INTERPHASE MODIFICATION BY TRANSCRYSTALLINITY PROMOTION INDUCED BY SUPRAMOLECULAR ASSEMBLY IN A HIGH PERFORMANCE THERMOPLASTIC COMPOSITE

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Abstract

This work addresses the challenging fibre-matrix compatibilization of a thermoplastic composite based on Poly(EtherEtherKetone) (PEEK) matrix reinforced with continuous high modulus pitch-based carbon fibre. An environmentally friendly methodology was applied in order to use PEEK matrix in high performance composites and dealt with the compatibilization of the matrix with the carbon fibre surface. This innovative and alternative method based on the so called “Layer-by-Layer” technic was used to modify the carbon fibre surface in order to improve the compatibility and the quality of the fibre-matrix interface. Particularly, electrostatic interactions were expected to promote the adhesion of polyelectrolyte species with the unsized and as received oxidized carbon fibre. Moreover, a mussel-based adhesive promoter, applied via a water-based process, was used to modify carbon fibre surface and to improve fibre-matrix adhesion. The innovative interface compatibilization method was successfully applied in the case of pitch-based carbon fibre reinforced PEEK matrix and resulted in an enhancement of crystallinity which probably occurred at the interphase and in an improvement of transverse tensile strength.

1. Introduction

The replacement of thermoset by thermoplastic is a major area of research in aeronautic and space industries particularly because of the recycling possibilities and the cost reduction obtained by the use of this class of polymer. Poly(EtherEtherKetone) (PEEK) is one of the most promising high performance thermoplastic polymer and has sufficiently good properties to be compatible to severe space conditions. The major challenge of its use as a matrix in high performance composites relies on the compatibilization of the matrix with a continuous high modulus pitch-based carbon fibre (CF). Therefore, the manufacturing of PEEK-based composites, which has to be performed at elevated temperatures between 380°C and 400°C, is challenging due to the following points: (i) the high melt viscosities 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 sizing has unsufficient thermal stability and, more generally, the fibre sizing has to be developed with a coating chemistry showing sufficient stability at such high temperatures, and (iii) the transcrystallinity of PEEK at the interface depends on the pitch-based carbon fibre surface properties and has to be taken into account to explain the interphase properties.

Applications of PEEK-based composites are increasingly popular and lead to the manufacture of primary and secondary structures such as PEEK/glass fibre laminates [1], carbon nanofiber composites [2] and carbon nanotubes composites [3]. However, PEEK-based composites reinforced with

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continuous carbon fibre are not yet reliable for high performance applications, as long as the material is reinforced with continuous high modulus pitch-based carbon fibre because of the issues linked to viscosity, thermal stability and transcristallinity, as previously described. Furthermore, to the best of our knowledge, there is a limited understanding about the compatibilization and adhesion mechanisms in such high performance composites [4]. More precisely it is assumed that fibre-matrix interface compatibilization is actually the key to improve these composites. Therefore, 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.

An innovative and versatile method, inspired by supramolecular assembly [5,6], is used to modify the carbon fibre surface. Indeed, coatings obtained by adsorption of polymer macromolecules onto solid surfaces have been studied for decades because they allow the fabrication of thin films having tailored structures and properties. Despite very promising results on solid substrates [7], this technique does not allow deposition of films onto large substrates and with a high throughput. Hence, the main objective of this work was to develop a versatile technique to enable carbon fibre surface modification for the development of environmentally friendly compatibilization and adhesion promotion. To this aim, we use an alternative method based on the so called “Layer-by-Layer” technique allowing to prepare a coating based on the coalescence and intermixing of complexes with or without thermostable thermoplastic polymer. The system was applied in the field of high performance composites and, in particular, for the improvement of pitch-based CF-PEEK matrix interface.

