

ENVIRONMENTAL DEGRADATION OF CARBON NANOTUBE-MODIFIED COMPOSITE LAMINATES: A STUDY OF ELECTRICAL RESISTIVITY

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The environmental durability of carbon nanotube (CNT)-modified carbon-fibre-reinforced polymers (CFRPs) is investigated. The key problem of these new-generation composites is the modification of their polymer matrix with nanoscaled fillers. It was recently demonstrated that the damage tolerance of these materials, as manifested by their fracture toughness, impact properties, and fatigue life, can be improved by adding CNTs at weight fractions as low as 0.5%. This improvement is mainly attributed to the incorporation of an additional interfacial area between the CNTs and the matrix, which is active at the nanoscale. However, this additional interface could have a negative effect on the environmental durability of the aforementioned systems, since it is well known that the moisture absorption ability of a matrix is enhanced by the presence of multiple interfaces, which serve as an ingress route to water. To examine this problem, CNT-modified CFRPs were exposed to hydrothermal loadings. At specified intervals, the composites were weighted, and the water uptake vs. time was recorded for both the modified and a reference systems. The electrical conductivity of the composites was registered at the same time intervals. After the environmental exposure, the interlaminar shear properties of the conditioned composite systems were measured and compared with those of unmodified composites, as well as with the shear properties of unexposed laminates.

1. Introduction

Carbon fibre-reinforced polymers (CFRPs) are widely used in many applications, such as aerospace, civil, and defence industries. This is mainly due to their low density and good mechanical properties. However, one of the greatest challenges associated with the applicability of these materials is their poor interlaminar toughness, fracture behaviour, and fatigue properties. The introduction of a nanoscaled reinforcement in otherwise conventional fibre-reinforced composites has opened an exciting new area in the mechanics of composite materials. The unique properties of these materials, combined with the de-

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sign versatility of fibrous composites, may offer both enhanced mechanical properties and multiple functionalities, which has been the focus of attention in the aerospace technology during the last decades. One of the most attractive nanofillers for the matrix modification of fibre-reinforced composites are carbon nanotubes (CNTs). CNTs possess unique properties, such as a high elastic modulus at the terascale, a huge aspect ratio, and an extremely large specific surface area (or the interfacial area when incorporated in the matrix) [1-3]. Moreover, the electrical conductivity of such systems has been reported to directly correlate with (i) the macroscopic strain applied to the material and (ii) the internal damage that accumulates in the material during its service life [4-8]. Recent research has focused on the use of nanoparticles as dopants for fibre-reinforced plastics (FRPs) [4, 6, 7, 9-14]. Specifically, it was found that the addition of CNTs to the matrix of CFRPs at weight fractions as low as 0.5% greatly improved the impact properties and fracture toughness of the material, as well as prolonged their fatigue life considerably [4, 11-13]. According to these studies, the improved damage tolerance of these systems can be attributed to the incorporation of an additional interfacial area, i.e., that between the CNTs and the matrix. This area is expected to activate the additional energy dissipation mechanisms related to the interfacial sliding, fibre pull-out, and bridging, as well as to crack bifurcation and arrest at the nanoscale. Other researchers studied the reinforcing mechanisms in CNT-reinforced polymers and concluded that these mechanisms involved the interfacial shearing between the CNTs and resin [15, 16], or even an additional sword-in-sheath mechanism, where the outer layer of multiwall CNTs (MWCNTs) breaks first, but the resin-MWCNT interface remains effective in load transfer [3, 17].

