

MULTI-WALL CARBON NANOTUBES CHEMICALLY GRAFTED AND PHYSICALLY ADSORPTED ON REINFORCING CARBON FIBRES

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Received 24 January 2008; accepted 19 May 2008

ABSTRACT

Carbon nanotubes (CNTs) because of their properties are alleged to be the key candidate additives for improving the mechanical properties of polymers and carbon fibre reinforced polymers (CFRPs). Nevertheless in order for the reinforcing effect of the nanotubes to be of practical use, the CNTs have to be mixed with the matrix material. In the current work an effort was made to chemically graft Multi-Wall Carbon Nanotubes (MWCNTs) on the actual reinforcing Carbon Fibres (CFs) in order to skip the sometimes complex mixing stage. Two different solutions were used in order to treat/prepare the CNTs; a) an acid solution of $\text{H}_2\text{SO}_4/\text{HNO}_3$ and, b) a toluene solution. The treated CFs were added to each solution, sonic bathed with deionised water and then dried in an oven. The resulting CFs were examined under SEM and both the solutions used proved to be reasonable successful with further investigation/optimisation to be necessary.

1. INTRODUCTION

Researchers globally have investigated the use of carbon nanotubes as reinforcements in polymer, ceramic and metal matrices. Based on their exceptional tensile strength and modulus, CNT are deemed to improve the tensile properties of the composite material and increase the fracture toughness [1-3]. CNT/polymer composites are usually prepared by dispersing CNTs into the polymer matrix through ultra-sonication, shear mixing, in situ polymerization or improvement of dispersibility in organic solvents via surface chemical functionalization, or polymer grafting [4-7]. However, during this process, not only a certain volume fraction of CNTs has to be dispersed into a matrix but it also has to be dispersed uniformly where many difficulties are faced.

The aim of this paper is to explore the possibility of skipping the mixing stage of the CNTs with the polymer matrix when preparing a CFRP enhanced with CNTs, by grafting the CNTs on the surface of reinforcing carbon fibres chemically. In the past, Kumar et al. [8] manufactured fibres from polypropylene/ vapour grown carbon fibre composite by using conventional melt spinning equipment. The resulting new fibres exhibited better mechanical properties compared with the plain polypropylene fibres. Other previous attempts by researchers involved

the actual growth of CNTs on CFs [9-10]. While, Laachachi [11] and He [12] used various chemical reactions including oxidation in order to graft CNTs onto the surface of carbon fibres. Recently Bekyarova et al. [13] used an innovative approach by using electrophoresis to selectively deposit SWCNTs and MWCNTs on woven carbon fabric. The CNT-coated carbon fabric panels were subsequently infiltrated with epoxy resin using vacuum-assisted resin transfer molding (VARTM) to fabricate multiscale hybrid composites in which the nanotubes were completely integrated into the fibre bundles and reinforced the matrix-rich regions. The carbon nanotube/carbon fabric/epoxy composites showed 30% enhancement of the interlaminar shear strength as compared to that of carbon fibre/epoxy composites without carbon nanotubes and demonstrated significantly improved out-of-plane electrical conductivity.

The proposed method by the current paper not only will dramatically reduce the time, energy and thus cost of the manufacturing of such a composite, but will also benefit from multi-scale reinforcement i.e. better interfacial bonding between the polymer matrix and the reinforcing fibre, enhanced interlaminar shear properties and better electrical properties [13-14]. The bonding between reinforcement and matrix is thus a crucial parameter controlling the load trans-

fer between the composite constituents. Moreover the electrical and the sensing/actuating abilities of the multi-scaled reinforced composite is believed to be improved leading thus to an overall enhanced composite material.

2. EXPERIMENTAL

2.1 Materials

The carbon fibres (CF) were by Toray Industries, Inc. (Japan) with tensile modulus of 233 GPa, elongation at break of 2.1%, weight of 300 gr/m² and, diameter between 6-8 µm. The multi-walled CNTs (MWCNTs) were produced by catalysed CVD and supplied by ARKEMA, France. Their diameter was about 10-16 nm and their length was larger than 500 nm. Also H₂SO₄ (98%) and HNO₃ (65%) and, Toluene (98%) by Merck Company, (USA) were used.