Based on our understanding of sizing processes and on the compatibility between surfaces with PEEK matrix, different criteria must be considered, both the compatibility of coating oligomers and main constituents with PEEK matrix and constraints linked to sizing implementation, procedures and composite material manufacturing. Indeed, polymers compatible with a PEEK matrix [8,9] present bad adhesion with pitch-based carbon fibre. The methodology presented here is expected to improve the interface and process compatibilization due to adhesion promotion of the carbon fibre surface with the matrix, which is essential to obtaining high performance materials [10]. Assuming that the carbon fibre surface of the as received and unsized carbon fibre is electro-oxidized, we expected that the surface contains some oxide functional groups conferring to the surface an electronegative potential which should allow the physisorption of cationic polyelectrolyte materials. This feature allows the deposition of an oppositely charged macromolecule to the previously adsorbed polyelectrolyte, hence modifying the surface properties. A second partner which presents exceptional adhesive performance in wet environment and derived from the mussel-based adhesion [6] is expected to play a role in interfacial adhesion. A major challenge has to be addressed to make this technique a key pillar and an applicable technology for high performance applications: the adsorption of these two partners at the surface of a high modulus pitch-based carbon fibre.

This paper will focus (i) on the carbon surfaces characterization and modifications by aqueous-based formulations applied in accordance to water-based sizing treatments, (ii) on the discussion about interphase modification and crystallinity promotion and (iii) on the mechanical performance of the high performance composites reinforced with the modified carbon fibres.

2. Material and Methods

2.1. Materials

2.1.1. Carbon fibre. Two high modulus and high strength fibres were used in this study, that were the GRANOC yarn high performance pitch-based carbon fibres YSH-50A-60Z and YSH-50A-60S produced by Nippon Graphite Fiber Corporation. Based on the supplier datasheet, these fibres were 6 k tow count (6000 monofilaments) with a tensile modulus of 630 GPa and a tensile strength of 3.9 GPa and were surface oxidized, unsized (CF-Z) and surface oxidized and thermoset-sized (CF-TS).

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2.1.2. Thermoplastic polymer matrix. The unreinforced and uncharged poly(etheretherketone) materials slected for this study were supplied in the form of a fine powder (PEEK 150XF) and thick films (300 μm) (APTIVTM 2000) by Victrex. The powder material was specifically used for the crystallinity investigation of the composite by x-ray diffraction, while the film material was used for the rest of the study. The remolding agent was CIREX 041WB from SICOMIN.

2.1.3. Chemicals. All chemicals were supplied by Sigma-Aldrich and were used as received in this study for the water-based surface treatment solutions.

2.2. Processes

2.2.1. Preparation of the water-based surface treatment solutions. The 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). A polyelectrolyte (PEtI) was used without further purification for physisorbed deposition and was added [1 mg/mL] to a buffer solution pH = 7.4 containing 10 mM Tris, 15 mM NaCl and ultrapure water. The solution was stirred under sonication for 10 min at room temperature. Fresh mussel-based adhesive partner solutions (PDA), at low concentrations, were prepared before use because the mixture reacted immediately upon addition to a 10 mM Tris–HCl (pH = 8.5) buffer solution.

2.2.2. Carbon fibre surface treatments. Continuous carbon fibres (substrates) were immersed in polyelectrolyte solution (PEtI) during times ranging from 10 s to several hours and rinsed with water before further use. Similarlyt, substrates (with and without PEtI surface treatments) were immersed in a mussel-based adhesive partner mixture (PDA) and rinsed with water.

2.2.3. PEEK-based composites implementation. We prepared 50 mm × 50 mm × 1 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 MPa and released and was finally subjected to 8 MPa 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.

2.3. Characterizations

2.3.1. Sessile drop test. 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. Elliptical model [11] was used to accurately estimate contact angle values, while 5 images were recorded to increase statistics.

2.3.2. X-ray photoelectron spectroscopy analysis. X-ray photoelectron spectroscopy (XPS) analyses of the carbon substrates were performed with a Hemispherical Energy Analyser SPECS (PHOIBOS 150) using a monochromatic source AlKα (1486.74 eV) as incident radiation. Scans were collected from 0 eV to 1300 eV with a power of 200 W and an anode voltage of 12 kV. The pressure in the analysis chamber was about 5.10^{-8} Pa and the pass energies were set to 80 eV and 20 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). The full width-at-half-maxima (FWHM) were fixed

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using XPSCASA software, excepted for the C-C sp² for which the spectrum was fitted allowing some variation of the FWHM. It is assumed that this method has a scanned depth close to 10 nm.

2.3.3. X-ray diffraction analysis. 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 kα 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 (2θ) 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 [12]. As amorphous peaks, we considered the large peaks 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.