Another challenge associated with the applicability of CFRPs is related to their environmental durability [18-31]. It is well known that epoxy-matrix composites are susceptible to heat and moisture, particularly when they operate in varying environments. The amount of moisture absorbed by the matrix is significantly different from that absorbed by the reinforcing phase. The presence of moisture and the stresses associated with the moisture-induced expansion may deteriorate the matrix-related properties of the composite and, as a result, adversely affect its damage tolerance and structural stability. It was found [18-31] that the higher the temperature, the higher the moisture uptake rate of the composites and the more intense the nucleation of delaminations. Furthermore, the interfacial adhesion degradation depends on the conditioning temperature and exposure time. Among the properties of polymer-matrix composites that are affected adversely by moisture uptake is the stiffness [18, 19], the interfacial strength [20], the interlaminar interface [21-29], the damping ratio [30, 31], etc. Some of the mechanisms occurring during moisture absorption include weakening of the fibre-matrix interface [21, 24, 28, 29], plasticization, swelling, and, in some cases, even softening of the matrix [24]. From the above-said, one can conclude that, in the case of CFRPs, the properties dominated by the matrix or the fibre/matrix interface are degraded by moisture absorption, whereas those dominated by fibres are less influenced.

Although CFRPs have attracted considerable attention, very few papers have been published on the environmental degradation of CNTs-reinforced composites [32-34]. The study by Zhang et al. [32-33] presents an analytical approach to describing the hygrothermal effects on the pull-out force and the interfacial stress transfer in CNT-reinforced composites, which takes into consideration the difference between the thermal and moisture expansion coefficients of CNTs and polymer. However, no experimental results are available about the effect of moisture absorption on the water uptake and mechanical properties of CNT-reinforced CFRPs. In a recent communication [35], it was emphasized that the specific surface area of nanosized particles is huge, indicating that a large proportion of the surrounding matrix will be in contact with the interface, or even a separate phase — an interphase — will be developed with properties different from those of the bulk matrix. One important point is that, in cross-linking resins, the ability of CNTs to absorb or donate electrons may well affect the cross-linking density. As discussed above, the matrix and reinforcement/matrix interface are more prone to absorb water and alter their properties. The fact that CNT-reinforced composites possess an increased interfacial area may be beneficial for their fracture toughness; however, this could also prove to be their weakest point in terms of the in-service durability.

Based on the above-said, the purpose of this study is twofold. The first aim is to evaluate the performance of CNT-modified CFRPs in extreme environments. The effect of water absorption on the interlaminar shear strength (ILSS) of the CFRPs is of special interest. To this end, MWCNTs are incorporated in a commercial epoxy system (EP), which is subsequently used for manufacturing quasi-isotropic CFRP laminates. The modified CFRPs are subjected to hydrothermal loadings. For comparison, unmodified CFRPs and the CNT-modified EPs are exposed to the same hydrothermal loading. During the en-

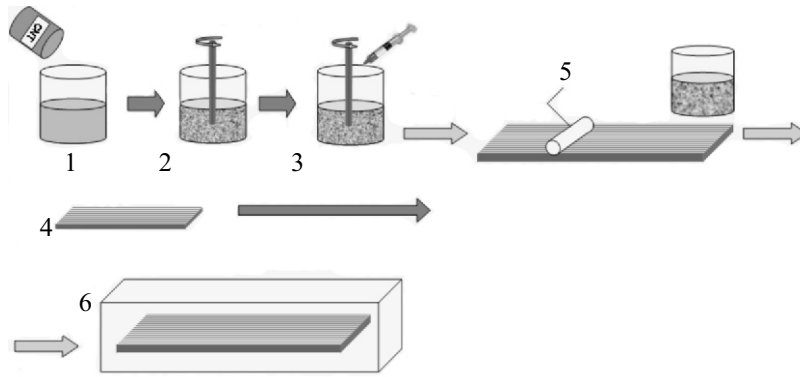


Fig. 1. Outline of specimen preparation: 1 — addition of MWCNTs to the EP; 2 — mixing in a torus mill device at 50°C in vacuum; 3 — addition of a curing agent and mixing; 4 — making CF-reinforced laminas; 5 — preparation of modified CFRP laminates by hand lay-up; 6 — curing in an autoclave (1 h at 80 C + 8 h at 140 C).

environmental conditioning, the composites are weighted at specified time intervals, and the water absorption vs. time is recorded for both the modified and the reference systems. After the exposure, the conditioned composite systems and the reference materials are both tested in interlaminar shear. The properties of the modified systems are compared with those of the unmodified composites and with CNT-modified matrices subjected to identical conditioning.