2.2 Carbon Fibre Treatment/Oxidation

Two strands of 70x50 mm² carbon fibres were cut. The carbon fibres were firstly treated so as to remove the sizing and therefore they were placed in an acetone bath for 24h. The next step involved the two-step oxidation process. The aim is to generate oxygen, carboxyl, carbonyl, or amine groups that will subsequently be used for the grafting with the CNTs [11-12]. The fibres were first placed in a HNO₃ solution of 100 ml, for 90 minutes in an oven at 140 °C and then for another 120 minutes at 120 °C. The last step involved the cleaning of the fibres with acetone in an ultrasonic bath for 5 minutes and finally washing with deionised H₂O.

2.3 Carbon Nanotubes Oxidation/Chemical treatment

As mentioned before the aim is to modify/functionalize the CNTs via oxidation or other chemical treatment in order to attach carboxylic acid groups to their surface since they tend to react with other molecules. Furthermore the chemical treatment would also help to promote any physical adsorption processes between the CFs and the CNTs. Therefore two different solutions were used; a) a toluene based solution and b) an acid based solution. The first solution is based on physical adsorption while the second on oxidation reactions. The mechanisms of the oxidation reactions are presented in Fig. 1.

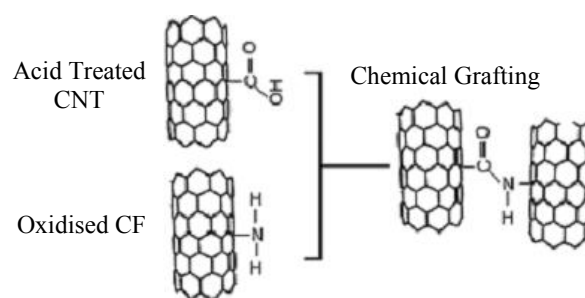


Fig. 1: Schematic presentation one of the oxidative reactions that is responsible for the chemical grafting of the CNTs on the CFs for the acidic solution

For the first solution 1gr of MWCNTs were placed in 200 ml of Toluene (C₆H₅CH₃) in an ultrasonic bath for 24 hours at 55°C. The resulting mixture was dried in an oven for one hour at 120 °C. The outcome was a thick black powder that was diluted with extra 80 ml of toluene. Then the carbon fibres were dipped in that solution and sonication for 30 minutes followed. The mixture was left to settle for 150 minutes at room temperature and then the carbon fibres were washed with deionised water and dried-out in an oven at 80 °C.

The second solution was a mixture of 3:2 by volume of H₂SO₄/HNO₃ respectively. 1 gr of CNTs was added to the acid solution and placed in the ultrasonic bath for 24h at 55°C. Next, the solution was then placed in an oven for 120 minutes at 120 °C. The carbon fibre strand was dipped into the acid solution and after was placed in the ultrasonic bath for 30 minutes. The mixture was afterwards left to settle for another 150 minutes at room temperature. The final step involved the neutralization of the remaining acid in a deionised water bath and drying out the fibres in an oven.

At this point it was essential to test if the grafting of the CNTs was successful. A way of doing that was to perform a *mechanical* test on the grafted CNTs so as to check the integrity of the grafting. Therefore the grafted carbon fibre strands were sonic bathed intensively in purified water for at least 24h at 680W. It is normally expected that only the CNTs that are successfully grafted onto carbon fibres surface will be able to withstand the forces applied during the sonication process [9,10-13]. Subsequently, the resulting carbon fibres were dried-out in a suitable

oven and were examined under SEM (LEO SUPRA 35V) in order to investigate if the CNT grafting was successful and at which extend.

3. RESULTS AND DISCUSSION

In Figs. 2 and 3 a comparison is made between the carbon fibre as received and the treated/oxidized carbon fibre. One can see the difference between the clean and round surface of the “as received” fibre against the treated/oxidized fibre where the sizing has been removed and the fibre surface has been altered via the oxidation process. The numerous SEM pictures taken on the fibres verified that the treatment/oxidation of the carbon fibre was successful.

