Plasma polymerized thin coating as a protective layer of carbon nanotubes grafted on carbon fibers

A Einig\textsuperscript{1,2}, P Rumeau\textsuperscript{2}, S Desrousseaux\textsuperscript{3}, Y Magga,\textsuperscript{1} J B Bai\textsuperscript{4}

\textsuperscript{1}Laboratoire MSSMat, CNRS UMR 8579, Ecole Centrale Paris, 92290 Châténay-Malabry, France
\textsuperscript{2}Institut Français du Textile et de l’Habillement, Avenue Guy de Collongue, 69134 Ecully, France
\textsuperscript{3}Laboratoire Chimie et Sécurité des Nanomatériaux, LITEN/DTNM/LCSN, Commissariat à l’Energie Atomique, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

Corresponding author: antinea.einig@ecp.fr

Abstract. Nanoparticles addition is widely studied to improve properties of carbon fiber reinforced composites. Here, hybrid carbon fiber results from grafting of carbon nanotubes (CNT) by Chemical Vapor Deposition (CVD) on the carbon fiber for mechanical reinforcement and conductive properties. Both tows and woven fabrics made of the hybrid fibers are added to the matrix for composite processing. However handling hybrid fibers may induce unwilling health risk due to eventual CNT release and a protective layer is required. A thin coating layer is deposited homogeneously by low pressure plasma polymerization of an organic monomer without modifying the morphology and the organization of grafted CNTs. The polymeric layer effect on the electrical behavior of hybrid fiber is assessed by conductivity measurements. Its influence on the mechanical properties is also studied regarding the interface adhesion between fiber and matrix. The protective role of layer is demonstrated by means of friction constraints applied to the hybrid fiber.

1. Introduction

In extreme conditions, such as for aeronautic applications, composites need to get higher properties than conventional materials as improved tensile strength and conductivity while being high performance lightweight structure. One of the key points of their properties is the interface between the fibers and matrix, which can be modified by nanoparticles addition. A possible solution is to graft carbon nanotubes (CNT) on the surface of carbon fibers (CF) to induce better interfacial properties in the composite [1]. Furthermore CNT have both high electric and thermal conductivities [2] and associated to carbon fibers they can bring more charges dissipation efficiency in the final composite [3]. During textile processing, fibers undergo different types of mechanical stresses before being incorporated into the matrix. In this step, nanoparticles can be released and breathed by operators [4] with unknown consequences on health. Within our study, the approach is to protect CNT with a thin polymeric layer on hybrid fibers. Deposit is made by plasma polymerization [5] under vacuum of an acrylic acid monomer leading to a plasma polymerized acrylic acid (ppAA). This process keeps confined grafted CNT in the vessel under vacuum instead of atmosphere and avoids direct exposure.
Layer of ppAA is also used to coat different substrates like PS spheres [6] and CNT [7]. It improves interface behavior of carbon fiber in composites [8].

2. Experimental

2.1. Plasma reactor and experimental conditions
Deposition process is carried out in a stainless steel reactor of 86 dm$^3$ as shown in Fig. 1. The microwave plasma source of 2.45 GHz is coupled to a surfaguide crossed by a quartz tube. The working pressure in the vessel is maintained under primary vacuum $5\text{-}20 \times 10^{-2}$ mbar by Roots pump and can be isolated by a valve. The monomer, acrylic acid (Acros Organic 99.5%, extra pure, stabilized) is injected by a mass flow controller for liquid (Bronkhorst Liqui-flow®) at 100% full scale. Simultaneously co-gas are introduced at 47 sccm for Argon (99.999%, Air Products) and 73 sccm for Oxygen (99.999%, Air Products). Pressure in the vessel is maintained at $10 \times 10^{-2}$ mbar and deposition time is 1 minute.

Carbon nanotubes are grafted to carbon fibers (Toray T700 GC 12k) by CVD process in a quartz reaction tube [9,10]. Unsizing of fibers is carried out by removing sizing at the same temperature used for CVD process.

CNT grafted carbon fibers and unsized carbon fibers are both positioned onto a home-made rotating drum (radius 10cm) inside the vessel with its axis at a distance of 37cm from the plasma source and with a rotating speed of 3 rpm.

2.2. Materials
Fiber morphology has been studied by Scanning Electron Microscopy Leo Gemini 1530 with Field Emission Gun. CNT morphology was observed by Transmission Electron Microscopy Philips CM20 Ultra-Twin at 200 kV. After ultrasonic treatment of ppAA coated hybrid fibers, released CNTs were collected and placed onto copper grids with holy-carbon film for TEM analysis.

Surface composition of ppAA treated unsized fibers were analysed by X-Ray Photoelectron Spectroscopy PHI Quantera SXM using monochromatic Al Ka X-rays (1486.6 eV) with spot diameter of 200µm. Standard take-off angle was 45° giving analysis depth in the range of 3-10nm. Survey spectra were recorded with a pass energy of 280 eV and carbon 1s high resolution spectra were recorded with a pass energy of 55 eV.