The second aim is to study the effect of hydrothermal loading on the mechanical properties of the materials by using nondestructive methods. The ultimate goal here is to relate the hydrothermally induced changes in the mechanical properties to the changes in the electrical resistivity. The electrical resistivity of FRPs [27, 36-42] and CNT-reinforced FRPs [4, 6-8, 13] has already been investigated as a function of damage, strain, and stiffness during static and cycling loadings, but very little has been done to study the moisture-caused changes in the resistivity of CFRPs and CNT-modified CFRPs [26, 27, 43]. To this end, during the environmental conditioning, the electrical resistivity was recorded at the same time intervals as the water uptake of the systems studied.

2. Experimental

2.1. Materials

The multiwall CNTs (MWCNTs) were supplied by ARKEMA, France. Their diameter was 10-15 nm and length more than 500 nm, resulting in aspect ratios (length/diameter) varying between 30 and 50. The nanotubes were dried in an oven overnight prior to use. The epoxy system used for the fabrication of CNT-doped resins and CFRPs was the Araldite LY564/Aradur HY2954 from Huntsman Advanced Materials, Switzerland.

2.2. Specimen preparation

The dispersion of MWCNTs in the epoxy resin was carried out in a torus mill device (VMA Getzmann GmbH). The mill creates high shear forces by a high-speed rotating disc, and the nanoparticle agglomerates are crushed owing to the milling effect generated by zirconium dioxide beads. The beads have a diameter of 1.2 to 1.7 mm and cause strong shear action and collision effects. The dissolver disc provides additional shear forces and maintains the vortex flow. The compound is stirred in a vacuum container to avoid the inclusion of air. The vortex flow, achieved by the geometry of the disc, leads to continuous mixing of the compound. The mixing speed was 2000 rpm for 3 h. Modified matrices with a CNT content varying from 0.1 to 1% were manufactured. All the modified resins were used to manufacture nonreinforced rectangular cast specimens. The resin with 0.5% CNTs was subsequently used for manufacturing modified CFRPs. This process is schematically shown in Fig. 1.

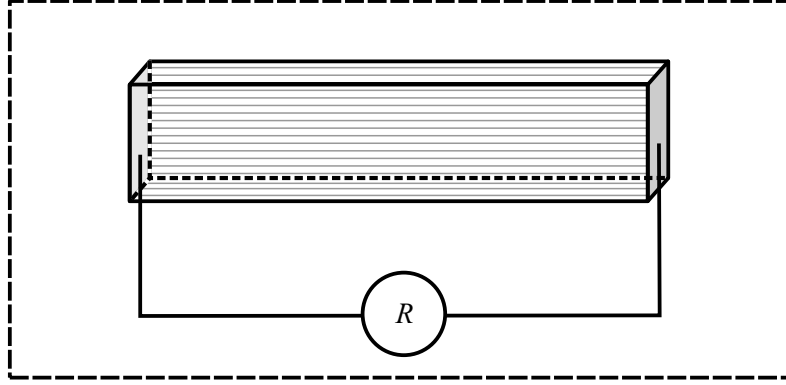


Fig. 2. Configuration of electrical resistance measurements.

16 plies of quasi-isotropic $[(0/+45/-45/90)_2]_s$ CF laminas, supplied by Hexcel, Germany, with a specific weight of 160 g/m^2 , were used for making CFRPs. Each panel was made by hand lay-up and then processed in an autoclave by employing the vacuum bag technique. A reference panel was also manufactured with a neat resin for a direct comparison. In all, two laminates of CFRP materials were tested: one having a CNT-modified matrix and the other with an unmodified (neat) matrix. Specimens for testing the interlaminar shear strength (ILSS) were cut, according to BS EN ISO 14130 [44], from the aforementioned laminates with a diamond saw.

