NANO-MODIFIED FIBER REINFORCED COMPOSITES: A WAY TOWARDS THE DEVELOPMENT OF NEW MATERIALS FOR SPACE APPLICATIONS.

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ABSTRACT

Composite materials are nowadays widely used in space applications. The introduction of nanotechnology in the field of composites has created new possibilities for the development of breakthrough materials with tailored functional properties. In this study, carbon nano-fibers (CNFs) were incorporated as a dopant into the matrix material of traditional carbon fiber reinforced plastics (CFRPs) having as a main goal the enhancement of their mechanical and electrical properties.

The first step towards this direction was the fabrication of isotropic CNF doped epoxy samples and the intensive characterization of their morphology and their mechanical-thermal-electrical behavior. In this way, a clear understanding of the doped matrix was obtained. The developed CNF doped epoxy mixtures were used as a matrix material for the preparation of unidirectional CFRPs. The mechanical characterization of the doped CFRPs showed remarkable increase in the fracture energy of the laminates and also higher elastic and storage modulus in comparison with the non-doped CFRPs. Furthermore, the use of CNFs as nano-sensors for the damage detection within the matrix material of the CFRPs was investigated. For this reason, the prepared doped CFRPs were submitted to fatigue tension-tension loading and the changes in the longitudinal resistance were monitored. Small increases in the resistance were reported much earlier than the macroscopic failure of the laminate indicating damage in the conductive network of the CNFs. Continuous acoustic emission (AE) monitoring was also applied during the fatigue tests and the captured AE signals were analyzed and correlated to the variation of the material's resistance.

INTRODUCTION

Multi-functionality is an aspect that space technology is focusing on the last decades. Space Systems design parameters like the mass reduction with increased system efficiency demand multifunctional approaches. The technology concept of multifunctional materials with sensing capabilities combined with enhanced mechanical properties could prove useful for the high requirements of the space sector. The incorporation of nanotechnology in the field of composites has opened new horizons towards the development of advanced materials with unique functional properties. Nano-composites are introducing the possibility of improved electrical and thermal properties combined with high mechanical efficiency.

Moreover, the non-destructive damage detection in carbon fiber reinforced polymers (CFRPs) during mechanical loading is a key parameter in many applications, especially in space structures. Previous studies within the last decade have shown that the mechanical deformation and the electric resistance of CFRPs are closely connected, so that the material can act an inherent sensor of his own damage [1]. In such composites with continuous carbon fibers, fiber breakage causes sudden increase in the axial resistance and in this way damage sensing is possible.

Carbon nanofibers (CNFs) are one of the most promising reinforcing materials for polymeric composites due to their high axial modulus and strength, high aspect ratio, large surface area, and excellent thermal and electrical properties [2]. In this study, CNFs were incorporated as dopants into the matrix material of unidirectional CFRPs. The target of this research is to set a point about the damage detection in a polymeric matrix by investigating the influence of the CNFs' incorporation in the mechanical, electrical and thermal properties of the CFRPs.

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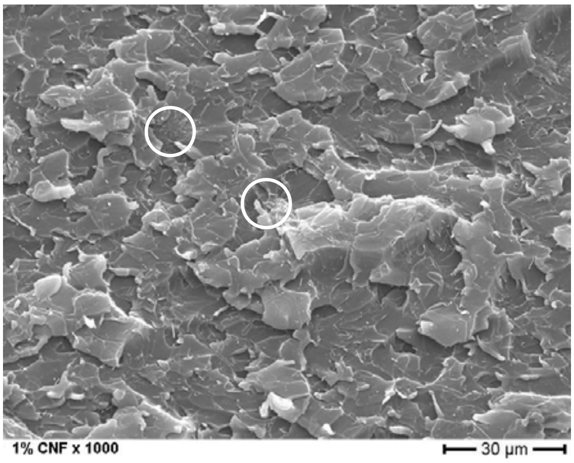
EXPERIMENTAL

