NP/ R matrix				
	R/ 1FS	X=5	X=10	X=15	X=20
75	923,753	332,154	400,312	1,794,074	724,111
80	58,860	21,983	26,804	78,826	48,604
85	3750	1457	1794	4662	3262

The normalised stiffness variation with the number of cycles at  $\sigma_{\max}=640$  MPa for the CFRP panels with the R/ 1FS and 5 CNBR-NP/ R matrices is shown in Figure 8. In general, materials exhibit a stiffness degradation with increasing number of cycles [22, 23]. The initial stiffness reduction for the two sets of specimens is significant, however the rate of this degradation was slightly higher for the CFRP panel with the 5 phr of nanorubber loading (5 CNBR-NP/ R). This may be attributed to the higher negative slope of the CFRP panel with the 5 CNBR-NP/ R matrix compared to the panel with the pristine matrix (Table 3). The stiffness degradation trend is directly related to the

presence of cracking in the matrix [18] and correlates well with the slope of the  $S-N$  curves of these panels.



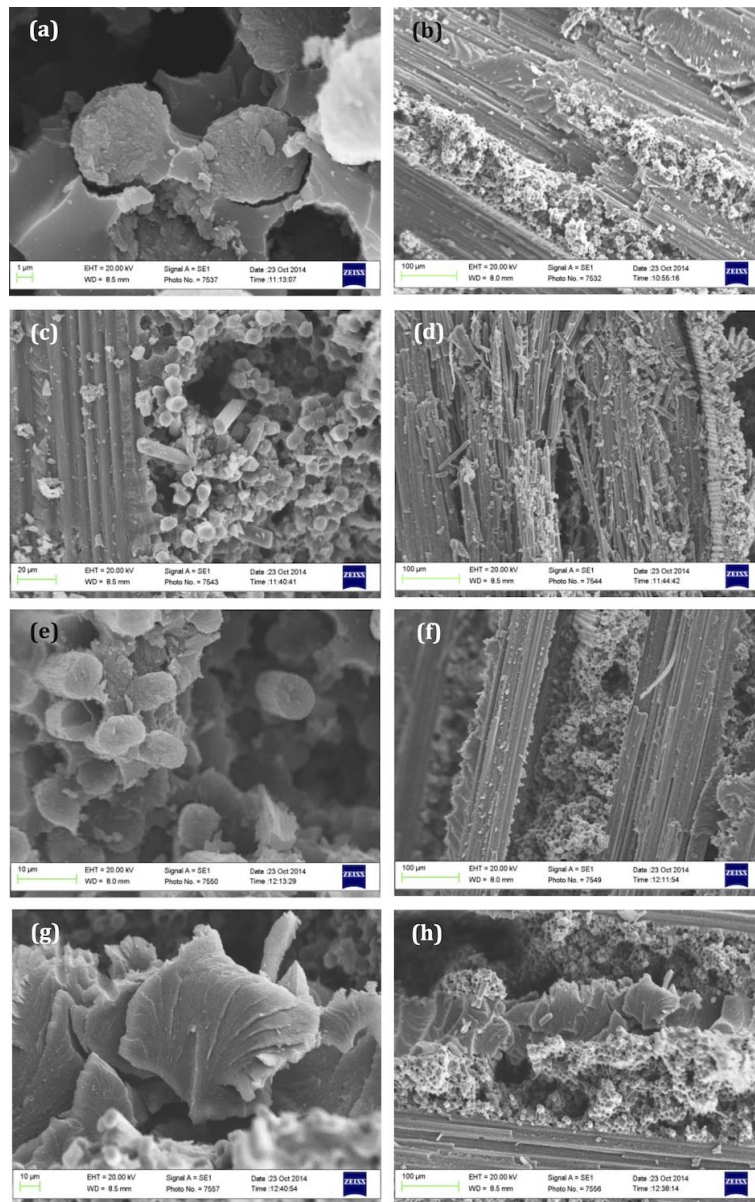
**Figure 8.** Normalised stiffness vs. number of cycles for CFRP panels with R/ 1FS and 5 CNBR-NP/ R matrices ( $\sigma_{\max}=640$  MPa,  $R=0.1$ )

Figure 9 shows some SEM images related to the fracture surfaces of the CFRP panels after fatigue failure. Fibre breakage, interface debonding and delamination were all observed in the CFRP panels with both pristine and nano rubber-toughened matrices. In Figures 9 (a) and (b) the damage mechanisms of the laminate with the neat matrix consisted of debonding at the fibre-matrix interfaces and of fracture of the fibres.



