

## Pitch-Based Carbon Fibre-Reinforced PEEK Composites: Optimization of Interphase Properties by Water-Based Treatments and Self-Assembly

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### Abstract

This work addresses the challenging fibre-matrix compatibilization and interface adhesion improvement of poly(etheretherketone) (PEEK) composites reinforced with pitch-based carbon fibre. An innovative and environmentally friendly method, inspired both by supramolecular "layer-by-layer" (LBL) assembly and by the composition of adhesive proteins in mussels was designed to modify the carbon fibre surface and improve the composites transverse properties by supramolecular interactions. The results proved that few sensitive carbon surfaces can be selectively modified by stable polyelectrolyte complexes and catechol amine polymer partners dispersed in water in such a way that a sizing treatment can be applied by techniques as simple as immersion or spraying procedure. It was shown that the combination of these solutions self-organized to form thin deposits containing compatibilization and/or crystallization promoter partners, thought transcrystallinity, onto carbon surface. This approach is an innovative and environmentally-friendly method which improves fibre-matrix interface quality in terms of compatibilization, adhesion and mechanical properties.

**Keywords:** Composite interphase; Fibre sizing; Interfacial adhesion; Interfacial microstructure; Polyelectrolyte; Polydopamine; PEEK/pitch-based carbon fibre composites; Surface modification

### Introduction

The advanced carbon fibre reinforced polymer (CFRP) composite market is dominated by materials based on thermoset polymer (TS) matrices such as epoxy, polyimides, bismaleimides and cyanate esters which have found many applications in aeronautic, space and military usages whose extreme environments demand high-performing materials. However, TS have limitations in terms of storage, hydrothermal ageing, insufficient toughness and have constraints in processing since long and strict multi-step processing by autoclave are needed [1]. This is why the replacement of TS matrices by thermoplastic polymers (TP) is an area of intense research with primarily use in short fibres reinforced composites. Currently, TP-based matrix composites associated with continuous fibres are growing rapidly and the TP used as matrix potentially present major competitive advantages over thermosets because of their ease of implementation and their intrinsic characteristics such as an extremely long shelf life as well as their recycling possibilities. Thermoplastics are usually high molecular weight, linear polymers which form bulk material by non-covalent bonds like hydrogen bonding, dipole-dipole, van der Waals and  $\pi$ - $\pi$  interactions, and linear structures with network possibility [2]. When high performance applications are targeted, thermoplastics with high thermal stability are required. One can cite space applications such as orbiting satellites, wherein investigations must not only be focused in space junk and orbital debris but also in material improvement with new multi-functionality and cost reduction in order to increase the application range.

The materials studied in this work include a continuous high modulus pitch-based carbon fibre with high thermal conductivity reinforcing a poly(etheretherketone) (PEEK) matrix. PEEK is one of the most promising high performance thermoplastic polymers and arouses a strong interest, not only for medical applications [3] but also as an alternative polymer for thermoset matrices replacement to the extent where it has sufficiently good properties to be compatible with severe conditions. Applications of PEEK-based composites are increasingly popular and lead to the manufacture of primary and secondary

structures such as PEEK/glass fibre laminates, [4] carbon nanofibre composites [5] and carbon nanotube composites [6]. However, carbon fibre-reinforced PEEK composites (CFRPEEK) only show sufficient performances for few CFRP developments and do not fully meet the requirements for high performance applications, in particular when the material is reinforced with continuous high modulus pitch-based carbon fibre because of issues linked to fibre-matrix lack of compatibility, viscosity, thermal stability and transcrystallinity. Indeed, the manufacturing process of PEEK-based composites, which has to be performed at elevated temperatures, i.e., between 380°C and 400°C, is challenging due to the following points: (i) the high melt viscosity is an obstacle to the lay-up of fibres combined with matrix into either a flat consolidated and oriented laminate or a three-dimensional shaped component, (ii) the fibre commercial sizings have insufficient thermal stability and, more generally, sizings have to be developed with a coating chemistry showing sufficient stability at such high temperatures, and (iii) the transcrystallinity of PEEK at the fibre-matrix interface depends on the pitch-based carbon fibre surface properties and has to be taken into account to explain the interphase properties. Furthermore, to the best of our knowledge, there is a limited understanding about the fibre-matrix compatibilization and adhesion mechanisms in such high performance TP composites [7]. More precisely it is assumed that fibre-matrix interface is actually the key to improve CFRP composites [8]. Indeed, one of the challenges linked to these materials relate to the fibre-matrix interface compatibilization, adhesion promotion, ageing and improvement of damage tolerance.

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In this context, the mechanical properties of high performance composites are dependent on several important microstructural properties [9,10]. It is well known that in carbon material reinforced polymer composites, local interactions between the fibre surface and the matrix at the vicinity of this fibre, can be transferred over longer distances thanks to the creation of an interphase area. In the specific case of semi-crystalline polymer-based matrix composites, this interphase, wherein the matrix properties are different than in the bulk matrix, is made of transcrystalline layers, also called transcrystallinity, and transition regions of decreasing or increasing segmental mobility within the amorphous phase [11]. Thus, the mechanical properties of CFRPEEK depend on the crystallinity of the matrix, the size of the spherulites but also on the microstructure transcrystallinity-related properties. Indeed, tensile modulus and tensile strength increase with increasing crystallinity up to a certain point after which the properties decrease because of crack propagation through the spherulites [12]. The formation and growth mechanisms of transcrystallinity have been published in a recent review and discussed for several semi-crystalline polymers [13]. It is important to note that it is well known that some fibres may act as heterogeneous nucleating agents and promote the nucleation of crystallization along the interface with a sufficiently high density of nuclei; where the crystals grow in perpendicularly direction to the fibre surface. Furthermore, many studies have shown that the composite properties, hence the transcrystallinity, can be greatly affected by the (melt) processing cycle [14]. Thus, interphase properties such as transcrystallinity are affected by the fibre-matrix interface quality that is directly connected to the fibre-matrix compatibility.