Carbon fiber tows conductivity is determined by standard NF EN 1149-2. A circular electrode is put on fibers with a controlled load and an auxiliary one under the same fibers. Both are connected to an electrometer (6517 Keithley). Conductivity perpendicular to the fibers direction was measured in this case.
Friction test is carried out on coated and uncoated hybrid carbon fibers tows. Fibers under fixed load are placed around mobile Teflon cylinder (turning on its axis in 480 rpm) and move on 60cm for 2 min. The setup is inside a glove box with a hole connected to an Electrical Low Pressure Impactor (ELPI Dekati).

3. Results and discussions

3.1. Characterization of ppAA coating on hybrid fiber

Morphology of grafted CNTs on carbon fibers before and after ppAA plasma treatment are shown in Fig. 2 and 3. Carbon nanotubes cover entirely carbon fiber as shown in Fig. 2 and hide its surface. CNT diameters are in the range of 8-12 nm and their length between 0.5-1µm. After plasma treatment as shown in Fig. 3, CNT’s density and their morphology are unchanged. Layer of ppAA overlays uniformly the hybrid fiber in combination with a possible slight agglomeration of CNT tips. The ppAA tends to wrap CNTs as shown in Fig. 4 with a thickness in this case of approximately 9nm. XPS C1s spectra of ppAA is decomposed into two peaks corresponding to bonding energy of C-O (286.7eV) and O-C=O (288.8eV) (Fig. 5). Percentage of ester groups or carboxylic acid groups in Table 1 suggests a high retention of carboxylic acid groups from the monomer of acrylic acid [11,12]. The presence of C-O in layer results from fragmented forms of monomer occurring during plasma polymerization [13].
Table 1. Chemical bond concentration of ppAA layer by XPS.

| % C-O (286.7eV) | % O-C=O (288.8eV) |
|-----------------|-------------------|
| 56              | 44                |

3.2. Layer effect on the hybrid fiber properties

The layer is supposed to modify the fiber surface as well as the fiber behavior at macroscopic scale. In order to quantify its effect, influence of ppAA coating on conductivity and fiber/matrix interface is studied on hybrid fibers.

The conductivity is one evidence of coating effect in electrical performance of fibers among others[14,15]. Grafting CNTs on carbon fibers highly increase the conductivity (X 10 000), as shown in Fig. 6, compared to that of the raw fiber. It results from the combination of unsizing and CNTs grafting of the carbon fiber and occurring in CVD process. After plasma coating of ppAA, hybrid fiber conductivity slightly decreases in comparison with CNT grafted carbon fiber but still has a much higher conductivity than the pristine one.

Figure 5. XPS C1s spectra from ppAA layer.

Figure 6. Conductivity evolution of CNT grafted CF and plasma treated CNT grafted CF compared to pristine carbon fiber.
Fragmentation samples were prepared with a single fiber extracted from the tows and embedded longitudinally in the epoxy matrix (resin WWA and hardening agent WWB4 from RESOLTECH) cured while 15 hours at 60°C. Dogbone shape specimen is loaded at 0.1 mm.min$^{-1}$ up to 1.8 mm displacement. The number of fragments is then counted by exposing specimen to transmission light (Fig. 6). Failure number in fragmentation test is an indication of the cohesive interface between matrix and fiber. Grafting CNT on the fiber seems to damage this interface compared to the pristine fiber, with a lower failure number. Concerning plasma coated hybrid fiber failure number increases and overtakes pristine fiber value. ppAA layer balances lost of adhesion at fiber/matrix interface observed after CNT grafting, and improves adhesion properties compared to the as received fiber. ppAA layer promotes bonds with epoxy matrix resin which improve level of adhesion of hybrid fiber [8,16].

![Figure 7. Results of fragmentation test for CNT grafted CF and plasma treated CNT grafted CF compared to pristine carbon fiber.](image)

3.3. **Protective layer effect measurement**

Electrical Low Pressure Impactor (ELPI Dekati) gives a real-time measurement of aerodynamic diameter particles distribution and concentration [17] emitted during friction test as shown in Fig. 7 and 8. For hybrid fibers, most of the particles sizes are below 28 nm with 3.10$^3$ particles.cm$^{-3}$. After ppAA plasma treatment on hybrid fibers, same amount of particles was detected but with a significant change of the particle size distribution showing a majority of particles in the ranges of [94-155nm] and of [155-260nm] referring to histograms of in Fig. 8. ppAA layer increases released particles size above nanoscale (i.e > 100 nm) certainly because of embedding CNTs blocks and avoiding releasing of single grafted CNTs. It reduces drastically the concentrations of particles size below 100nm when frictions are applied to hybrid fiber.
4. Conclusions
The plasma polymerized acrylic acid (ppAA) coating, with a thickness of about 10 nm, wraps uniformly carbon nanotubes grafted on carbon fibers with no modification of hybrid fiber aspect and more specifically, no morphology modification of carbon nanotubes. ppAA polymeric layer slightly reduces hybrid fibers conductivity which still remains clearly higher than in the case of the pristine fibers. Considering interfacial properties, ppAA contributes to the compatibility with epoxy and induce improvement of adhesive properties between hybrid fibers and epoxy. The protective role of the ppAA layer is demonstrated under friction test. ppAA coating prevents single CNT releasing probably by embedding CNTs blocks. It induces a decreasing of the particles concentrations and a shift of the particles diameter distribution beyond nanoscale (i.e. >100 nm).

