Thin Solid Films 616 (2016) 220–227

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Dielectric barrier discharge assisted continuous plasma polypyrrole deposition for the surface modification of carbon nanotube-grafted carbon fibers

Hande Yavuz *, Grégory Girard, Jinbo Bai

Laboratoire de Mécanique des Sols, Structures et Matériaux, École Centrale Paris, CNRS UMR8579, Grande Voie des Vignes, 92290, Châtenay-Malabry, France

ARTICLE INFO

Article history:
Received 29 December 2015
Received in revised form 11 August 2016
Accepted 11 August 2016
Available online 12 August 2016

Keywords:
Plasma assisted deposition
Dielectric barrier discharge
Carbon nanotube grafted fiber
Plasma polypyrrole

ABSTRACT

The incorporation of carbon nanotube-grafted carbon fibers (CNT-CF) into polymer matrices provides highly-enhanced physical properties to the materials. They could be ideal candidates to be integrated into multi-functional composites applications in several industries. However, in order to take advantage of carbon nanotubes (CNTs), it is essential to keep all the CNTs on the surface of fibers during their implementation phase in the composite manufacturing process. Besides, some unresolved safety issues remain during the integration phase of such hybrid forms into polymer matrices. This research is making an attempt to develop an effective plasma surface treatment method either to keep the maximum possible amount of CNTs on the fibers and to modify the surface properties of CNT-CF which is highly necessary prior to the composite fabrication. In order to provide better understanding of the modified structures in a domain ranging from microscopic to atomic scales, several characterization studies were realized by X-ray Photoelectron Spectroscopy (chemical structure) and Scanning Electron Microscopy (microstructure). This research is expected to provide valuable information for further studies to develop hybrid composites where multifunctionality is the main concern.

1. Introduction

Carbon nanotubes (CNTs) vary in their morphology and their structural characteristics. Resulting from these properties; chiral angle, tube diameter, C—C bond length of the hexagonal lattice, tube length, tube-end configuration (end-caps), as well as nanotube wall structure are some of the parameters which can be used to characterize the nanotubes [1,2].

Regarding their configuration (i.e., chiral angle and diameter), these nanotubes can possess different level of metallization (i.e., metallic, semi-metallic or semiconducting) [1]. They can produce conductive capabilities which can be characterized by several techniques [3–5]. CNTs can also ensure high elastic and strength properties [1,6]. It has been found that when uniform forces are applied on the outer layer of multi-walled carbon nanotubes, the inner layer exhibits small axial displacements. This revealed that the force acting on the outer layer is transferred to the inner layer through long range intermolecular forces such as Van der Waals interactions [1]. Thanks to CNTs' superior mechanical, electrical and thermal properties, they have found great potential to be embedded in a wide variety of structural applications in order to obtain high performance, multi-functional, and lightweight components [7].

When CNTs are desired to be used in structural composites, one of the most important criteria is to increase their surface adhesion capability prior to manufacturing phases such as weaving and impregnation. In order to enhance the interfacial strength between the CNTs and polymer matrix, the amount of good bonding between CNTs and polymer matrix must be reached, and less graphitized more rough CNT surfaces should be provided. Therefore, the integration of functional groups such as hydroxyl, carboxyl, nitrogen or fluorine groups on the outer layers of CNTs by plasma modification [8–20] and the incorporation of nanowires [21] are the promising methods within the field of functionalization processes which may further give possibility to improve the micro/nanomechanical properties of polymer composites. Either to quantify or qualify such properties of composites, nanoindentation tests can be combined with imaging techniques such as atomic force microscopy and scanning electron microscopy [22].

Plasma processing can be considered as a promising tool in materials surface treatment because of the comparatively straightforward scale-up to larger dimensions, possibility of continuous surface treatment and compatibility of any type of substrate. Moreover, with well-designed plasma conditions, functional structure deposition on materials is also possible in a very short time. This research demonstrates the possibility of plasma polypyrrole deposition at atmospheric pressure and characterization of the chemical and morphological properties. It is also stated that the encapsulation of CNTs diminishes the risk to inhale free CNTs that exists on the carbon fibers subsequent to chemical vapor deposition (CVD).

* Corresponding author.
E-mail address: hande.yavuz@centraliens.net (H. Yavuz).

http://dx.doi.org/10.1016/j.tsf.2016.08.028
0040-6090/

2. Experimental

2.1. Materials

Polyacrylonitrile based Hexcel AS4-12K (AF) and Toray T700-12K (TF) fibers were used throughout the investigation. CNT-grafted fibers were chosen to be prepared from TF fibers (TF/CNT) by a CVD method [23]. Pyrrole (C_4H_5N, 98 + %, liquid at STP) and p-toluene sulfonic acid monohydrate ($C_7H_8O_3S \cdot H_2O$, 98 + %, solid at STP, referred as dopant or pTSA.H_2O throughout the paper) were purchased from Sigma-Aldrich. Both precursor was heated prior to plasma treatment and was fed easily into the plasma post-discharge region in the vapor phase. Nitrogen (Alphagaz B50, 9.4 m^3, 20 MPa) which was used as a process gas for the initiation of plasma discharge and as a carrier gas for the feeding of precursors contained the following impurities: H_2O < 3 ppm, O_2 < 2 ppm, C_nH_n < 0.5 ppm.