A very limited number of sizing formulations compatible with thermoplastic-based matrices and particularly with PEEK matrix has been reported so far [15]. However, sizing agents proved necessary for making fibre handling and prevent fibre degradation but they also are very interesting as a way to fibre-matrix compatibilization, to adhesion promotion and to enhance interphase properties [16,17]. Based on our understanding of sizing chemistry and processes and on the compatibility between fibre surfaces with PEEK matrix, it seems suitable to develop sizing formulations from thermostable thermoplastics [18]. Different criteria must be considered, both the compatibility of coating oligomers and main constituents with PEEK matrix and constraints linked to sizing implementation and composite material manufacturing. Indeed, polymers compatible with a PEEK matrix [19,20] present a poor adhesion with pitch-based carbon fibres. The fibre-matrix interface chemical engineering methodology presented here is expected to improve the interface by reactive compatibilization due to adhesion promotion of the carbon fibre surface with the PEEK matrix through growth of crystallinity directly onto the fibre, which is essential to obtain high performance materials [21-24]. In order to develop an effective solution to improve the fibre-matrix compatibility, particular attention was paid to the reinforcement material and to the methodology for coating deposition of a material able to promote the compatibilization and/or the adhesion with the matrix.

Assuming that the surface of the as-received and unsized carbon fibre is electrochemically-oxidized, we expected that the surface contains some oxide functional groups conferring to the surface an electronegative potential, which shall allow the physisorption of cationic polyelectrolyte materials. To this end, an innovative and environmentally friendly method, inspired by supramolecular layer by layer (LBL) assembly, [25] is used to modify the carbon fibre surface. The LBL technique relies upon the deposition of an oppositely charged macromolecule to the previously adsorbed polyelectrolyte, hence modifying the surface properties. Recent relevant reviews have

been published detailing the advantages of LBL technique [26-29]. This surface modification technique is suited for the deposition of multilayered films covering a broad range of applications. Nevertheless, to our knowledge this method can only be applied to small surface areas. Another important aspect concerns the fact that LBL films can not only be deposited from polyelectrolytes (due to electrostatic interactions) but also from all kinds of molecules or particles owing to mutually complementary interactions, such as hydrogen donor-acceptors, [30,31] covalent coupling through click chemistry, [32] complementary stereoregular polymers, [33] and nanomaterials [34] justifying the use of a mussel-based adhesive promoter namely polydopamine (PDA) due to its exceptional adhesive performance in wet environment and its role in interfacial adhesion[35,36]. A major challenge needs to be addressed to make this technique a key-pillar and an applicable technology for high performance applications: the adsorption of these two partners (polyelectrolyte and PDA) and particularly their complexation at the surface of a high modulus pitch-based carbon fibre.

Thus, this contribution aims at focusing on (i) the carbon fibre surface modification investigation by sessile drop testing, scanning electron microscope (SEM) observations, X-ray photoelectron spectroscopy (XPS) and multi-mode atomic force microscopy (AFM) characterization to identify and quantify the chemical modifications prior and after surface treatments, (ii) the influence of the fibre-matrix interface chemical engineering on the interphase properties of the composites reinforced with the so-modified carbon fibres by X-ray diffraction measurements to assess any crystallinity change, and (iii) the investigation of the impact of the reactive compatibilization on the CFRP composite mechanical properties by transversal tensile strength testing. We assume that this environmentally friendly methodology is an innovative challenge that allows the possibility to improve fibre-matrix interface quality and CFRP composite mechanical properties.

## Experimental Section

### Materials

**Carbon fibres:** Two carbon fibres were used in this study: high performance GRANOC yarn pitch-based carbon fibres YSH-50A-60Z and YSH-50A-60S produced by Nippon Graphite Fiber Corporation. Based on the supplier datasheet, these are high modulus and high strength 6 k tow count fibres (6000 monofilaments) with a tensile modulus of 630 GPa and a tensile strength of 3.9 GPa. One fibre was surface oxidized and not sized (CF-Z), the other was surface oxidized and thermoset-sized (CF-TS) with a sizing chemistry based on epoxy polymers.

**Thermoplastic polymer:** One thermoplastic polymer was used in this study. An unreinforced and uncharged poly(etheretherketone) (PEEK) was selected and used as a matrix of the composites. The PEEK materials were supplied in the form of a fine powder (PEEK 150XF) and thick films (300  $\mu\text{m}$ ) (APTIVTM 2000) by Victrex. The powder material was specifically used for the crystallinity investigation of the composites by x-ray diffraction, while the film material was used for the rest of the study. The remolding agent was CIREX 041WB from SICOMIN.

**Chemicals:** All chemicals (detailed in the section 2.2) were supplied by Sigma-Aldrich and used as received.

### Processes

**Preparation of the water-based surface treatment solutions:** Water (W/Milli-Q or ultrapure water) used in all experiments (with the exception of fibre rinse cycles) was prepared in a three-stage Millipore

Milli-Q purification system and was air-equilibrated before use. All glassware was submitted to cleaning steps using ethanol and acetone and rinsed with ultrapure water (W/Milli-Q). Poly(ethyleneimine) (PEI) was used without further purification as the polyelectrolyte for physisorbed deposition and was added (1 mg/mL) to a buffer solution pH=7.4 containing 10 mM tris(hydroxymethyl)aminomethane (THAM), 15 mM NaCl and ultrapure water. The solution was stirred at room temperature. Fresh dopamine hydrochloride (PDA) solutions were prepared before use because the mixture reacted immediately upon addition to a 10 mM THAM-HCl (pH=8.5) buffer solution.

**Carbon fibre surface treatments:** Continuous carbon fibres (substrates) were immersed in polyelectrolyte solution (PEI) during times ranging from 10 s to several hours and rinsed with water before any further use. Similarly, substrates (with and without PEI surface treatments) were immersed in polydopamine mixtures (PDA) (during times ranging from 10 s to 24 h) and rinsed with water.

**PEEK-based composites implementation:** We prepared 50 mm × 50 mm × 0.8 mm plates of PEEK composites reinforced with 2 unidirectional (UD) plies of as received or modified carbon fibres by compression-molding. To this end, a hydraulic manual press Carver equipped with heating plates and a Carver tile mold with an insert for 50 mm × 50 mm specimens were used. 50 mm × 50 mm UD plies of as received and modified carbon fibres were produced by the winding methodology. To fabricate a composite, two UD plies of fibres were subsequently sandwiched between three films of PEEK, then placed in the mold and pressed at 400°C for 30 min. To remove trapped air, the material was first sequentially pressed to 2 Tons and released and was finally subjected to 8 Tons for 30 s. The cooling step is performed by switching off the heating and leaving the material under pressure until the temperature reached room temperature.