Materials

The thermosetting matrix consisted of a bisphenol F-epichlorohydrin epoxy resin (Epikote 862, Resolution Performance Products) cured with a BF3-complex catalytic curing agent (Anchor 1170, Air Products). The carbon nanofibers (Pyrograf-III, Applied Sciences Inc.) had a typical diameter of 50 to 200 nm and lengths varying from 50 to 100 μm. As such, their diameter were much smaller than the conventional continuous or milled carbon fibers but significantly larger than the carbon nanotubes their tensile strength was around 720 MPa. The fillers were used as received and were dried in oven over night before mixing in order to eliminate humidity. For all the EP mixtures the curing cycle was the following; heating at 50^{o}C for an hour and then up to 70^{o}C with a rate of 10^{o}C/hr, where it remained for 2 hours. The next curing step involved heating up to 130^{o}C (same rate as above) and the temperature remained constant for 1 hour. Finally, the samples were left to cool-down in the autoclave.

Preparation and Characterization of isotropic CNF doped epoxy samples

The mixing of the EP resin with the CNFs took place in a vacuum dissolver (Dispermat AE, VMA-Getzmann) in order to achieve a good dispersion of the fillers in the resin. The curing agent was added then and mixed by hand. Finally, the samples were cured in an oven using the same temperature profile for all of them. The final concentration of CNFs was 1 vol. %. The produced test specimens were examined by systematic scanning electron microscopic (SEM). In Figure 1a it is observed that a good level of uniformity and homogeneity is achieved in the EP/CNF mixture. Nevertheless, some rich-in-CNFs areas are visible (marked by circles). The observation of these areas in larger magnification (Figure 1b) reveals that the CNFs are well wetted by the EP matrix and no pure CNF agglomerations are formed.



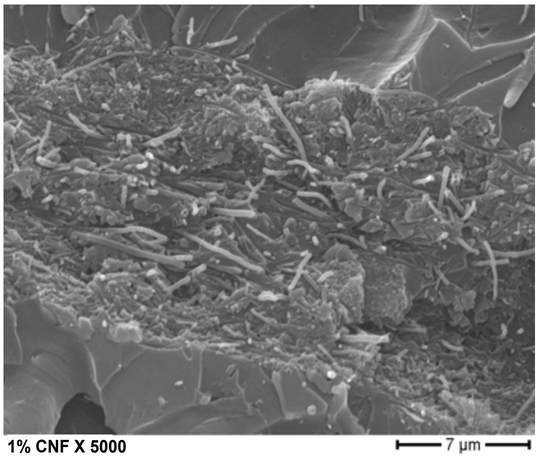


Fig. 1 SEM results of CNF-doped epoxy samples. A) x1000 magnification B) x5000 magnification of rich with CNFs area.

Tensile tests of dog-bone specimens were performed at a MTS 858 testing device with cross-head rate of 1 mm/min. The visco-elastic response of the various EP matrix samples was studied by dynamic mechanical thermal analysis (DMTA). An Eplexor TM 150N (Gabo Qualimeter) DMTA device was employed to carry out the tests. The specimens were subjected to oscillating dynamic loading consisting of a static preload of 4N on which a sinusoidal wave of 2 N at a constant frequency was superimposed. The measurements were made under tension loading with testing frequency of 10 Hz. Heating occurred at a rate of 2°C/min and in a temperature range between 20 to 150°C. The volume resistivity measurements were carried out by a resistivity meter (Hiresta UP, Mitsubishi Chemicals).

Preparation and Characterization of Doped CFRP Laminates

The next step involved the manufacturing of CFRP laminates having as matrix material the neat EP and the 1 vol.% CNF-doped resin mixture described above. The carbon fibers (CF) laminas were chosen to be unidirectional (UD) by Toray Industries, Inc. (Japan) with tensile modulus of 233 GPa, elongation at break of 2.1 %, and weight of