The Fig. 4 illustrates two random carbon fibres with

CNTs grafted using the of $\text{H}_2\text{SO}_4/\text{HNO}_3$ solution. It can be seen that there are some regions spread on the whole surface of the fibre where the CNTs are successfully grafted. The following Fig. 5 is actually a zoomed-in SEM micrograph of the previous Fig. 4 where the CNT grafting is more obvious. Furthermore indicative measurements of CNT diameter was performed using the software tools of the SEM facility for comparison purposes (Fig. 6). The diameters of the CNTs remained unaffected from the chemical process. It has to be noted that the grafted CNTs seem to be compacted on the carbon fibre’s surface. Moreover the SEM images of CNT grafted using the Toluene solution can be seen in Figs. 7, 8 and 9. Once again it is visible that the CNTs are successfully grafted on the carbon fibre’s surface with

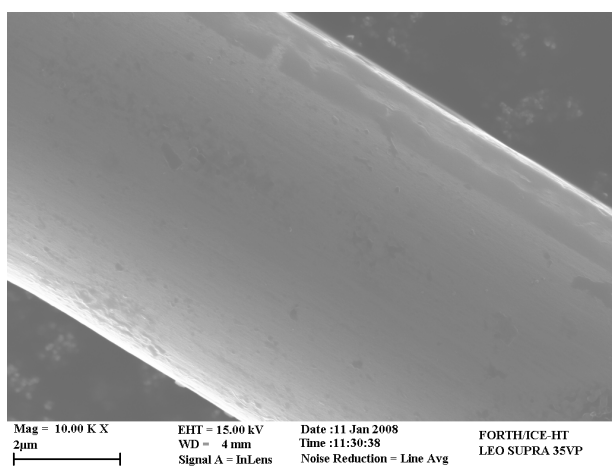


Fig. 2: *As received* carbon fibre with clean surfaces where, the difference with the treated/oxidized carbon fibre in Fig. 2 is obvious.

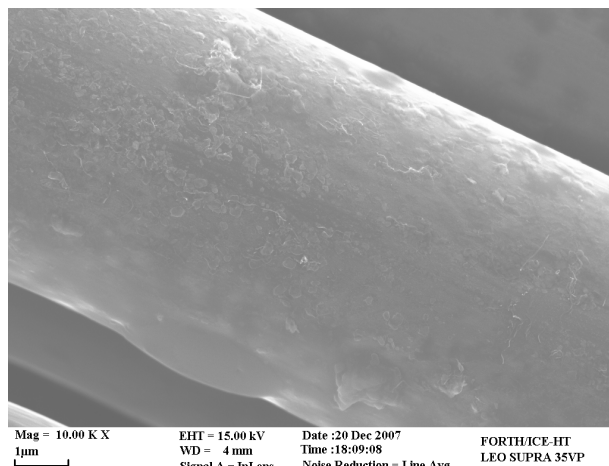


Fig. 3: Treated/ oxidized carbon fibre where the sizing has been removed and the surface of the carbon fibre has been oxidized with HNO_3

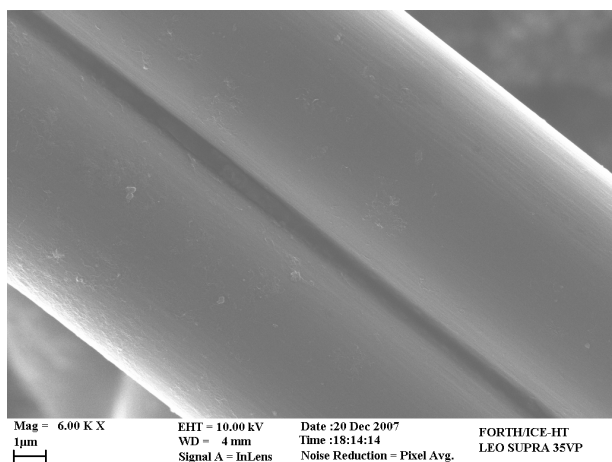


Fig. 4: Carbon fibres with CNTs grafted using the of $\text{H}_2\text{SO}_4/\text{HNO}_3$ solution after the intense sonication. The arrows indicate CNT grafted areas while the dotted circle indicates the area where Fig. 4 and 5 SEM pictures are taken.