## Characterizations

**Scanning electron microscopy:** A pressure-controlled Quanta FEG 200 environmental scanning electron microscope (SEM) from FEI Company Europe BV was used in secondary electron detection mode to get information about the carbon substrate surface topography, the fibre diameter, the surface treatment deposition quality and the fibre-matrix interface quality after transverse tensile strength testing of the composites. The environmental mode, with gaseous secondary electron detector (GSED) enables wet samples to be observed through the use of partial vapour pressure in the microscope specimen chamber to analyze the drop growth and geometry at the surface of the treated fibres. All observations were directly performed on specimens without any particular preparation procedure (no conductive coating).

**Sessile drop testing:** The wettability of the fibres prior and after surface treatment was investigated by static contact angle measurements (apparatus OCA 15 from Dataphysics) using the sessile drop method and distilled water as a liquid. Droplet volume is 2 µL. Elliptical model [37] was used to accurately estimate contact angle values, while 5 images were recorded to increase statistics.

**Atomic force microscopy:** A new generation of Bruker Atomic force microscopy (AFM) (Multi Mode 8 AFM with nanoscope 5 controller) was used to measure profiles of the surface of some samples at ambient conditions in order to investigate the electrostatic, structural and mechanical properties. Surface potential was measured in Peak Force (PF) KPFM in amplitude and frequency modulation modes (in conjunction with peak force tapping), topography in PF tapping mode, Young's modulus and adhesion in PF quantitative nano-mechanical mapping (QNM) mode.

**X-ray photoelectron spectroscopy:** X-ray photoelectron spectroscopy (XPS) analyses of the carbon substrates were performed with a Kratos AXIS Ultra DLD instrument using a hemispherical energy analyzer and a monochromatic Al K $\alpha$  X-ray source (1486.6 eV) as the incident radiation. For each samples, at least two measurements were performed at different locations. Scans were collected from 0 to 1300 eV with a power of 225 W and an anode voltage of 12 kV. The pressure in the analysis chamber was about 5.10<sup>-8</sup> Pa and the pass energies were set to 160 eV and 40 eV for survey and higher resolution scans, respectively. The binding energy scale was referenced from the carbon contamination using the C (1s) peak signal at 284.6 eV. Core level peaks were analyzed using a nonlinear Shirley-type background. Concerning the analysis of the C (1s) high resolution spectra, the peak positions and areas were optimized by a weighted least-square fitting method using a GL function (product of a Lorentzian by a Gaussian) by fixing the full width-at-half-maximum (FWHM) using XPCASA software, except for the C-C sp<sup>2</sup> for which the spectrum was fitted allowing some variations of the FWHM. It is assumed that this method has a scanned depth approximately between 5 nm and 10 nm.

**X-ray diffraction:** X-ray diffraction (XRD) experiments were conducted with a Panalytical X'Pert Pro MPD in reflection configuration, equipped with a temperature chamber (reference TTK 450). The X-ray beam corresponding to the K $\alpha$  copper radiation (1.54 Å) was generated at 40 kV and 45 mA. As primary optics, a programmable divergent slit was used with a constant sample irradiated length of 5 mm, a 0.04 rad Soller slit, and a mask of 5 mm. As secondary optics, a Pixcel detector was used with a constant programmable antiscatter slit of 5 mm, a 0.04 rad Soller slit, and a reception slit of 0.1 mm. The samples, consisting of 10 mm-continuous fibre on which was deposited a thin layer of PEEK powder, were positioned on the TTK 450 sample holder and subjected to a temperature program. The latter consisted of an heating step from 25°C to 400°C at 10°C/min to erase the thermal history of the PEEK matrix and enable the composite consolidation, and then to a cooling step from 400°C to 25°C with a cooling rate of -30°C/min. The intensity (I) - 2 theta ( $\theta$ ) diffractogram of the composite was first measured at 400°C to verify that the melting was totally achieved and then at the end of the program to calculate the material crystallinity. The crystallinity was calculated as the ratio between the area of crystalline peaks to the total area of crystalline and amorphous peaks. As crystalline peaks, we considered the (110), (113), (200), (213), (216) reflections positioned at 18.7°, 20.8°, 22.7°, 28.8°, 32.9° and 38.8°, respectively, corresponding to the orthorhombic phase of PEEK [38]. As amorphous peaks, we considered the bump centered at 20° and 28.6°. The mathematical deconvolution was done with the software PeakFit by using a Gaussian equation for each peak. The influence of the fibre/matrix compatibilization on PEEK crystallinity was evaluated.

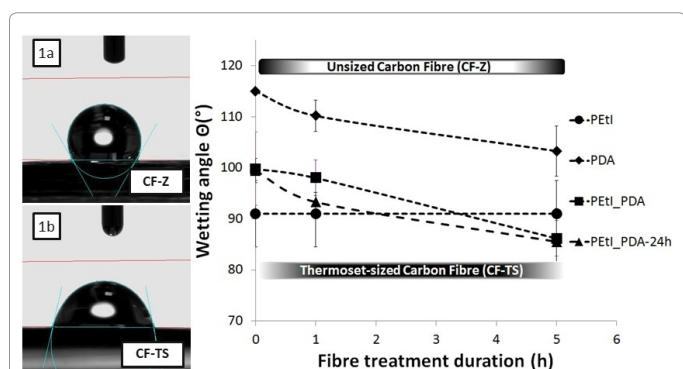
**Transverse tensile testing:** A miniature tensile/compression testing machine from Kammrath and Weiss was utilized to characterize the tensile behavior of PEEK/carbon fiber composites in the transverse direction. Tensile bars of dimensions 50 mm × 10 mm × 1 mm were machined perpendicular to fibre direction from the initial molded plates with a precision saw (Struers). The mechanical testing was performed at room temperature (20°C) and at a displacement rate of 10 µm.s<sup>-1</sup>, corresponding to a strain rate of 10 µm/28000 µm = 0.00036 s<sup>-1</sup>. The tensile strength, corresponding to the maximum stress at failure, was measured and discussed as a function of the fibre-matrix compatibilization parameters while at least 5 tastings were performed to increase statistics.

## Results and Discussion

In this work, influence of water-based surface treatments on carbon fibre, particularly an environmentally friendly methodology consisting of water-based solutions of polyelectrolytes, of mussel-inspired adhesive promoter and thermostable thermoplastic polymer, was investigated in the field of high performance materials. To this end, the following fibres were studied: i) the as received unsized carbon fibre (CF-Z), ii) the as received carbon fibre with commercial thermoset sizing (CF-TS), iii) the poly(ethyleneimine) treated carbon fibre (CF-PETI), iv) the carbon fibre treated with hydrochloride polydopamine solutions (CF-PDA) and v) the carbon fibres modified with a combination of the two treatments (CF-PETI-PDA). The interphase properties and interface mechanical performances of the composites have been investigated using PEEK as TP matrix.