300 g/m^2. Plates consisted of 6 plies carbon fiber laminas, were prepared and processed in an autoclave using the vacuum bag technique. The resins prior to the stacking process were heated up to 60°C so as to lower their viscosity and make the infiltration of the particles in the fiber bundles easier. The final fiber volume fraction (V_f) values of the laminates were; 52.9%, and 42.5% for the neat, and CNF-doped epoxy matrix panels, respectively.
Tensile tests of rectangular composite specimens (20 x 200 x 3 mm^3) were performed at a MTS 858 testing device with cross-head rate of 1 mm/min. Mode I and Mode II fracture behaviour was studied using the double cantilever beam (DCB) and end-notched flexural (ENF) method. The critical strain energy release rates for mode I and mode II remote loading were calculated accordingly. Moreover, coupons of the prepared laminates were subjected to tension-tension fatigue loading and the changes in the longitudinal electric resistance were monitored via a digital Multimeter (Keithley 2002). Continuous acoustic emission (AE) monitoring also applied during the fatigue tests and the captured AE signals were analyzed and correlated to the variation of the material's resistance. The electrodes used, were placed 100 mm apart, symmetrically to the specimens middle length after polishing to remove the insulating EP matrix surface layer (Figure 2)

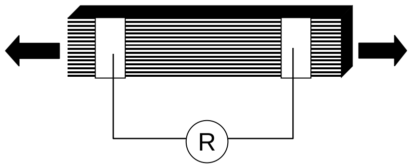


Fig. 2 Location of the electrodes used during the mechanical testing.

RESULTS AND DISCUSSION

Isotropic Epoxy Samples

The volume resistivity of neat epoxy samples was higher than 10^{13} Ω·cm. The addition of 1% CNFs led to a reduction of 5 orders of magnitude (about 10^8 Ω·cm) in volume resistivity. Similar results have been observed by other researchers for the same kind of CNFs [3-5].
The DMTA analysis of the isotropic samples prepared in this study showed no significant changes in the glass transition temperature (Tg), as determined by the peak in loss factor, tanδ, when CNFs were added (Figure 3). The width of the peaks remains also stable after the incorporation of the CNFs, suggesting that their influence on the quality the cross-linked epoxy network was negligible. The storage modulus, E' increases by the addition of CNFs compared to the neat epoxy sample.

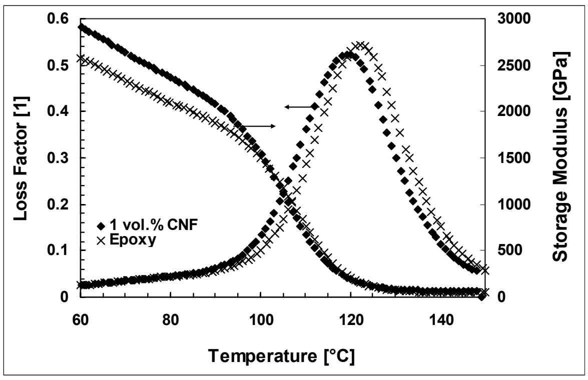


Fig. 3

In Figure 4a, the values of elastic modulus of the neat and CNF-doped epoxy samples are compared. An improvement in the tensile properties by the use of CNFs as additives is observed. The tensile modulus was increased in comparison with the reference resin due to the high inherent modulus of the nanofibers. The interfacial area between the resin matrix and the nanofibers is increased because of the high aspect ratio of the CNFs, which in turn led to enhanced tensile properties. By direct comparison in Figure 4b, it is noticed that the CNF doped epoxy samples has lower elongation at break compared with the neat epoxy sample.