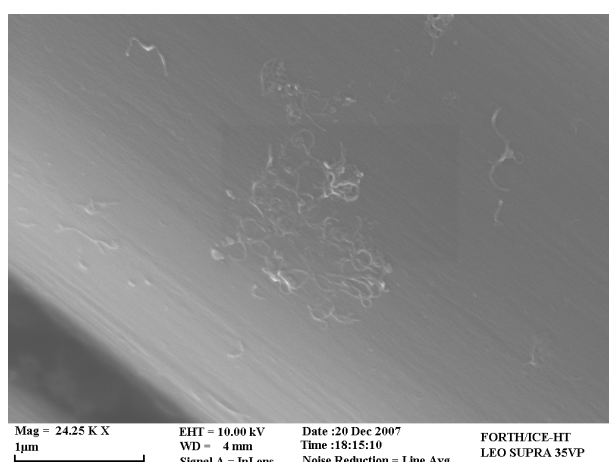


Fig.5: Zoomed-in area of Fig. 3 where an area of grafted CNTs is visible. Single grafted CNTs can also be seen around the central area.

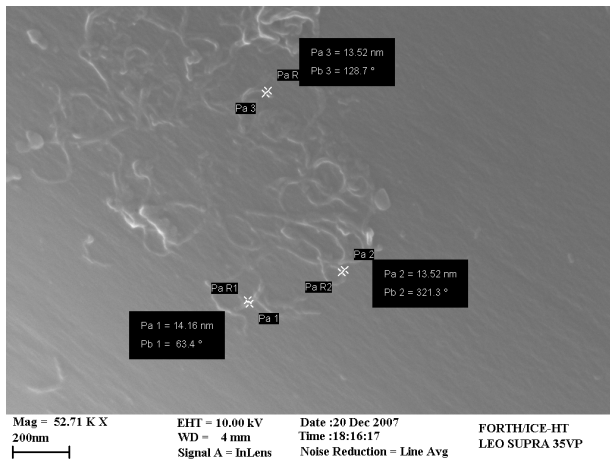


Fig. 6: Zoomed in SEM micrographs of Fig. 4, where the grafting of the CNTs is more visible and their diameters are measured for comparison purposes.

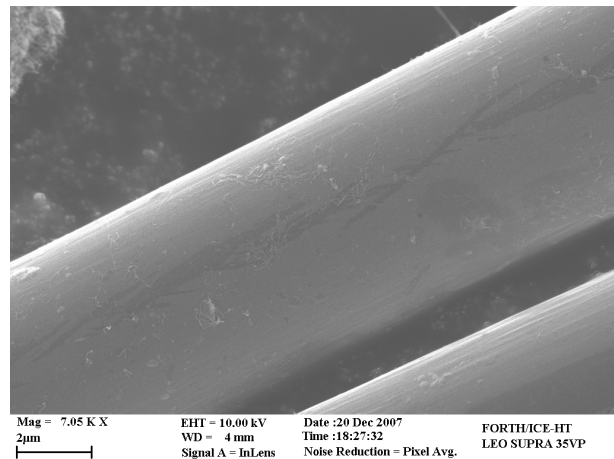


Fig. 7: Carbon fibres with CNTs grafted using the of the Toluene solution after the intense sonication. The arrows indicate CNT grafted areas while the dotted circle indicates the area where Fig. 7 and 8 SEM pictures are taken.