Carbon fibre surface properties were first investigated by measuring the water contact angle (WCA, sessile drop tests) before and after surface treatments. This surface characterization allowed us to identify the influence of surface treatments on carbon roving wettability (Figure 1) and to illustrate the wetting difference between the untreated fibre (CF-Z) with the commercial-sized fibre (CF-TS) (Figure 1).

The as-received unsized carbon fibre (CF-Z) is hydrophobic with a contact angle of about 120°. As expected, the thermoset-sized CF (CF-TS), with a sizing chemistry based on epoxy polymers, is more hydrophilic with a contact angle close to 80°. The results obtained on the treated CF (Figure 1) show a decrease of the hydrophobic character with all the surface treatments whatever the treatment duration. Regarding the fibres treated with PDA solutions (CF-PDA), there is a decrease of the hydrophobic character from 115° to 103° as a function of the treatment duration indicating CF surface property modifications through self-assembly of the polydopamine onto the surface. With the polyelectrolyte treatments (CF-PETI) the contact angle was about 90° whatever the treatment duration, which proved the existence of electrostatic interactions between the polyelectrolyte chains and the CF surface. Moreover, this result seems to prove that physisorption of the polyethyleneimine is effective even after rinses cycle and occurs very rapidly comparing to some industrial processes, which could even require thermal treatments.



**Figure 1:** Contact angle values (averaged from 5 measurements with standard deviation) of pitch-based carbon fibre (CF) as a function of the nature and treatment duration (from 10 s to 5 h) with CF-Z: unsized CF, CF-TS: thermoset-based sized CF, PETI: CF treated with PETI solution [1mg/mL], PDA: CF treated with PDA solution [0.05 mg/mL], PETI\_PDA: CF treated with solutions of PETI [1 mg/mL] then fresh PDA [0.05 mg/mL] and PETI\_PDA-24h: CF treated with solutions of PETI [1 mg/mL] then 24h aged PDA [0.05 mg/mL]. Sessile drops from experimental set (image 1a): as received unsized CF; (image 1b): as received thermoset-sized CF. Black dashed lines are given as guides to the eye.

The steady value of contact angle with treatment duration shows that the covering of the fibre is immediate and complete and that a prolonged time treatment is not necessary to further modify the surface properties. Indeed, the overcompensation of the surface charge, which will be demonstrated further down this contribution, avoids the addition of the polyelectrolyte and an oppositely charged partner can be added in order to tune the CF surface modification. Thus, with a combination of the two treatments (CF-PETI\_PDA), the hydrophobic character decreases with treatment duration as expected since the PDA lies at the top of the surface. Moreover, with aged PDA (PETI\_PDA<sub>24h</sub>), contact angle faster decreases than with fresh PDA obviously because self-assembly of the polydopamine occurred in solutions yielding larger amount of macromolecules physisorbed at the surface. Therefore, at short treatment time, the amount of polydopamine trapped in the coating is certainly higher than in the case of aged solutions. Nevertheless, with longer treatment the properties became almost the same indicating that self-assembly occurred with fresh solution, which improves PDA concentration and homogeneity of deposition at the surface. However, surface topography should be different and will be discussed (*vide infra*). These results indicate that the fibre water-based surface modification is due: i) to the electrostatic interaction of the fibre surface with the polyelectrolyte (PETI) certainly resulting into charge overcompensation at the surface, and ii) to the self-assembly of the polydopamine at the carbon fibre surface. Moreover, it seems that PDA is more compatible with the CF surface after PETI surface treatment. These measurements were completed with environmental SEM observations of the carbon fibres in wet conditions to get results on monofilaments of the carbon fibres (Figure 2).

To this end, drop growth and geometry at the micrometer scale were obtained by SEM observations, using partial vapour pressure in the sample chamber. Results of the CF-Z fibres are presented on Figures 2a and 2b. One can specify that these are qualitative observations and no quantitative measurements because of the difficulty to control the drop volume when the images were observed and the difficulty to calculate the contact angle when substrate is curved. Thus CF-Z monofilament wetting was clearly hydrophobic confirming results obtained on roving. The drop geometry was almost spherical (Figure 2b) and the contact angle (Figure 2a) appeared to be >90°. Regarding fibres treated with the polyelectrolyte solutions (CF-PETI), Figures 2c and 2d confirmed a decrease of the hydrophobic character with drops more homogeneously spread onto monofilament and particularly, Figure 2c exhibited a good reproducibility with almost the same geometry for all droplets confirming WCA results. Figures 2e and 2f allowed observation of the PDA concentration influence for the same duration of fibre treatment. The higher was the PDA concentration (2f), the less spherical was the drop shape highlight that the surface wetting was clearly influenced by the PDA concentration and PDA surface treatment duration (self-assembly). Figure 2g showed that a PETI treatment prior to PDA self-assembly was relevant and enabled a more suitable coating of the droplet onto the monofilament than without polyelectrolyte physisorption confirming that, for such carbon fibres, a surface priming (pretreatment) of the substrate with a polyelectrolyte complex-based film triggers a more efficient subsequent deposition and self-assembly of hydrogen-bonded film [39]. Influence of aged PDA (24 h) is presented on the Figures 2h and 2i and it seems that a large quantity of PDA effectively covers the monofilaments after 24h duration, making the surface hydrophilic. These observations confirmed the WCA results obtained on roving.