Debonding at the fibre-matrix interfaces occurred as a result of local stresses that develop at the interfaces during loading. This debonding was correlated with some individual fibres becoming prematurely overloaded and then failing [24]. As the fibres continue to undergo a premature failure, stress concentrations and local stresses at the interface are developed. The high amount of fibre pull-out resulting from the weak fibre-matrix interfacial strength is easily noticeable in the panel with the unmodified matrix (Figure 9 (a)). The pristine epoxy shows a relatively smooth fracture surface, devoid of any indications of large-scale plastic deformation. In Figures 9 (c) and (d), the presence of extracted carbon fibres on the fracture surface is clearly observable, and this feature indicates that the bonding between the fibres and the matrix is rather weak in the sample with the 5CNBR-NP/ R matrix, causing therefore a severe delamination. In Figures 9 (e) and (g) it is possible to observe the presence of a high amount of plastic deformation at the fibre-matrix interface in the panels with relatively higher nano rubber concentration matrices. The plastic deformation may act as an energy dissipation mechanism that provides an improved interfacial strength. In CFRP composites, the difference between the elastic moduli of the carbon fibre and the resin matrix is quite significant (Figure 4), and the stress transfer between the two phases is weak, leading to the presence of residual stresses at the interface. However, the relatively soft and compliant nanorubber toughened matrix can develop the plastic deformation to relax in part the stress concentrations. This fact suggests that the soft CNBR-NP particles

actually developed a resistance to fibre-matrix failure because of the creation of an interphase between the fibre and the matrix that can be clearly seen in Figure 9 (f). In Figures 9 (g) and (h) a “lotus leaf” formation is observed in the sample with the 20 CNBR-NP/ R matrix. This particular microstructure architecture provides an enhanced bonding between fibres and matrix.