In order to facilitate the electrical resistance measurements during the environmental conditioning, specimen ends were grinded using a grinding wheel to ensure the exposure of carbon fibres. The ends (across which the electrical resistance was measured) were coated with a conductive silver paint. Then, electrodes were pasted on specimen ends with a conductive epoxy glue (Fig. 2). Finally, specimen ends were coated with silicone. This procedure effectively eliminated the fluctuations in resistance measurements caused by differences in connector clamping pressures, or by deterioration of electrode properties.

2.3. C-scan

A C-scan system manufactured by the Physical Acoustics Corporation was used to evaluate the integrity of the laminates manufactured. The system consists of a single-bridge ultrasonic immersion tank with five computer-controlled coordinate axes (x , y , z , gimbal, and swivel), a 1- m step, a computer-controlled pulser-receiver, a high-speed A/D converter with a 100-Msps digitizing rate, and multiple software gates. A 10-MHz transducer was used in the pulse-echo mode. The laminates were evaluated in the amplitude mode on the laminate back surface.

2.4. Environmental conditioning and resistance monitoring

A water bath with temperature control was used for the hydrothermal conditioning of test specimens. Before placing the specimens into the water bath, they were dried in an oven at $50 \text{ }^\circ\text{C}$ up to a stable weight. The weight was measured using an analytical balance with an accuracy of $\pm 0.1 \text{ mg}$. The specimens were then placed in distilled water at a temperature of $80 \text{ }^\circ\text{C}$, controlled to $\pm 1 \text{ }^\circ\text{C}$, and left to stand for about 1200 h. The specimens used for moisture uptake measurements were removed at specified time intervals (see Table 1), wiped, air-dried for five min, and then weighted. The moisture uptake kinetics was measured at different intervals of conditioning time. The weight gain was calculated from the formula

$$M(t) (\%) = \frac{m_w - m_d}{m_d} \cdot 100,$$

where m_d is the dry weight and m_w is the wet weight of the specimen.

The specimens used for resistance measurements were inserted in a sealed container with distilled water, which was placed in the water bath. The electrodes were passed through holes in the container lid, which were then sealed using silicon to avoid evaporation losses. This set-up was created in order to avoid any disturbances in resistance measurements stemming

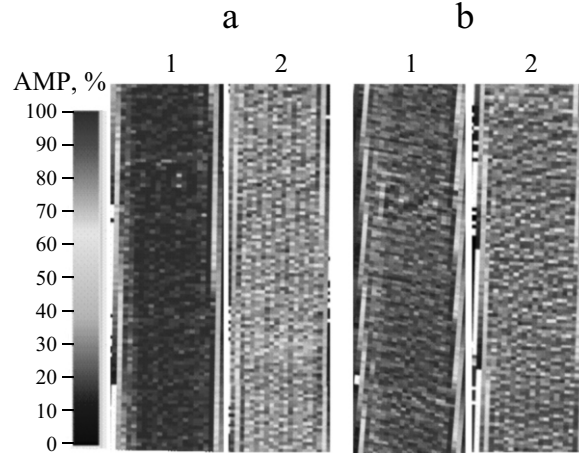


Fig. 3. C-scans of neat (a) and CNT-modified (b) laminates before (1) and after (2) a hydrothermal exposure.

from the disturbance of the environment or the connections. The specimens were not removed from the container during the course of the experiment. The resistance measurements were performed simultaneously with the weight gain measurements by using a digital Keithley multimeter of accuracy 0.1 m . The relative change in the electrical resistance was calculated as

$$\frac{R(t)}{R_0} (\%) = \frac{R(t) - R_0}{R_0} \cdot 100,$$

where $R(t)$ is the time-dependent electrical resistance, and R_0 is the initial resistance.