2.3.4. 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 dimension 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^{-1}, corresponding to a strain rate of 10 µm / 28000 µm = 0.00036 s^{-1}. The tensile strength, corresponding to the maximum stress at failure, was measured and discussed as a function of the fibre-matrix compatibilization parameters.

2. Results and Discussions

In this work, influence of water-based surface treatments on carbon fibre, particularly eco-friendly solutions of polyelectrolyte and solutions containing a mussel-inspired adhesive promoter were investigated for the following fibres: i) the as received carbon fibre (CF-Z), ii) the polyelectrolyte physisorbed carbon fibre (CF-PEtI), iii) the carbon fibre modified with mussel-inspired adhesive promoter (CF-PDA) and iv) the fibres modified with a combination of the two treatments (CF-PEtI-PDA). Discussion about the influence of carbon fibre surface modifications on the surface properties is done for these four kind of samples. Thermoplastic composite interphase properties and interface mechanical performances are also investigated. Additionnaly, a carbon fibre with commercial thermoset sizing (CF-TS) was also considered for thew sake of comparison.

Thus, carbon fibres surface properties are 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 fibre wettability (Figure 1) and to illustrate the wetting difference between the untreated fibre (CF-Z) with the commercial-sized fibre (CF-TS) (images 1a and 1b).

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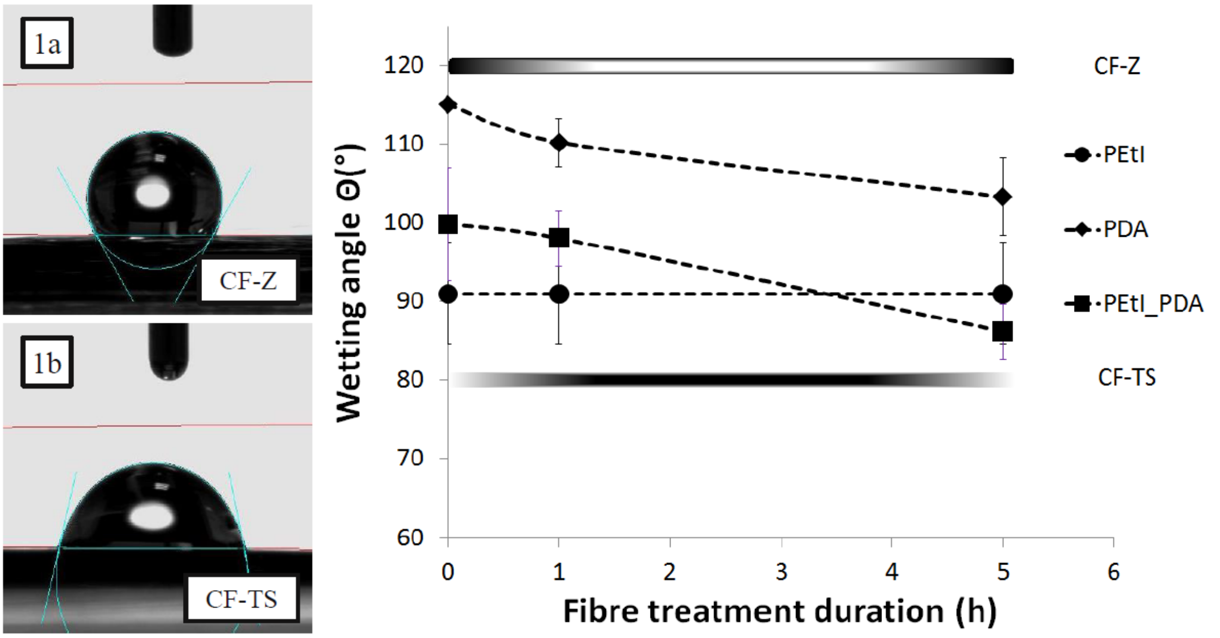

Figure 1. Contact angle values of the studied carbon fibres including the thermoset sized fibre as a function of the duration of the treatments (the first treatment correspond to several seconds). **Images 1a and 1b.** Sessile drops from experimental set (a): as received unsized fibre; (b): as received thermoset-sized fibre.