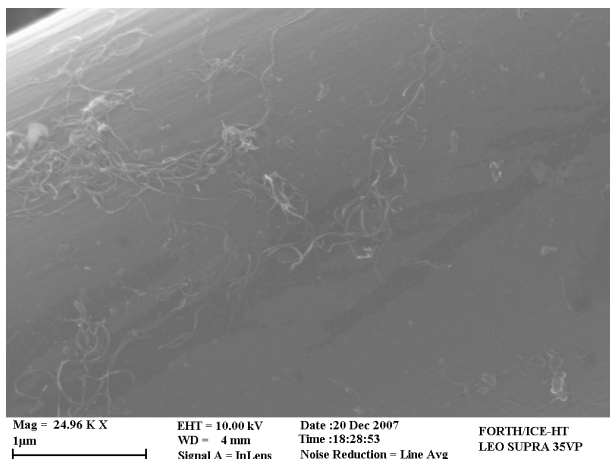


Fig. 8: The zoomed in area of Fig. 6 where many grafted CNTs are visible.

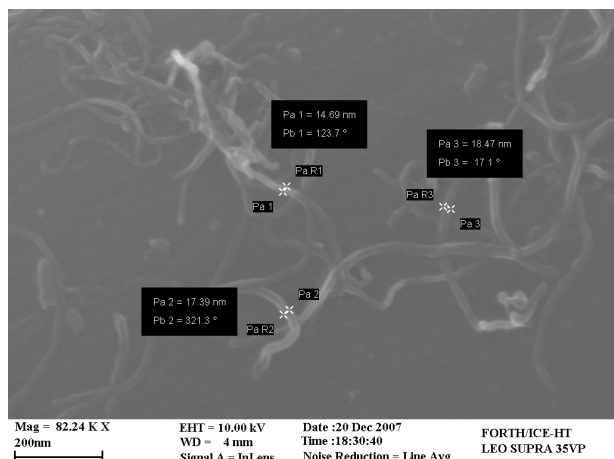


Fig. 9: Zoomed in SEM micrographs of Fig. 7 at high magnification, where the grafting of the CNTs is more visible and their diameters are measured for comparison purposes.

their diameter to remain practically unchanged by the chemical treatment. One should underline that the investigation of the SEM pictures leads to the remark that the grafted CNTs are not fully compacted on to the carbon fibre's surface as in the previous case. A part of their length is not grafted on to the carbon fibre, therefore it is speculated that the interfacial properties with resin polymer matrix material would lead to better properties when directly compared with the $\text{H}_2\text{SO}_4/\text{HNO}_3$ solution since extra energy will be needed so as to pull them out of the matrix material. All the aforementioned Figs. 4-9 were taken after the intense sonication had been performed proving thus that the grafting was successful in both methods.

Since this work is preliminary and the purpose was

at this point, only to investigate the feasibility of the grafting methods used. The future work is of vital importance and will involve the optimization of the two methods in order to achieve a more homogeneously dispersed grafting. Weight measurements also to take place prior and after the grafting so as to have quantitative comparison between the two methods. Furthermore fibre pull-out test to be performed to investigate the adhesion properties with the resin and finally conductivity measurements to be also conducted to examine the effect of the MW-CNTs on the electrical properties of the CFs.

4. CONCLUSIONS

Two different chemical grafting methods of carbon nanotubes onto carbon fibres were presented. The

grafting proved to be reasonably successful with both the methods presented here, even after intense sonication. The method based on the toluene solution despite the fact that involves one additional step during the process than the acid based one, is actually easier to control since it affects less the structure of the whole CF strand. Also it is expected to produce more promising results since the grafted CNTs are not fully compacted on carbon fibre's surface leading thus to enhanced interfacial properties. Both the carbon nanotubes and the carbon fibres were functionalized in order to form surface carbonyl, carboxyl and amine groups. These functions are vital for the grafting. Even though the carbon fibres after the grafting process were ultra-sonicated and washed intensively the CNT grafting remained unaffected. Moreover the CNTs' diameters remained unchanged during the chemical treatments. While on the other hand the grafting was not homogeneously dispersed and did not cover the whole surface of the carbon fibres.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. V. Drakopoulos and the Institute of Chemical Engineering and High Temperature Chemical Processes (FORTH/ICE-HT) for their contribution with the Scanning Electron Microscope facilities.

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