2.5. Mechanical characterization

To determine the interlaminar shear strength (ILSS), three-point bending tests were run, according to the BS EN ISO 14130 [44], on a 100-kN Instron hydraulic universal testing machine at a crosshead speed of 1 mm/min. The value of ILSS for each specimen was calculated by the formula

$$\frac{3F}{4bh},$$

where F is the load applied; b and h are the width and thickness of the test specimen, respectively.

3. Results and Discussion

In Fig. 3, the ultrasonic images of the modified and unmodified laminates before and after the hydrothermal exposure are shown. As can be seen, the laminates were defect-free both before and after the exposure. The exposed laminates exhibited an increased attenuation of ultrasound due to the water uptake. However, the difference in the amplitudes before and after the exposure was more pronounced in the case of the unmodified laminates. This fact can be attributed to the presence of CNTs in the epoxy matrix, which mediated between the effect of water uptake by the neat matrix and the acoustic impedance of the modified system (Fig. 3b).

Figure 4 shows the weight gain of the neat and CNT-modified epoxy matrices. All the systems reached saturation during the hydrothermal exposure. Within the limits of experimental error, all the systems reached 95% of their saturation value after 400 h of exposure. The neat epoxy exhibited the least weight gain at saturation compared with all the modified systems, reaching approximately 1.6%. The CNT-modified epoxies exhibited an increased water uptake, ranging from 1.7 to 1.9%. This

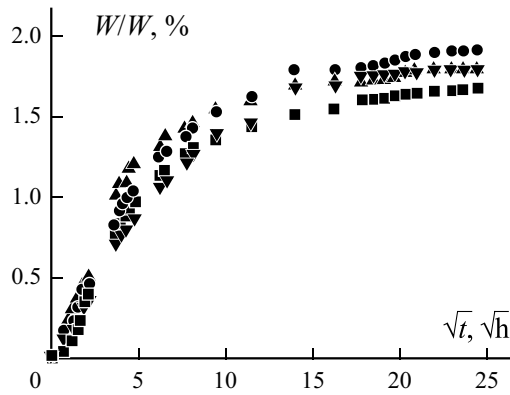


Fig. 4. Weight gain W/W versus the square root of time \sqrt{t} for the neat and modified epoxy matrices: neat resin (■) and resins containing 0.3 (▲), 0.5 (●), and 1.0% CNTs (▼).

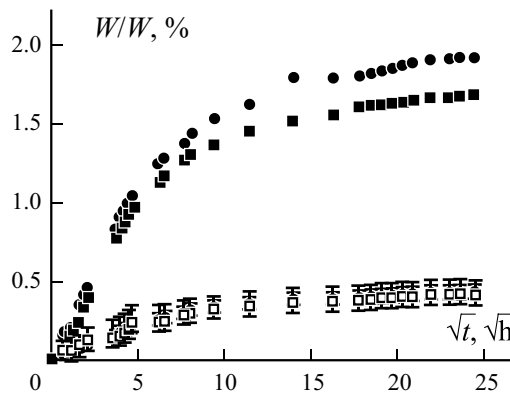


Fig. 5. The same for the neat (■) and 0.5% CNT-modified (●) epoxy and neat (□) and modified CFRPs (○).

was to be expected, since an interface was created between the CNTs and the epoxy matrix, which served as a route for water uptake. However, no clear correlation was observed between the CNT content and the relative weight gain for the modified matrix systems.

Figure 5 depicts the weight gain versus the square root of time for the neat and 0.5% CNT-modified CFRP laminates. For comparison purposes, results for the neat and 0.5% CNT-modified matrices are also shown in the figure. A 95% saturation was reached approximately in 400 h, as in the case of the nonreinforced matrices. The saturation for the laminates occurred at an approximately 0.4% weight gain. The pronounced difference in the water uptake between the matrices and laminates was due to the presence of CFs, which did not exhibit any water absorption. In this regard, there were no visible differences between the two laminates. It can therefore be concluded that the presence of the carbon fibre reinforcement was masking any increase in the water uptake created by the CNTs. It is interesting to note that the introduction of an interface at the microscale,