2.2. Experimental set-up

The plasma generation system used to treat AF and TF/CNT fibers was based on dielectric barrier discharge technique. Plasma generator and plasma source (Model ULD-120, processed length is 120 mm) was developed by Acxys Technologies (Saint-Martin-le-Vinoux, France). Plasma generator consists of electric supply, gas control and touch screen; plasma source consists of process gas distribution chamber and water cooled co-axial cylindrical electrodes. The atmospheric pressure glow discharge was produced between two co-axial water-cooled cylindrical electrodes located inside the source. An insulator material covers the inner metal electrode and surrounded by a cylindrical slotted metal electrode. The inner electrode was connected to a power supply consisting of a low frequency generator (120 kHz), a high voltage transformer (±3.5 kV) and a power amplifier. The injected power can be adjusted from 1000 to 2000 W. The treatment duration per 120-mm-long sample was chosen to be between 45 s (treatment speed: 0.16 m/min) and 60 s (treatment speed: 0.12 m/min) for this study. N_2 was used as process gas, pyrrole and pTSA.H_2O were used for plasma deposition (Fig. 1). Flow was adjusted by means of mass flowmeters and recorded using the LabView software. In the presence of dopant, injection points of precursor and dopant were separated from each-other in order to avoid possible oxidation reactions between them. After each experiment, plasma treated fibers were washed with acetonitrile (Cas no. 75-05-8) and the solution was injected into a gas chromatograph in order to identify the solubility of the deposited layer. According to the results, no peaks were observed except acetonitrile which was an indication of insolubility of coating in that solvent.

2.3. Apparatus

2.3.1. X-ray photoelectron spectroscopy (XPS)

The sample surfaces were analyzed with the Physical Electronics PHI 5000 Versaprobe X-ray photoelectron spectrometer. The spectra were collected using a monochromatic Al Kα X-ray source (hv = 1486.6 eV) operated at 15 kV and 25 W. The pass energy for collecting survey and high resolution spectra were 187.85 eV (step size = 0.4 eV, time/step = 20 ms) and 29.35 eV (step size = 0.1 eV, time/step = 50 ms), respectively. A combination of 1 eV electrons and 6 eV Ar+ ions were used for the charge neutralization. For calibration purposes, the C 1s electron binding energy was referenced at 284.8 eV. Curve fitting was performed using Multipak software (developed by Ulvac-Phi). The quantitative analysis of atomic surface composition of carbon fibers (C 1s, O 1s and N 1s photoelectron peaks) was calculated by integration of the peak areas with Shirley method on the basis of Wagner and Scofield sensitivity factors.

2.3.2. Scanning electron microscopy (SEM)

The topography of unmodified and plasma modified AF and TF/CNT surfaces was examined by LEO Gemini 1530 scanning electron microscope. Fiber samples were fixed on aluminum holders without any

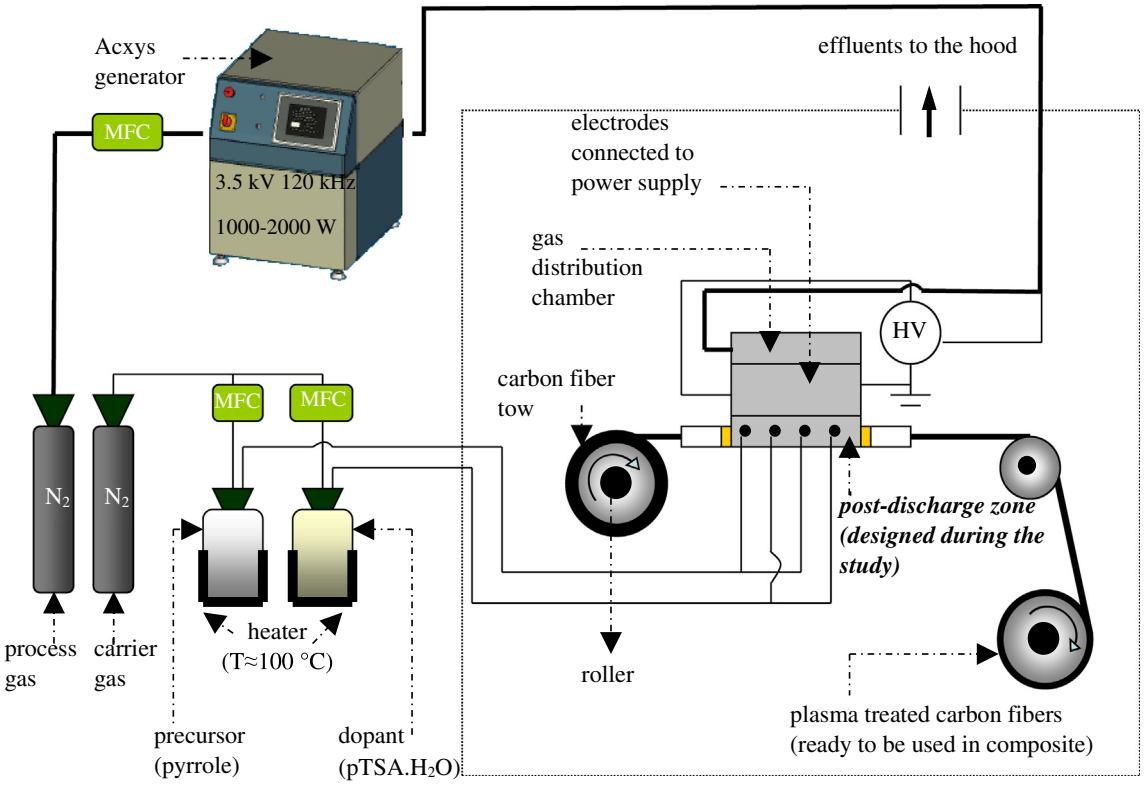

Fig. 1. Plasma treatment system used for the modification of CFs and CNT-CFs.