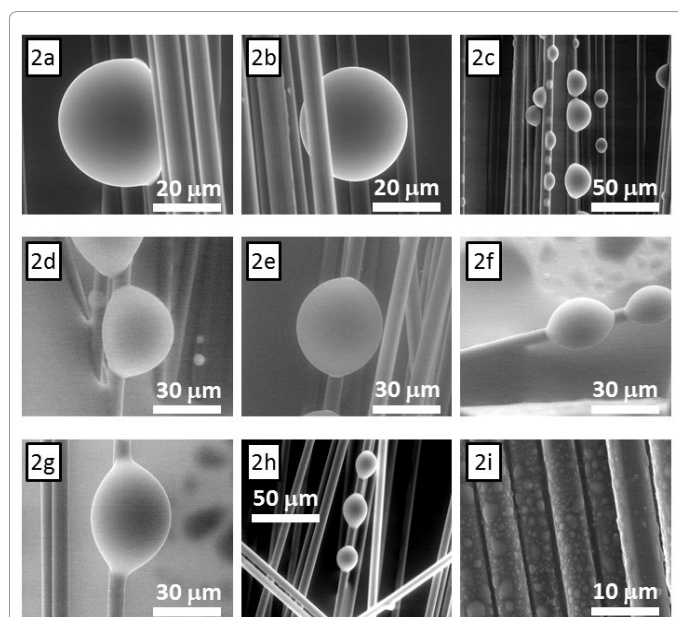
The main difficulty concerning the fibre-matrix interface compatibilization by fibre dipping or spraying is the understanding of

the carbon surface chemistry and its influence after surface treatments. Indeed, these treatments trigger surface modifications which may introduce functional groups onto the surface able of interact and/or react with the matrix. Thus, in order to go deeper into the characterization of surface properties, X-ray photoelectron spectroscopy (XPS) testing was performed on the fibres to determine the atomic composition of the extreme surface by measuring the elemental composition and calculating the O/C and N/C ratios. The elemental compositions and the calculated surface atomic O/C and N/C ratios prior and after water-based treatments are presented in Figure 3. Assuming that the carbon was homogeneously distributed in the mass of the carbon fibre and that the XPS sampling depth was approximately 10 nm, the results confirmed the success of the water-based surface modifications by chemical modification onto the fibre surface. Indeed, the untreated carbon fibre (CF-Z) contained about 2.4%-At of oxygen (O/C=0.024) and no nitrogen as expected with a pitch precursor. For all treated samples, the oxygen concentration is different from the case of bare fibres and nitrogen was detected, which was obviously a consequence of the surface modifications by the polyelectrolyte and polydopamine solutions. Indeed, PETI treatment induced an increase of oxygen atom amount to about 8.3%-At (O/C=0.095) and identification of nitrogen functional groups (4.1%-At; N/C = 0.047). Moreover, making the assumption that the film thickness was bigger than the depth of analysis of XPS, [25] the ratios allowed to calculate the polyelectrolyte complexes (PETI and THAM) ratio in the covering through equations (1) and (2):

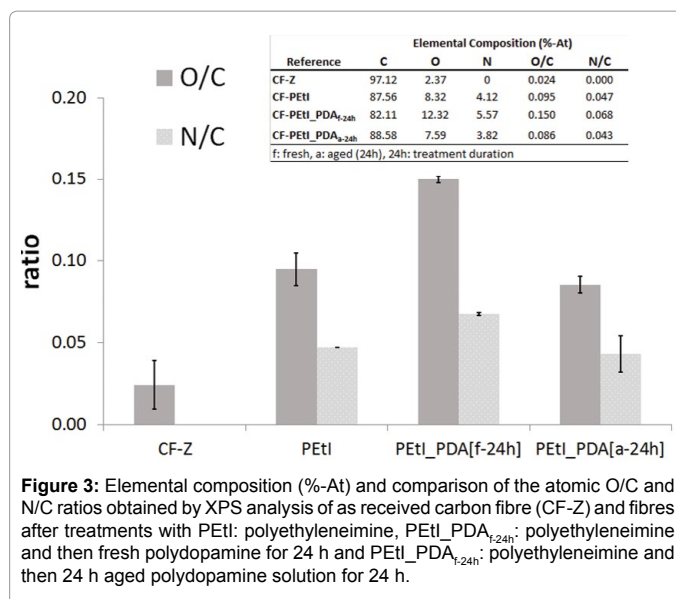
$$[O/C]_{CF-PETI} = a \cdot [O/C]_{PETI} + b \cdot [O/C]_{THAM} \quad (1)$$

$$[N/C]_{CF-PETI} = a \cdot [N/C]_{PETI} + b \cdot [N/C]_{THAM} \quad (2)$$

Where  $[O/C]_{CF-PETI}$  and  $[N/C]_{CF-PETI}$  are the polyelectrolyte complexes covering measured by XPS (corresponding to respectively 0.095 and 0.047),  $[O/C]_{PETI}$  and  $[N/C]_{PETI}$  are the carbon and nitrogen atom concentration in pure PETI (corresponding to respectively 0



**Figure 2:** Wet environmental SEM observations of carbon fibres monofilaments with 2a and 2b: as received unsized CF, 2c and 2d: CF-PETI, 2e and 2f: CF-PDA[0.1] and CF-PDA[1.0] and CF-PDA[1.0]<sub>f,24h</sub>, 2g: CF-PETI\_PDA<sub>f,24h</sub>, 2h and 2i: CF-PETI\_PDA<sub>f,24h-s</sub> and <sub>a,24h-24h</sub> ([x]<sub>y-z</sub>, x: PDA concentration [mg/mL], y: fresh "f" or 24h aged PDA solutions and z: treatment duration several seconds "s" or 24 hours "24h").



**Figure 3:** Elemental composition (%-At) and comparison of the atomic O/C and N/C ratios obtained by XPS analysis of as received carbon fibre (CF-Z) and fibres after treatments with PETI: polyethyleneimine, PETI\_PDA<sub>f,24h</sub>: polyethyleneimine and then fresh polydopamine for 24 h and PETI\_PDA<sub>a,24h</sub>: polyethyleneimine and then 24 h aged polydopamine solution for 24 h.

and 0.5),  $[O/C]_{THAM}$  and  $[N/C]_{THAM}$  are the carbon and nitrogen atom concentration in pure THAM (corresponding to respectively 0.75 and 0.25),  $a$  the total amount of PETI measured by XPS and  $b$  the total amount of THAM measured by XPS.

It derived from (1) and (2) that the polyelectrolyte complex-based film contained a THAM/PETI ratio of approximately equal. Considering that we used a poly(ethyleneimine) solution with a relative molar mass, based on the supplier documentation,  $M_r$  of about 600000-1000000, it is not surprising that the deposited film had such composition by adsorption of complexes formed from polyanion interacting and/or trapped in the branched polycation. This result paves the way to the development of tailored fibre-matrix interfaces by using other polyanionic species and suitable (nano) fillers.