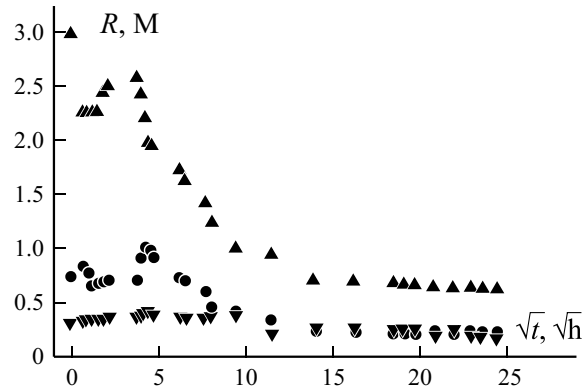


Fig. 6. Electrical resistance R versus the square root of time \sqrt{t} for the CNT-modified epoxy specimens: 0.3 (▲), 0.5 (●), and 1.0% (▼) CNTs.

i.e., that between the CF reinforcement and the matrix, diminished the effect of the interface at the nanoscale, i.e., that between the CNTs and the matrix, despite the fact that the latter was larger by some orders of magnitude.

In Fig. 6, the electrical resistance R of the modified epoxy systems as a function of the square root of exposure time t and CNT content is illustrated. The resistance of the specimens with 0.3% CNTs fell rapidly with exposure time from an initial 3 M to approximately 0.75 M, which was the resistance measured at saturation. The specimens with 0.5% CNTs behaved in a similar manner; however, their initial resistance was much lower, i.e., at approximately 0.75 M, and the saturation was reached at approximately 0.25 M. As can be seen, the behaviour of the aforementioned specimens was nonmonotonic up to 25 h of exposure. On the other hand, when using the same resistance scale, the resistance of the system with 0.1% CNTs appeared almost constant in the course of exposure. As the CNT content increased, the resistance drop became less pronounced. This fact can be attributed to the electrical percolation threshold of the modified resins, which was experimentally defined at approximately 0.3% CNT [45]. As the CNT content of the modified systems moved well above the percolation threshold, the specimens became less sensitive to the water uptake as far as their electrical resistance values were concerned. On the other hand, the nonmonotonic behaviour of the lower concentration systems may be linked to the existence of two competitive mechanisms affecting the electrical resistance. As should be noted, the hydrothermal exposure generally reduces the resistance, whereas the tensile strain have an opposite effect, i.e., the resistance increases [45].

In Fig. 7, the resistance versus the square root of time is depicted for the unmodified and CNT-modified laminates. The resistance of the modified specimens increased monotonically with exposure time. The resistance of the unmodified CFRPs increased for about the first 20 h of exposure, and thereafter decreased to approximately the initial resistance. At this point, it should be noted that the resistance of the CFRPs was of the order of 1, whereas the order of resistance magnitude of the modified matrices was six times higher, namely 1 M. The principal conductive phase of the laminates was the carbon fibres, which dominated the electrical behaviour of the material. However, the CNT modification dramatically altered the electrical resistance of the laminates, which was monotonic in the case of the modified system, whereas for the unmodified ones, it reached a pick at about 20 h and fell thereafter.

Figure 8 presents the relative electrical resistance versus weight gain for the CNT-modified epoxy specimens. The scaling to the initial R value revealed that the trend noticed in Fig. 6 was the same for all CNT contents. However, this trend was masked by the small resistance variations in the case of 1% CNT content. The relative resistance increased for all three configurations until a 1% weight gain was reached. From this point onwards, all the systems became more conductive. A similar effect was reported by Singh et al. [46], where the conductance of glass fibre/epoxy laminates increased with exposure to a