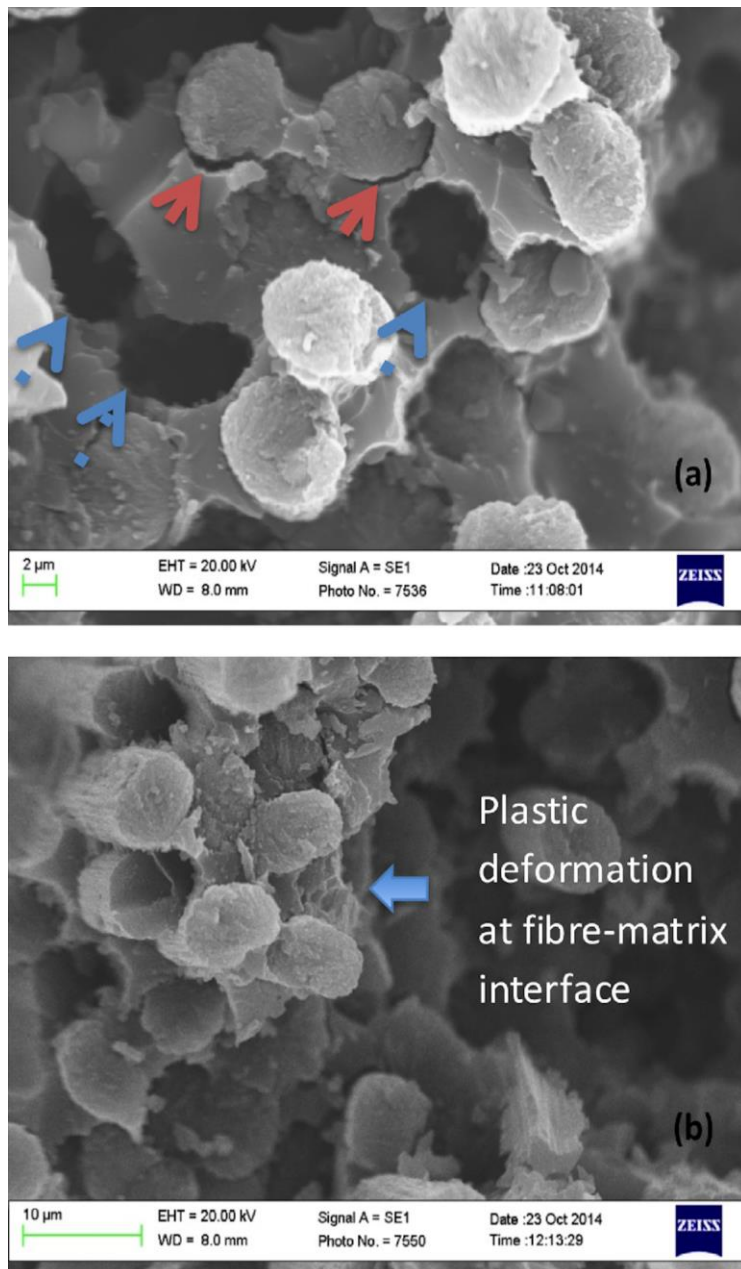


**Figure 9.** SEM images of the fracture surfaces of the CFRP panels tested in tensile fatigue, (a), (b) laminates with R/ 1FS matrix, (c), (d) laminates with 5 CNBR-NP/ R matrix, (e), (f) laminates with 15 CNBR-NP/ R matrix, (g), (h) laminates with 20 CNBR-NP/ R matrix

Figure 10 shows a close-up SEM image of the axial fibre-matrix interface of the CFRP panels. The most distinctive differences in the fracture surfaces of these two laminates are the extent of the fibre pull-out and the plastic deformation close to the interface. Both fibre-matrix debonding and fibre pull out were suppressed with the dispersion of nanorubber. The fracture surface is also noticeably rougher in the rubber-toughened composites, and this feature may lead to an increased efficiency of the load transfer between the matrix and the fibres and also to lower stress concentrations in the structure [16]. The primary role of the nanorubbers is to create a high amount of interface that may affect the curing/ crosslinking process and modify the structure of the polymer in the neighbourhood of the particle surface. Verma et al. indeed observed similar features in epoxy-alumina nanocomposites, and the presence of roughness on the fracture surfaces was deemed to be an indicator of higher energy dissipation that leads to an increase in fatigue life [25]. It is also possible that the functional carboxyl groups of CNBR-NP particles promoted a covalent bonding between the CNBR-NP particles and the carbon fibres, resulting in an enhanced fibre-matrix interfacial strength. Tiwari et al. have noticed that the carboxyl (COOH) groups promote the bonding between the fibre and the matrix by increasing the chemical activity of the fibre [26]. Usually the surface treatment of the carbon fibres (either by reactive functional groups or roughening the surface) improves the fibres' wettability and leads to better bonding with the matrix. In our case, the functional -COOH groups already exist on the nanoparticles' surface. In

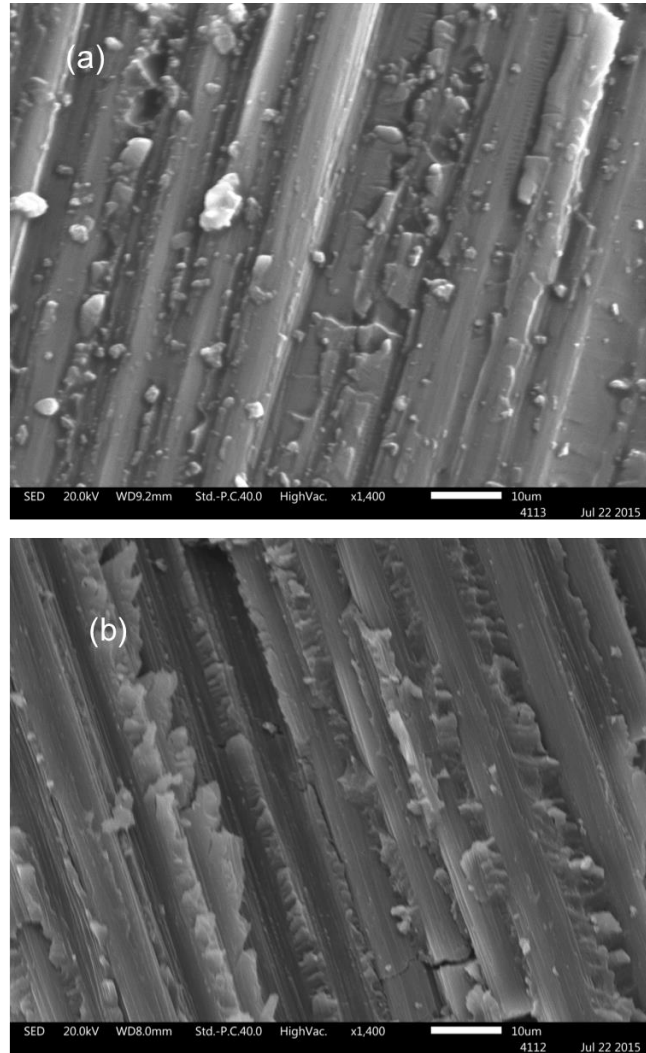
Figure 10 (b), it is noticeable that the nano rubber toughened matrix is well bonded to the carbon fibres, and this feature has been observed in several studies related to nano silica tougheners [27, 28].