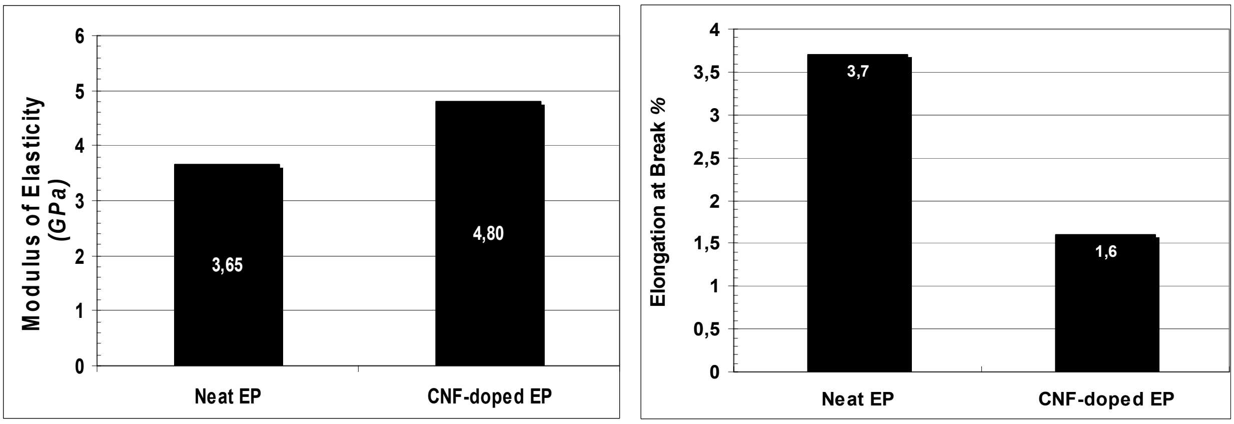


Fig. 4

Doped CFRP Laminates

The longitudinal resistance of composite sample with neat EP matrix was about 0.8 kOhms. The addition of CNFs led, as expected, to a reduction in resistance (about 0.2 kOhms). The tensile properties of the materials are fiber dominated [6] and therefore the differences were expected to be small if not negligible. Even though, the addition of the CNFs led to an improvement in the modulus of elasticity of the CFRPs (Figure 5a). This is attributed to the stiffened matrix of these laminates (cf. Figure 4a).
The DMA analysis showed similar tendencies as for the isotropic samples. The results are summarized in Table 1. Tg remains almost stable, while CNFs lead to an increase in storage modulus, E', compared to the laminate with the neat EP matrix.

Sample	Tg [°C]	E' [GPa] at 30°C
Epoxy	119.8	27.7
CNF	119.3	30.5

Table 1 Tg and E' values of CFRPs with neat and CNF-doped EP matrices.

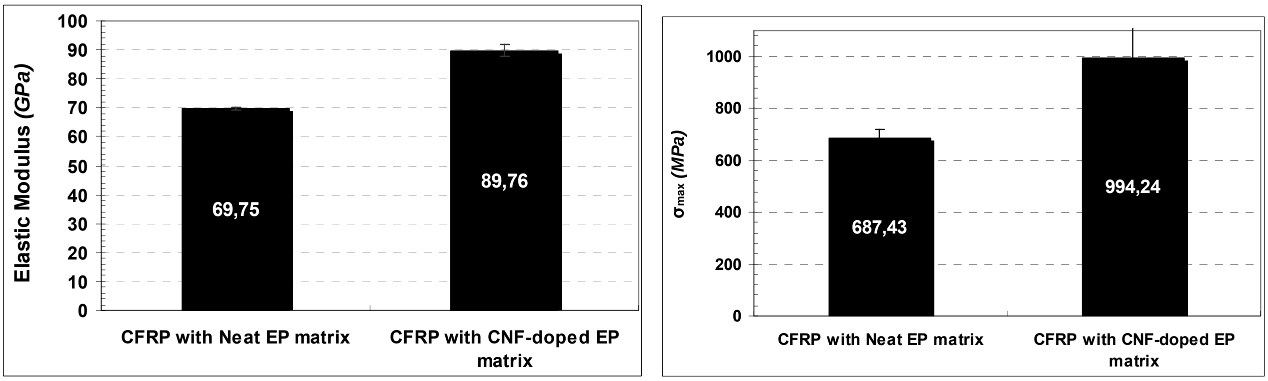


Fig. 5

Fig. 6 shows the G_{IC} and G_{IIC} values of laminates with matrix of neat and CNF-doped EP. It is observed that the fracture energy increases remarkably after the addition of the CNFs in the matrix of the laminates (100% and 45% increase for Mode I and Mode II, respectively). Increase in fracture toughness is directly related to different crack growth processes. The initial cracks may deviate around the nanofibers contributing in this way to higher fracture toughness. In unidirectional systems the initial crack growth and propagation proceeds parallel to the fibers or fiber-matrix interface, and therefore tougher matrix will result in higher G_C value. CNFs bridge the crack surface and thus contribute to the increase in critical strain energy release rate.