Regarding the combination of PETI and PDA treatments, we used fresh and 24-h aged polydopamine solutions to modify the CF-PETI fibres. XPS analysis showed that significant improvements in O/C and N/C ratios were obtained with fresh polydopamine solution treatment and tended to confirm the success of the surface modification and self-assembly onto the carbon fibre surface and thus the presence of PDA. Concerning 24-hour aged PDA treatment, the O/C and N/C ratios determined by the technique are respectively 0.086 and 0.043. It can be observed that these ratios are lower than that of PETI surface priming and of PDA reference in solution (0.25 and 0.125), which means that the excess of carbon measured could come from fibres which are not fully covered. Indeed, PDA treatment is performed in solution with higher pH and lower salt concentration increasing the negative surface charge of the fibre and inducing higher interaction between the surface and the PETI, which could modify the film structure and thickness. Moreover for aged-PDA, self-assembly occurred in solution. The PDA deposited onto the fibre is built on larger macromolecules assembled in solution and not self-assembled directly onto the fibre. The topography between both samples and their surface chemistry are thus different as confirmed by XPS, WCA and wet-ESEM results.

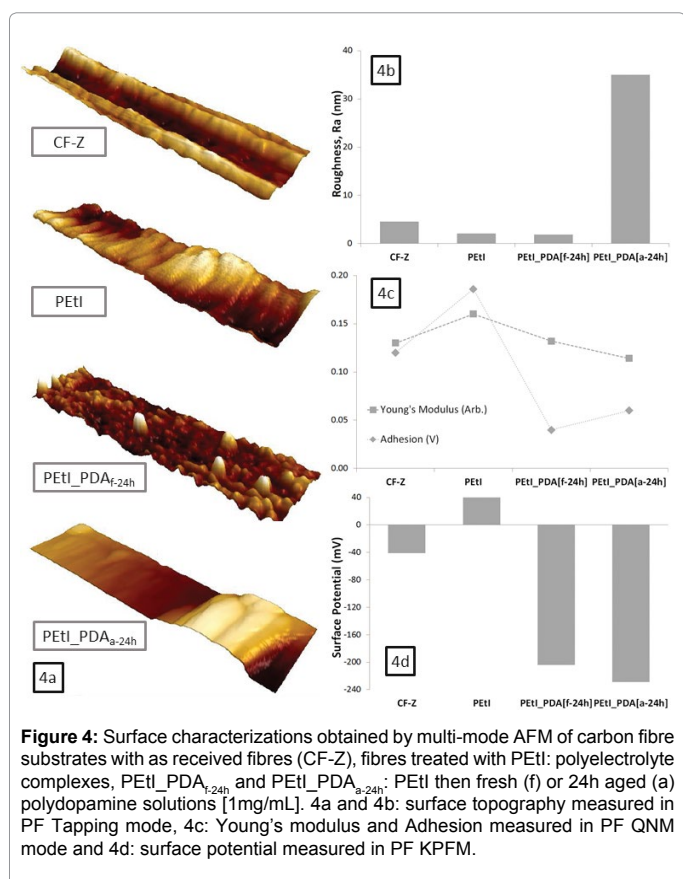
After the successful surface treatments and chemical property modification of the carbon fibres with PETI and PETI\_PDA solutions, multi-mode Atomic Force Microscopy (AFM) characterizations were performed to confirm and finely identify the physico-chemical surface modifications and particularly the charge overcompensation of the

surfaces after treatment. Peak force AFM was used to measure surface profiles of the CF-Z, CF-PETi, CF-PETi\_PDA<sub>f-24h</sub> and CF-PETi\_PDA<sub>a-24h</sub> carbon fibres at ambient conditions in order to investigate the electrostatic, structural and mechanical properties of the treated fibre surfaces.

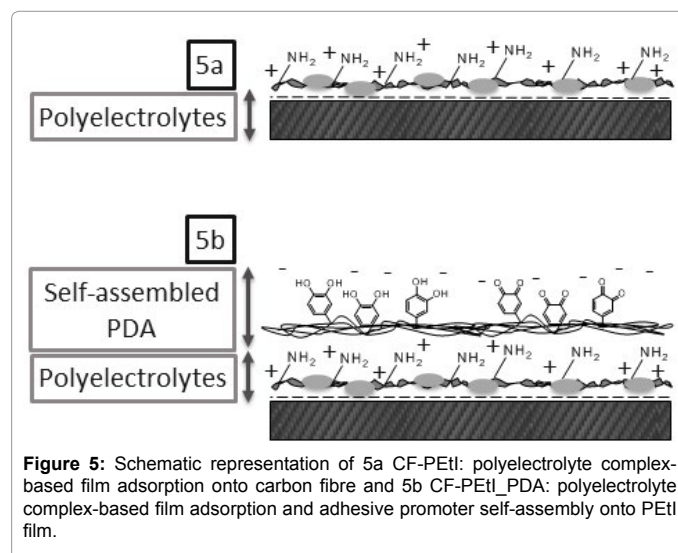
Surface topography (Figures 4a and 4b) was measured in PF tapping mode. Seemingly, the change of surface roughness indicated the change of the carbon fibre surface morphology with respect to the as-received unsized carbon fibre. The polyelectrolyte complex-based film and the combination of the polyelectrolyte complex with fresh polydopamine solution induced a subtle decrease of the fibre roughness (respectively Ra=2.1 nm and 1.9 nm against 4.6 nm for the reference). This could indicate a suitable coating of a polyelectrolyte complexes film onto the fibre and a PDA self-assembly onto the nanoscale roughness of the physisorbed film. On the contrary, the aged PDA solution induced deposition of large PDA molecules (self-assembled in solution) improving surface roughness. These results demonstrated that the PDA self-assembly was distinctly different if it occurred directly onto the fibre surface or in the solution. Surface Young's modulus and adhesion properties were measured in PF QNM mode (Figure 4c). Regarding PF QNM measurements, modulus and adhesion were only compared one with the others in a qualitative manner. Interestingly, the Young's modulus remained almost constant for all fibres (CF-Z: 0.13 Arb.; PETi: 0.16Arb.; PETi\_PDA<sub>f-24h</sub>: 0.132Arb. and PETi\_PDA<sub>a-24h</sub>: 0.114Arb.). The slight improvement measured with the PETi treatment must be triggered by the polyelectrolyte complex-based physisorbed film, which was obviously of a different nature than the self-assembled PDA deposit. This suggests that all over changes of the PDA deposits were extreme surface related. Moreover, the decrease

in adhesion of PDA-treated substrates indicates a change of the surface functional groups of these fibres (CF-Z: 0.12V; PETi: 0.186V; PETi\_PDA<sub>f-24h</sub>: 0.04V and PETi\_PDA<sub>a-24h</sub>: 0.06V). Finally, the surface potential (Figure 4d) was measured in Peak Force (PF) KPFM in frequency modulation mode (in conjunction with peak force tapping). The consistent changes of surface potential (CF-Z: -41mV; PETi: 69mV; PETi\_PDA<sub>f-24h</sub>: -204mV and PETi\_PDA<sub>a-24h</sub>: -229mV) showed a modification of the fibre surface electrostatic properties after treatment (with respect to the reference). Moreover, the charge modification with PETi treatment demonstrated the charge overcompensation induced by the physisorption of the polyelectrolyte film onto the carbon fibre. These results clearly demonstrated the efficiency of our methodology inspired by the LBL technique. Finally, the charge modification and surface potential improvement with PETi\_PDA treatment seemed to prove that the hydroxyl functional groups of the adhesive promoter are exposed at the top surface of the coating. The interaction mechanism and the polyelectrolyte and adhesive promoter conformations are schematically explained in Figure 5.