The as-received carbon fibre (CF-Z) is hydrophobic with a contact angle about 120°. As expected, the thermoset-sized (CF-TS), with a sizing chemistry probably based on epoxy polymers, is more hydrophilic with a contact angle close to 80°C. The obtained results on the modified fibres (Figure 1) show a decrease of the hydrophobic character with the mussel-inspired adhesive promoter treatments (PDA) as a function of the fibre treatment duration. With the polyelectrolyte treatments (PEtI) the contact angle was about 90° whatever the treatment duration, which seems to prove that the electrostatic interactions between the polyelectrolytes and the carbon surface are strong and occur rapidly. With a combination of the two treatments, the hydrophobic character decreased and, when treatment duration increased, the fibre surface becomes hydrophilic close to the commercial sizing (CF-TS) wetting properties. This result signifies that the fibre surface modification is due: i) to the electrostatic interaction of the fibre surface with the polyelectrolytes resulting into charge overcompensation at the surface, ii) to the self-assembly of the mussel-inspired adhesive promoter at the carbon surface with a more suitable organization than without the polyelectrolyte. It seems that the mussel-inspired adhesive promoter is more compatible with the carbon fibre surface after surface treatment with the polyelectrolyte solution.

In order to go deeper into the characterization of surface properties, 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 composition and the calculated surface atomic O/C and N/C ratios prior and after water-based treatments were presented in Figure 2. 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 confirm the success of the water-based surface modifications. Indeed, the untreated carbon fibre (CF-Z) contained about 5.3 % of oxygen and no nitrogen like expected with a pitch precursor. For all treated samples, the oxygen concentration presented a difference and nitrogen was detected, which is obviously a consequence of the surface modifications by the polyelectrolyte and adhesive promoter solutions.

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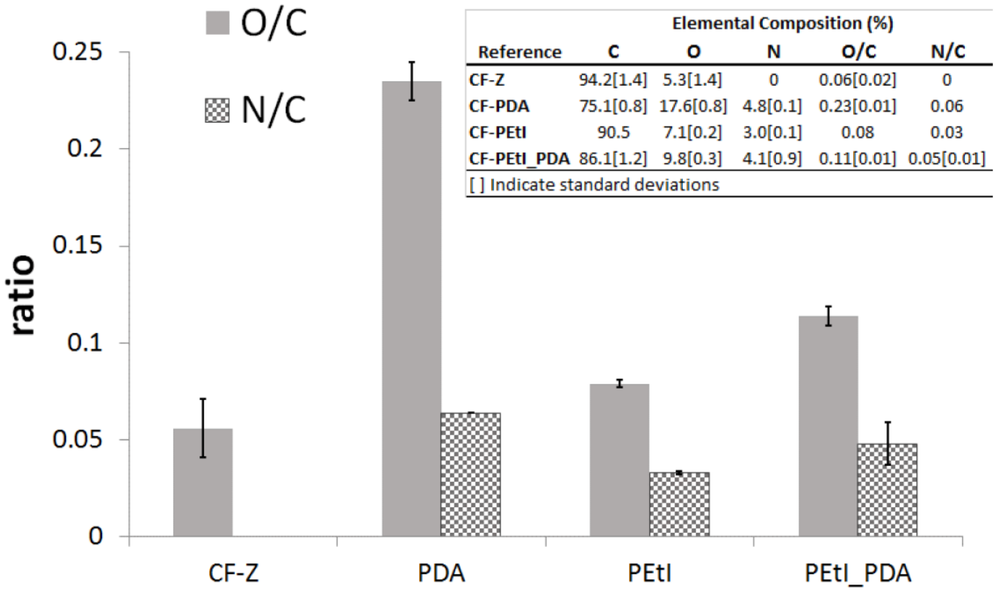

	Elemental Composition (%)				
Reference	**C**	**O**	**N**	**O/C**	**N/C**
CF-Z	94.2[1.4]	5.3[1.4]	0	0.06[0.02]	0
CF-PDA	75.1[0.8]	17.6[0.8]	4.8[0.1]	0.23[0.01]	0.06
CF-PEtI	90.5	7.1[0.2]	3.0[0.1]	0.08	0.03
CF-PEtI_PDA	86.1[1.2]	9.8[0.3]	4.1[0.9]	0.11[0.01]	0.05[0.01]

[ ] Indicate standard deviations

Figure 2. Elemental composition (%) and comparison of the atomic O/C and N/C ratios obtained by XPS analysis for reference and modified carbon fibres.