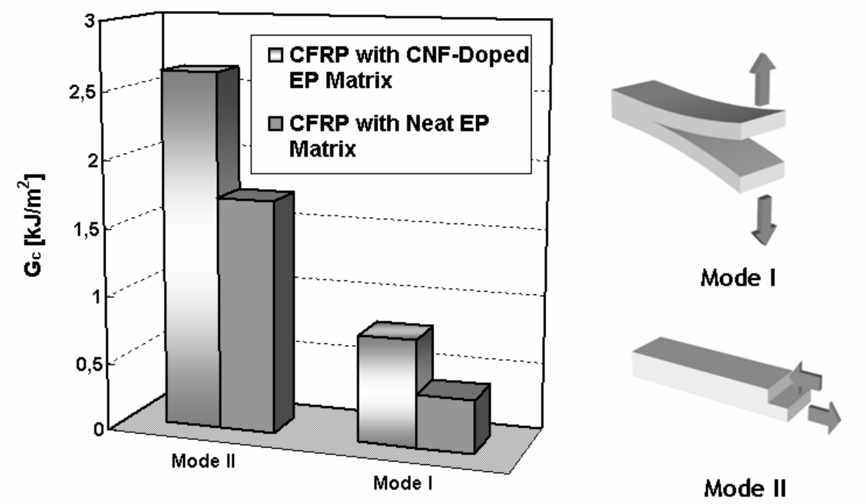


Fig. 6 Mode I and Mode II critical strain energy release rate of unidirectional laminates with neat and CNF-doped EP matrix.

The main goal of the present work was to go a step further and to use CNFs as a nano-sensor for the damage detection of the CFRPs. For this reason a set of electrodes was place on the surface of the samples using conductive silver epoxy adhesive.

Specimens were subjected to increasingly loading-unloading-reloading tension and the resistance was measured at the maximum load and at the lower unloading point of each loading cycle. In Figure 7, the changes in resistance have been plotted versus the applied loading for each loading cycle. The maximum failure load was 39 and 61 kN for the laminate with neat EP and CNF-doped, respectively. Significant changes can be noted in the resistance of both specimens. With increasing applied load the resistance increases due to the damage of the fibers and the resulting progressive damage of the percolating network. During the unloading phase of the specimens the broken fibers and the cracked percolation net are coming in contact and consequently the resistance decreases slightly. Similar results have been observed during the post buckling bending tests of CFRPs [1]. For the doped sample smaller changes of resistance increase are shown. The presence of CNF results in conductive matrix material with a much finer percolative network compared to the micro-scale on the CFs. During the first loading cycles small cracks in the matrix cause slight changes in the resistance which are visible with a closer look at the $\Delta R/R_o$ vs P/P_{max} diagram (Figure 7b). Although the variation of the longitudinal normalized electric resistance versus normalized applied load shows much more prominent in the case of CFRPs with neat epoxy resin, it is evident that in both cases electric resistance variation follows well the produced damage.