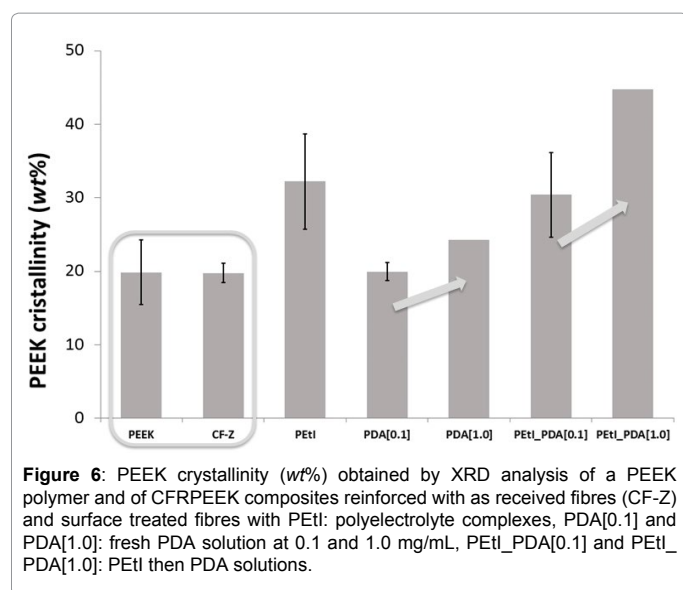
The influence of the water-based surface treatments onto the carbon fibre surface properties has been investigated and detailed. Surface modification, particularly in terms of wettability, chemical composition at the extreme surface, roughness and surface potential have been measured and discussed. It has been proven that polyelectrolyte complex-based film, in combination or not with the adhesive promoter self-assembly directly onto the carbon surface by dipping in water-based solutions containing these chemicals, modified the physico-chemical properties of carbon fibre surface. After these successful surface modifications of carbon fibres with PETi and PETi\_PDA, XRD analysis has been approached to study the crystallization behavior of PEEK with constant processing parameters, as a function of fibre surface treatments. The composite heating treatment and cooling steps were directly performed in the XRD apparatus. Specific cooling step parameters have been designed in such a way that crystallinity could not grow at the interface. This procedure allowed the investigation of surface modifications by water-based solutions on the fibre-matrix interphase properties through the monitoring of the crystallinity behavior. Indeed, it is well known that to erase the thermal history of PEEK matrix, a thermal treatment at 400°C was required [40] and we verified that cooling step affected PEEK crystallization (results not presented here). A cooling rate of 30°C/min was chosen which was



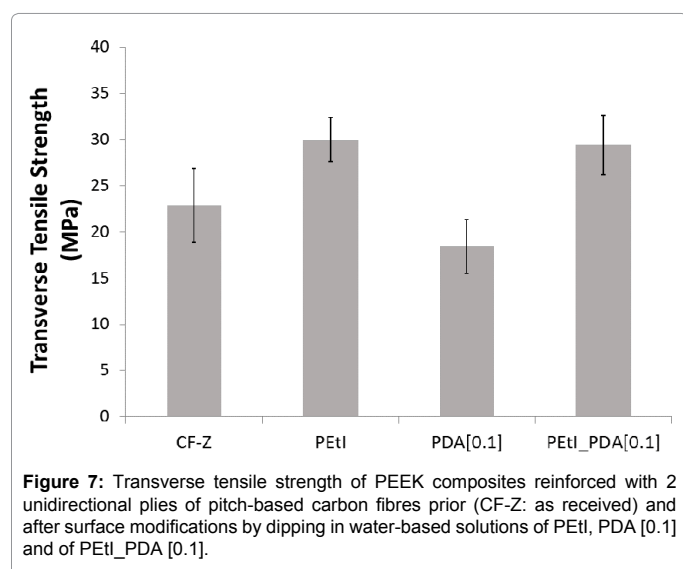
**Figure 4:** Surface characterizations obtained by multi-mode AFM of carbon fibre substrates with as received fibres (CF-Z), fibres treated with PETi: polyelectrolyte complexes, PETi\_PDA<sub>f-24h</sub> and PETi\_PDA<sub>a-24h</sub>; PETi then fresh (f) or 24h aged (a) polydopamine solutions [1mg/mL]. 4a and 4b: surface topography measured in PF Tapping mode, 4c: Young's modulus and Adhesion measured in PF QNM mode and 4d: surface potential measured in PF KPFM.



**Figure 5:** Schematic representation of 5a CF-PETi: polyelectrolyte complex-based film adsorption onto carbon fibre and 5b CF-PETi\_PDA: polyelectrolyte complex-based film adsorption and adhesive promoter self-assembly onto PETi film.



**Figure 6:** PEEK crystallinity (wt%) obtained by XRD analysis of a PEEK polymer and of CFRPEEK composites reinforced with as received fibres (CF-Z) and surface treated fibres with PETI: polyelectrolyte complexes, PDA[0.1] and PDA[1.0]: fresh PDA solution at 0.1 and 1.0 mg/mL, PETI\_PDA[0.1] and PETI\_PDA[1.0]: PETI then PDA solutions.



**Figure 7:** Transverse tensile strength of PEEK composites reinforced with 2 unidirectional plies of pitch-based carbon fibres prior (CF-Z: as received) and after surface modifications by dipping in water-based solutions of PETI, PDA [0.1] and of PETI\_PDA [0.1].

the faster controlled process representative of an air cooling because of the mold temperature gradients. Crystallinity assessments presented in Figure 6 showed that, as expected, unreinforced PEEK polymer and CFRPEEK composites reinforced with as received carbon fibres (CF-Z) had almost the same crystallinity, i.e. about 20 wt%. XRD results confirmed that with typical industrial scale parameters, there is a lack of compatibility and interaction between the matrix and the surface of the CF-Z fibres since crystallinity improvement through transcrystallinity is not detected. Indeed, as far as authors know, transcrystallinity has only been observed by microscopy with very slow cooling parameters [41] with pitch-based carbon fibre-reinforced PEEK composites.