Acknowledgments
The authors thank Mr. Jacques Maguin for technical support at IFTH. The authors are grateful to Mrs. F. Garnier for performing SEM and Dr. P. Haghi-Ashtiani for performing TEM observation at Ecole Centrale Paris. The authors want also thank Mr. A. Guiot for ELPI measurements for friction test at the Laboratoire Chimie et Sécurité des Nanomatériaux, CEA Grenoble. This work was financially supported by national ANR-PROCOM project.

References
[1] Qian H, Bismarck A, Greenhalgh ES, Shaffer MSP. Carbon nanotube grafted carbon fibres: A study of wetting and fibre fragmentation. Composites Part A: Applied Science and Manufacturing. 2010 sept;41(9):1107-14.

[2] Dominiczak M, Otubo L, Alamarguy D, Houzé F, Volz S, Noël S, et al. Evaluation of the nanotube intrinsic resistance across the tip-carbon nanotube-metal substrate junction by Atomic Force Microscopy. Nanoscale Research Letters. 2011;6(1):1-10.

[3] Allaoui A, Hoa SV, Evesque P, Bai J. Electronic transport in carbon nanotube tangles under compression: The role of contact resistance. Scripta Materialia. 2009 sept;61(6):628-31.

[4] Cena LG, Peters TM. Characterization and Control of Airborne Particles Emitted During Production of Epoxy/Carbon Nanotube Nanocomposites. Journal of Occupational and Environmental Hygiene. 2011;8(2):86-92.
[5] Yasuda H. *Plasma polymerization*. Academic Press; 1985.

[6] Jafari R, Tatoulian M, Arefi-Khonsari F. Improvement of the stability of plasma polymerized acrylic acid coating deposited on PS beads in a fluidized bed reactor. *Reactive and Functional Polymers*. 2011 avr;71(4):520-4.

[7] Zhao J, Shi D, Lian J. Small angle light scattering study of improved dispersion of carbon nanofibers in water by plasma treatment. *Carbon*. 2009 août;47(10):2329-36.

[8] Kettle AP, Beck AJ, O’Toole L, Jones FR, Short RD. Plasma polymerisation for molecular engineering of carbon-fibre surfaces for optimised composites. *Composites Science and Technology*. 1997;57(8):1023-32.

[9] Zhao Z-G, Ci L-J, Cheng H-M, Bai J-B. The growth of multi-walled carbon nanotubes with different morphologies on carbon fibers. *Carbon*. 2005 janv;43(3):663-5.

[10] Li H, He D, Li T, Genestoux M, Bai J. Chemical kinetics of catalytic chemical vapor deposition of an acetylene/xylene mixture for improved carbon nanotube production. *Carbon* 2010 déc;48(15):4330-42.

[11] Morent R, De Geyter N, Van Vlierberghe S, Vanderleyden E, Dubruel P, Leys C, et al. Deposition of Polyacrylic Acid Films by Means of an Atmospheric Pressure Dielectric Barrier Discharge. *Plasma Chemistry and Plasma Processing*. 2009;29(2):103-17.

[12] Zanini S, Ziano R, Riccardi C. Stable Poly(Acrylic Acid) Films from Acrylic Acid/Argon Plasmas: Influence of the Mixture Composition and the Reactor Geometry on the Thin Films Chemical Structures. *Plasma Chemistry and Plasma Processing*. 2009;29(6):535-47.

[13] D’Agostino R. Advanced Plasma Technology. John Wiley & Sons; 2008.

[14] Tzeng S-S, Chang F-Y. Electrical resistivity of electroless nickel coated carbon fibers. *Thin Solid Films*. 2001 juin 1;388(1–2):143-9.

[15] Athanasopoulos N, Kostopoulos V. Prediction and experimental validation of the electrical conductivity of dry carbon fiber unidirectional layers. *Composites Part B: Engineering*. 2011 sept;42(6):1578-87.

[16] Lopattananon N, Kettle AP, Tripathi D, Beck AJ, Duval E, France RM, et al. Interface molecular engineering of carbon-fiber composites. *Composites Part A: Applied Science and Manufacturing*. 1999 janv;30(1):49-57.

[17] Marjamäki M, Keskinen J, Chen D-R, Pui DYH. Performance evaluation of the electrical low-pressure impactor (ELPI). *Journal of Aerosol Science*. 2000 févr;31(2):249-61.