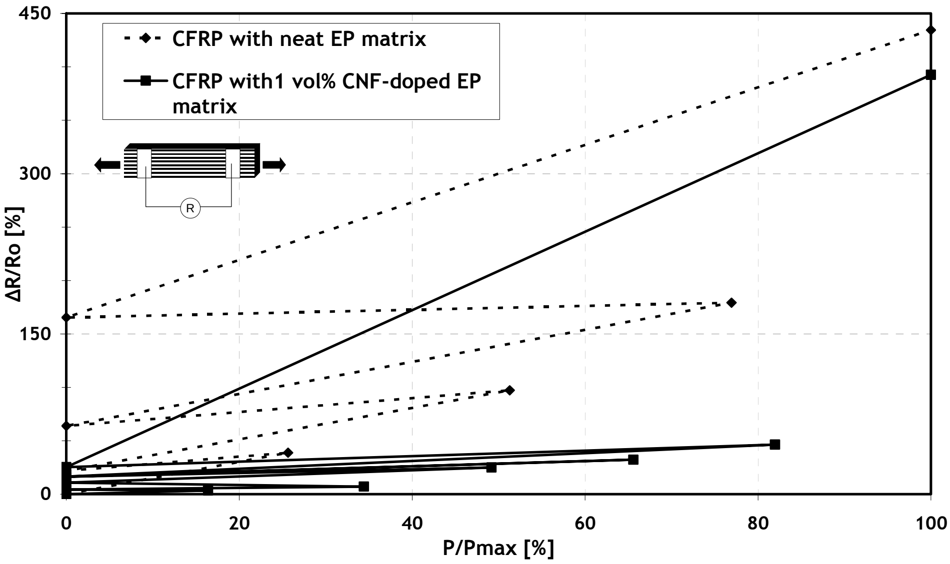


Figure 7a

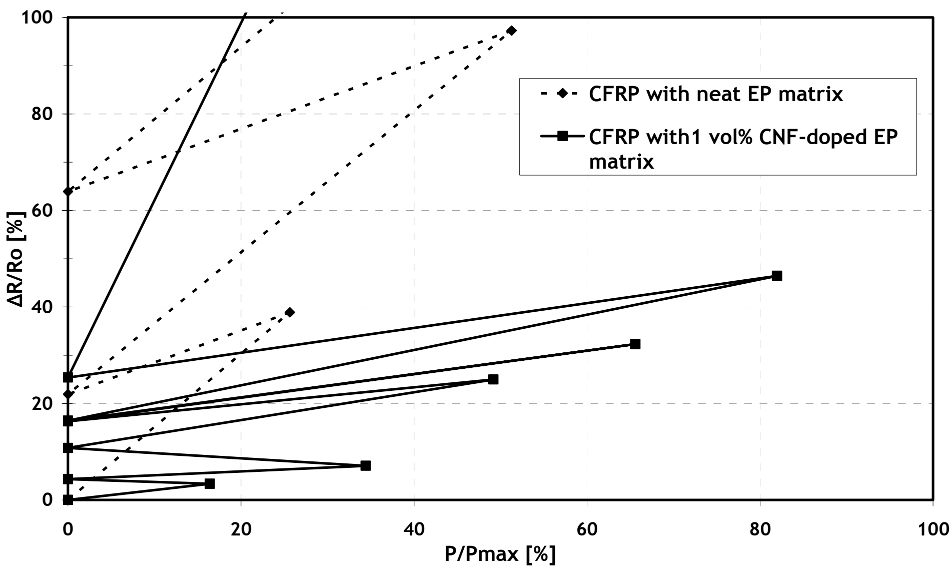


Figure 7b

Fig. 7 Changes in electrical resistance as a function of the applied load during loading-unloading cycles of CFRPs with neat EP and CNF doped EP as matrix. (Figure 7b is a closer view of Figure 7a)

The fatigue life data are presented in Fig. 8. They show that the fatigue life is prolonged by the addition of the CNFs in the matrix of the composite laminates. In Fig. 9a the changes of electric resistance during fatigue loading for both neat and CNF-doped EP matrix laminates are presented. In this case, the maximum applied load was 33 and 44 kN for the neat and the doped matrix laminate, respectively. It can be noted that the doped sample is more sensitive to resistance changes especially during the first cycles (Figure 9b). It is speculated that the presence of CNFs can give evidence of the matrix cracking which take place at the earlier stages of fatigue loading.

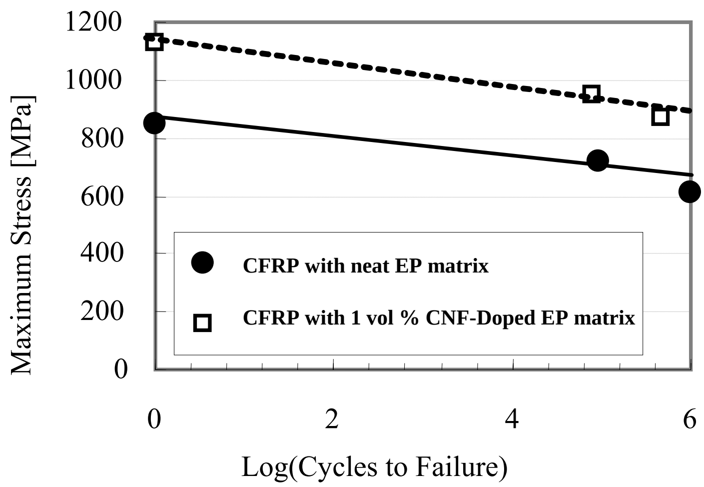


Fig. 8 Plot of S-logN fatigue life of laminate with matrix of neat and CNF doped EP.