Concerning the fibres treated with fresh PDA solutions at 0.1 mg/mL and 1.0 mg/mL, the lower PDA concentration samples did not show any influence on the composites crystallinity. This experiment did not provide the anticipated results because even at low concentration and without pre-surface treatment, PDA treatment induced chemical and physical properties modification onto the fibre surface. But, with the improvement increase of the PDA concentration (to 1 mg/mL), the PEEK crystallinity increased from 20 to about 24 wt% highlighting that

the PDA self-assembly onto the fibre influenced the total crystallinity of the PEEK. Furthermore, the fibres treated with the polyelectrolyte complex solution (PETI) proved to increase the matrix crystallinity in the composites up to ca. 32 wt%. This significant improvement seemed to demonstrate that transcrystallinity occurred at the fibre-matrix interface creating an interphase area. This interphase should be an area of strong interaction between PEEK polymer and carbon fibre surface. Interestingly, as far as the fibres treated with both solutions, i.e. PETI then PDA, a substantial some improvement to about 30 wt% and even 45 wt% was determined. These improvements of PEEK crystallinity demonstrated that PETI permitted a higher interaction between PEEK and the fibre surface and that PDA did not interfere with matrix crystallinity improvement and the very likely creation of an interphase area. These results could demonstrate an enhancement of fibre-matrix interface compatibilization and improvement of adhesion of the PEEK onto the fibre through the formation of a transcrystalline interphase which was influenced by the fibre surface properties. Indeed, we assume that the presence of the polyelectrolyte complex-based film forces the PEEK to get very close to the carbon fibre surface owing to electrostatic interactions and hydrogen bonding. During the cooling phase, the PEEK macromolecules (containing aromatic rings) close to the fibre surface (also made of aromatic rings due to the high density graphitic sheet-like microstructure of the fibre and high preferred orientation in terms of crystallite size [42,43] create  $\Pi$ - $\Pi$  stacking and electrostatic interactions making the fibre surface an effective nucleating site and a large number of nuclei can be induced directly onto the surface. The crystal structure similarity, the high thermal conductivity of the fibre increasing the nucleation, and the high degree of molecular orientation inducing by the polyelectrolyte complex-based coating, allowed a nucleation growth at the interphase, which is thus referred to as transcrystallinity. Moreover, this  $\Pi$ - $\Pi$  stacking interaction effect was not obstructed by the presence of PDA and could be even more pronounced by the self-assembly of PDA resulting from  $\Pi$ - $\Pi$  stacking assembly. Actually, fibres treated with the higher PDA concentration [1.0 mg/mL] proved to increase the crystallinity of the composites to around 24 wt% and the higher crystallinity to about 45 wt%, was obtained with PETI\_PDA [1.0 mg/mL] samples, which tended to support our proposed mechanism. These results seem to confirm that PDA improved PEEK crystallinity by improving the  $\Pi$ - $\Pi$  stacking interaction concentration induced by its self-assembly especially as when it optimized (by the presence of the polyelectrolyte complex-based film, for example).

Assuming these promising results, the water-based surface treatments were proposed as a convenient method for the sizing treatment of the high modulus pitch-based carbon fibres. Indeed, sizing process was considered as the simplest procedure to modify the carbon fibre surface [44-46]. The use of these modified carbon fibres was expected to improve the composite mechanical properties, particularly because of better adhesion between the fibre and the matrix as a result of interface compatibilization by interphase area formation at the vicinity of the fibres. The identified matrix crystallinity improvement was assumed to be transcrystallinity and was obtained by fibre surface modifications, was expected to generate interaction responsible for the PEEK adhesion on the fibre surface.

The transverse tensile strength at failure obtained with as received carbon fibres (CF-Z) and surface treated fibres were reported in Figure 7. Enhancements were actually obtained on the transverse tensile strength at failure, as measured via transverse tensile testing of unidirectional composites, by applying the PETI and PETI\_PDA surface treatments. Indeed, 30 MPa and 29.4 MPa were respectively measured, whereas

transverse tensile stress of 22.9 MPa was recorded for the composites reinforced with the reference (CF-Z). The effect of the influence of the transcrystallinity (inducing fibre-matrix compatibilization and adhesion promotion at the interface) on the composite mechanical behavior is confirmed. The influence of the crystallinity improvement, which is certainly a transcrystalline interphase, on the mechanical behavior is strongly assumed. The poor mechanical properties (18.5 MPa) obtained with the composites reinforced with mussel-inspired adhesive promoter-treated fibres confirmed the poor fibre-matrix interface quality and the lack of crystallinity with low concentration of adhesive promoter. Encouraging results allow the use of PEEK composites reinforced with high modulus pitch-based carbon fibres as structural materials for high performance applications by the use of fibres sized applying this environmentally friendly methodology.

## Summary and Conclusions

This study showed an innovative and environmentally friendly methodology for fibre-matrix compatibilization and adhesion promotion in the case of PEEK composites reinforced with pitch-based carbon fibres. The composite interphase properties were improved by the carbon fibre surface modification using water-based treatments. Transcrystallinity at the interphase, which was successfully improved by means of incorporating polyelectrolyte complex-based film and self-assembled adhesive promoter coating by water-based sizing procedure, allowed the improvement of the composite transverse mechanical properties. Indeed, carbon fibre surfaces were modified thanks to the physisorption of polyelectrolyte complex-based film. This film adsorption, based on electrostatic interaction, had a positive effect on the adhesive promoter self-assembly onto the fibre. The influence of these water-based surface treatments onto the carbon fibre surface properties (tow and monofilament) have been investigated and detailed. Surface modification particularly in terms of wettability, chemical composition at the extreme surface, roughness and surface potential have been measured and discussed and an interaction mechanism was proposed. Interestingly enough, this is the first time that PETA/PDA/pitch-based carbon fibre were used in a real continuous pitch-based carbon fibre reinforced PEEK composite. Finally, this environmentally friendly methodology appeared to be very interesting and efficient ways to the development of reactive compatibilization and high performance eco-sizing. This work paves the way to the formulation of cost efficient thermoplastic sizing easily processed by water-based solutions/process.

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