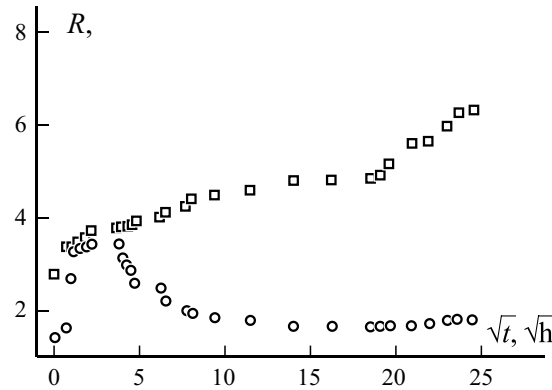


Fig. 7. The same for the neat (○) and 0.5% CNT-modified CFRP (□) specimens.

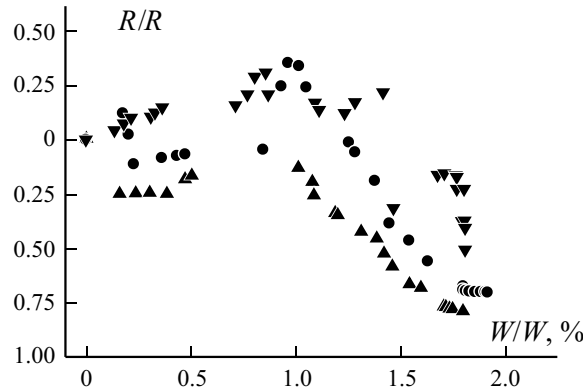


Fig. 8. Relative change in the electrical resistance R versus weight gain W/W for the CNT-modified epoxy specimens: 0.3 (▲), 0.5 (●), and 1.0% CNTs (▼).

hydrothermal environment and exhalate vapours. However, to our knowledge, this is the first time that the irreversible damage processes are found to decrease the electrical resistance of systems where carbon in any form (fibre, nanotube, or carbon black) is the conductive phase. This nonmonotonic behaviour can be attributed only to the epoxy resin or the CNT/resin interface, as the conductivity of the CNTs was not expected to change as a result of the hydrothermal exposure.

Similar observations can be made in relation to Fig. 9, albeit in a different context. The relative resistance as a function of weight gain for the specimens of neat CFRP was clearly nonmonotonic. It is notable that the inclusion of only 0.5% CNTs in the matrix material was enough to completely efface this effect. In the former case, the conductivity reached a plateau at approximately 0.2% relative weight gain and rapidly decreased thereafter, but in the latter one, there was a clear monotonic increase in the resistance.

As already mentioned in connection with Figs. 6 and 8, the increasing CNT content masked the nonmonotonic behaviour of the modified matrix systems. However, this behaviour was always present. In terms of the absolute resistance (Fig. 6), since the modified systems were more conductive due to the increased conductive phase, this nonlinearity tended to diminish within the system noise. On the other hand, as shown in Fig. 9, the unmodified laminates exhibited behaviour similar to that of the doped resin systems. Moreover, as can be safely assumed, the total water absorption was only due to the polymer and the

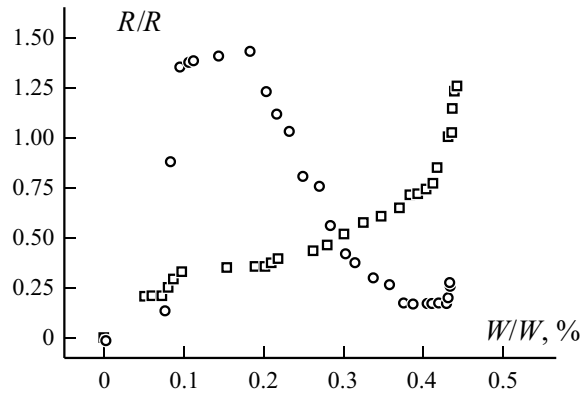


Fig. 9. The same for the neat (○) and 0.5% CNT-modified CFRP (□) specimens.