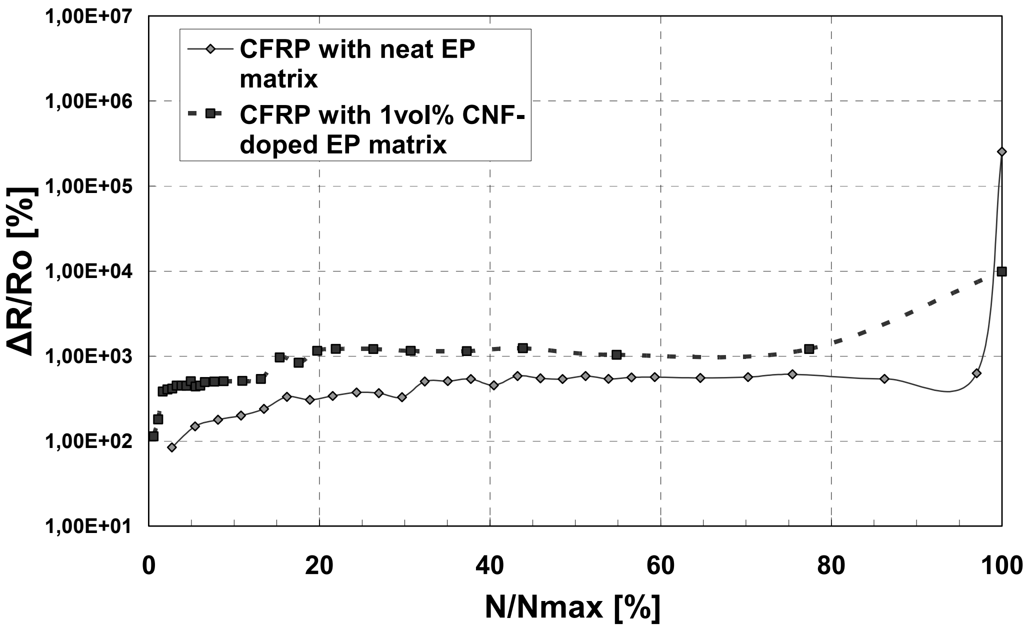


Figure 9a

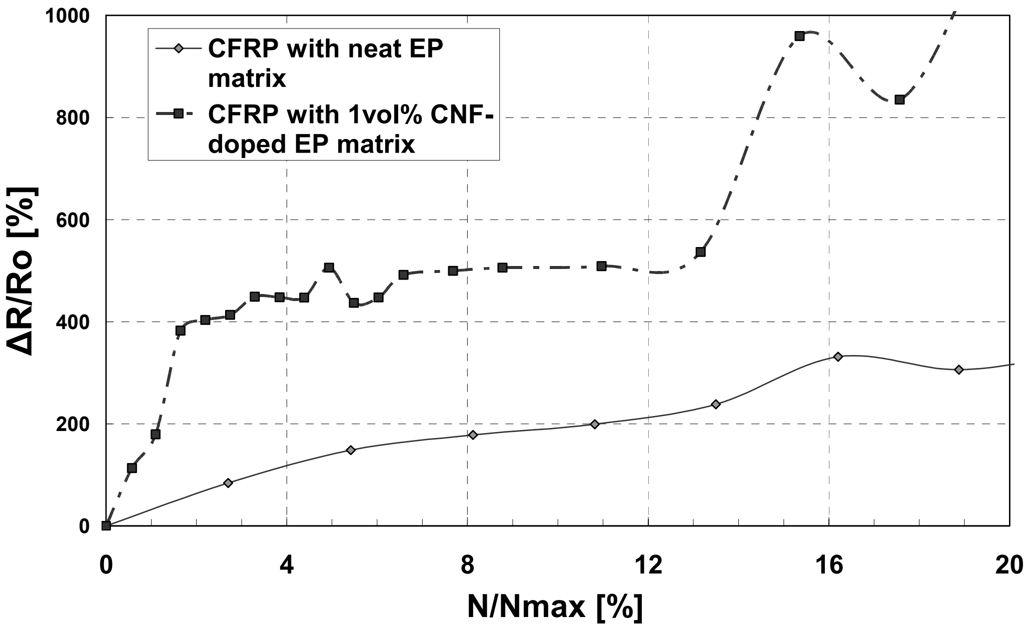


Figure 9b

Fig. 9 Changes in the resistance versus the normalized number of cycles for laminates with neat and CNF-doped EP matrix.

However, these preliminary tests need systematic development and optimization in order to obtain clear correlation between the fatigue behaviour and the resistance changes of the laminates. The AE data recorded during fatigue experiment are shown in Fig. 10 where AE counts versus number of fatigue cycles are presented for the same specimens presented in Figure 9. For the samples made of neat EP matrix high amount of hits appeared almost after the half of the fatigue life of the samples. For the CNF doped laminates important AE activity is monitored at the very early stages of the fatigue loading and this is possibly attributed to the presence of CNFs. However, the complex behaviour of the doped laminates cannot be easily interpenetrated with conventional AE theories and further research need to be undertaken towards this direction.