Although plastic deformation can be observed in the laminate with the 15 CNBR-NP/ R matrix when compared to the smooth and glassy fracture surface of the laminate with the pristine resin matrix, neither the tensile strength nor the fatigue performance was strongly affected by the nanorubber modification of the matrix. This may be due to the fibre-dominated nature of the tensile and fatigue properties of the composites. The results may have been different if the analysis was carried out on a flexible glass fibre reinforced composite, in which the energy dissipation mechanism due to nano rubber toughening of the matrix may have accounted more on the fatigue behaviour of the composites [29].



**Figure 10.** SEM images of the fracture surfaces of the CFRP panels tested in tensile fatigue, **(a)** laminate with R/ 1FS matrix, blue dashed arrows point to fibre pull-out, red arrows point to fibre-matrix debond **(b)** laminate with 15 CNBR-NP/ R matrix

There is also a noticeable difference between the fracture surfaces of the laminate with the R/ 1FS matrix and the ones with the 20 CNBR-NP/ R resin (Figure 11). The high amount of fibre bridging in Figure 11 (b) is usually attributed to the strong interfacial bond between the fibre and the matrix [21, 19]. The presence of an interphase is a further indication of a strong bonding, and the cracks propagated through the fibres. The fracture surface of the sample with 20 phr of nanorubber in its matrix also displays more resin and broken carbon fibres, proving further the strong matrix/ carbon fibre adhesion. Fibre bridging is a mechanism to delay crack growth. In the case of the pristine epoxy composite the crack propagated along the fibre/matrix interface for long distances with little resistance and produced almost no plastic deformation. On the contrary, the rubber-toughened matrices were characterised by a stronger bonding, where the cracks propagated along the fibres (Figure 11 (b)).



**Figure 11.** SEM images of the fracture surfaces of CFRP panels tested in tensile fatigue, **(a)** laminate with R/ 1FS matrix, **(b)** laminate with 20 CNBR-NP/ R matrix

## Conclusions

The following conclusions can be drawn based on the results obtained in this work.



1. Unlike the case of low-modulus glass fibre composites [27, 28], the high moduli of the carbon fibres prevent the transfer of strains to the matrix and hence inhibit the matrix failure due to fatigue loading. The specimens showed rather a failure of the fibres, and the matrix modification did not have a significant effect on the fatigue behaviour of the laminates at low cycle fatigue.
2. High amount of fibre bridging and interphase formation was observed in the SEM image of the fracture surface of the laminate with the highest amount of nanorubber loading in its matrix that was attributed to the enhanced fibre-matrix adhesion. There was also a difference in the fracture mechanism in the laminate with the pristine resin matrix and that with the 20 phr of nanorubber loaded matrix, where the cracks propagated towards the weak fibre-matrix interface in the former, and along the strong fibres in the latter.
3. Normalised test data showed that the high cycle fatigue life was enhanced by a factor of 2 for the composite panel with the 15 CNBR-NP/ R matrix. Nano rubber toughening of the resin can improve the energy dissipation capacity of the matrix and the extent of the plastic deformation at the fibre-matrix interface [30, 31]. Therefore, the modified matrix can act as a stress relief medium, resulting in improved strain transfer between the fibre and the matrix phase and an enhanced fatigue life.

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