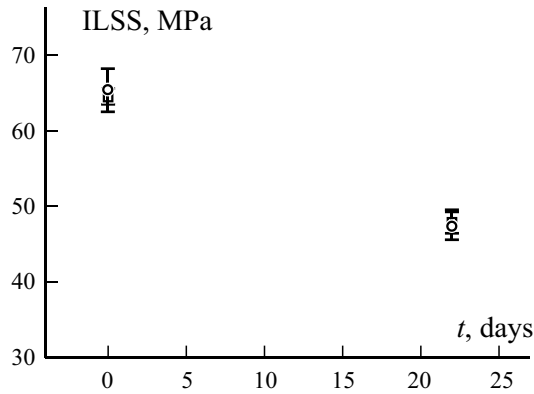


Fig. 10. Interlaminar shear strength ILSS before and after the hydrothermal exposure for all the laminates tested.

polymer/inclusion interface. The weight gain at the maximum resistance was approximately 1% for the modified resins and 0.2% for the neat CFRPs (Figs. 8 and 9, respectively). This was already expected, as the volume fraction of carbon fibres was 55% and the carbon fibre to resin density ratio was approximately 1.8.

In view of the above-said, one would expect that the inclusion of both carbon fibres and CNTs in the epoxy would affect the electrical resistance of the composite in the same way, regarding its response to the hydrothermal exposure. However, in the case of the modified CFRP laminates, a paradox was observed. This paradox manifested in the fact that the electrical resistance increased monotonically with weight gain. The inclusion of a small weight fraction of a conductive phase (CNTs) in an already conductive material (due to the presence of carbon fibres), although it is unlikely that this affected the initial resistance of the system (Fig. 7), totally altered its electrical behaviour. This phenomenon can be attributed only to a synergistic effect caused by interaction between the main carbon fibre reinforcement and the CNTs included in the epoxy matrix. Last but not least, the monitoring of hydrothermally induced damage via the resistance technique for composite laminates may be made feasible with inclusion of CNTs. However, this method is not directly applicable to the conventional composite systems.

Finally, in Fig. 10, the interlaminar shear strength of all the composite laminates before and after the hydrothermal exposure is depicted. The inclusion of 0.5% CNTs in the composite matrix did not affect the interlaminar performance of the composite systems. This observation is consistent with the fact that there was no obvious difference in the water uptake between the

modified and neat specimens (Fig. 5). Although the inclusion of an additional interface was expected to deteriorate the interlaminar shear strength, this was not verified in the experimental investigation.

4. Conclusions

The current study was focussed on the effect of hydrothermal exposure of epoxy matrices and carbon fibre/epoxy composites modified and unmodified with CNTs. The weight gain and the electrical resistance of the exposed systems were measured as a function of exposure time.

There were very little differences between the neat and modified epoxy resins in terms of weight gain. The neat epoxy system exhibited a slightly lower water uptake than the modified systems. In the case of composite laminates, there was practically no difference in terms of weight gain versus time. This observation is consistent with the fact that there was no notable difference in the interlaminar shear strength of the composite laminates before and after the hydrothermal exposure.

The modification of epoxy resins rendered them conductive, enabling the monitoring of the electrical resistance throughout the exposure. For all the systems studied, the resistance reached a peak value after about 20 h of exposure, or at a 1% weight gain. Thereafter, the resistance decreased monotonically until the end of exposure, i.e., at 600 h. A similar behaviour was observed for the neat CFRPs, with the peak value reached at almost the same exposure time, i.e., at 20 h and at a 0.2% weight gain. On the contrary, in the case of the CFRP laminate modified with 0.5% CNTs, the resistance increased monotonically throughout the experiment. This can be explained by a synergistic effect caused by the interaction between the two conductive phases, i.e., the carbon fibres and carbon nanotubes.

Furthermore, the inclusion of CNTs in the matrix of otherwise conventional carbon fibre/epoxy composites is promising as far as the monitoring of hydrothermal degradation of the materials by means of electrical resistance measurements is concerned.

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