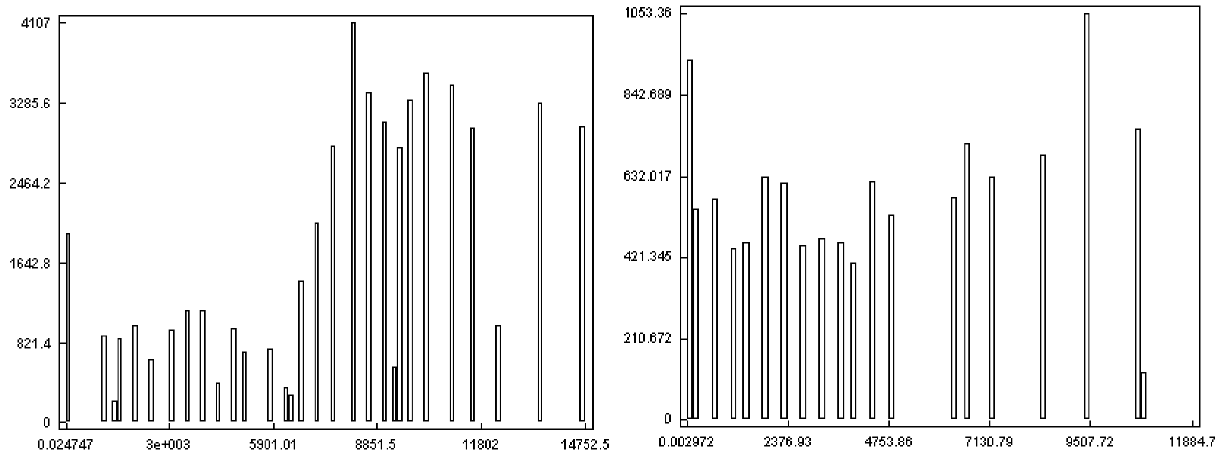


Fig. 10 Distribution of number of AE hits vs. test time for samples with a) neat EP matrix and b) CNF doped EP matrix.

CONCLUSIONS

This study dealt with the use of CNFs as dopants for the EP matrix of CFRP laminates. The presence of CNFs led to a remarkable increase in the fracture energy of the laminates (about 100% in Mode I and 50% in Mode II). This trend is closely connected to fiber bridging and fiber pull-out phenomena which were verified by SEM analysis. Additionally, CNFs resulted to increase in the fatigue life of the laminates of about 40 %. Preliminary tests of resistance monitoring during loading showed that CNFs can give evidence for matrix failure during the first cycles of the fatigue life. Moreover the increased stiffness of the doped laminate was depicted by smaller resistance changes compared to the neat EP laminate. Finally, AE data for the doped laminate showed also more intensive activity for the early stages of the fatigue loading.

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