WCA and XPS were done and surface modifications by using water-based solutions of polyelectrolyte and/or mussel-inspired adhesive promoter have been demonstrated. We used XRD analysis to study the crystallization behavior of PEEK with constant processing parameters, as a function of these surface treatments. The cooling step parameters were chosen in such a way that crystallinity could not grow at the interface. This 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 [13] and we verified that cooling step affected PEEK crystallization. The composite's heating treatement and cooling steps were directly performed in the XRD. Crystallinity assessments presented in Figure 3 showed that, as expected, PEEK polymer and PEEK matrix reinforced with as received CF-Z fibres had almost the same crystallinity of about 20 wt%.

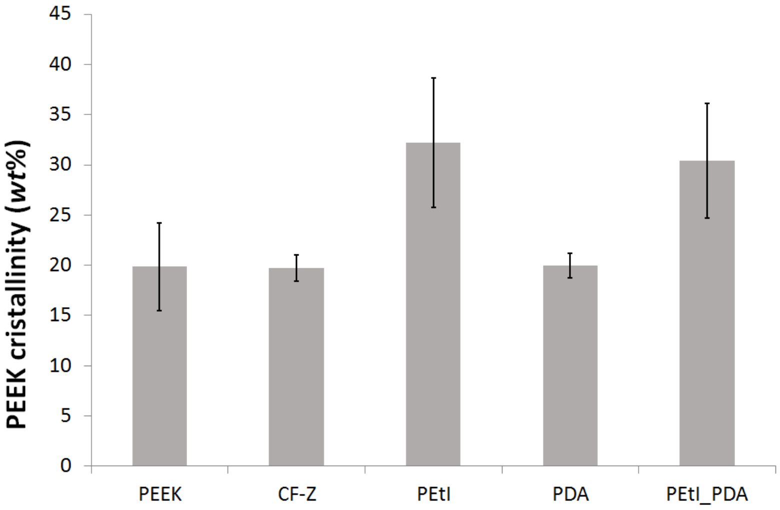

Figure 3. PEEK crystallinity (wt%) obtained by XRD analysis of a PEEK polymer and of pitch-based carbon fibre reinforced PEEK composites with the 4 studied carbon fibres.

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XRD results confirmed that there is a lack of compatibility and interaction between the matrix and the surface of the CF-Z fibre since transcristallinity is not detected. Indeed, as far as the authors know, transcrystallinity has only been observed by microscopy with very slow cooling parameters [14] on pitch-based CF. Concerning the fibres treated with low concentration of mussel-inspired adhesive promoter, results show no influence on the crystallinity of the composites. However, fibres treated with polyelectrolyte solution (PEtI) allowed improvement of the crystallinity of the composites to around 32.2 wt%. This significant improvement seems to demonstrate that transcrystallinity occurs at the fibre-matrix interface, thus creating an interphase area of strong interaction between PEEK polymer and the carbon fibre surface. Moreover, fibres treated with both solutions showed improvement to 30.4 wt% even though the mussel-inspired adhesive promoter was at the top of the fibre surface. This result demonstrates that PEtI permits a higher interaction between the PEEK and the fibre surface and that the adhesive promoter does not significantly influence transcrystallinity. These results could demonstrate that PEEK molecules (containing aromatic rings) close to the fibre surface (also made of aromatic rings) and due to the high density graphitic sheet-like microstructure of the fibre and high preferred orientation in terms of crystallite size [15], create π-stacking interaction making the fibre surface an effective nucleating site. Thus a large number of nuclei can be induced directly onto the surface. This study is under development with XRD measurements performed with modified fibres with higher concentration of adhesive promoter and will be discussed in details in a next paper.

The transverse tensile strength at failure obtained with CF-Z and modified fibres were reported in Figure 4. Enhancements were actually obtained on the transverse tensile strength at failure, as measured via transverse tensile strength mechanical testing of unidirectional composites, by applying the PEtI and the 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 composite with untreated fibres. 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 bad interface quality and the lack of crystallinity with low concentration of PDA. A next step will consist in further understanding the interface/interphase properties as a function of fibre treatement, and to associate this understanding with better mechanical and ageing properties.

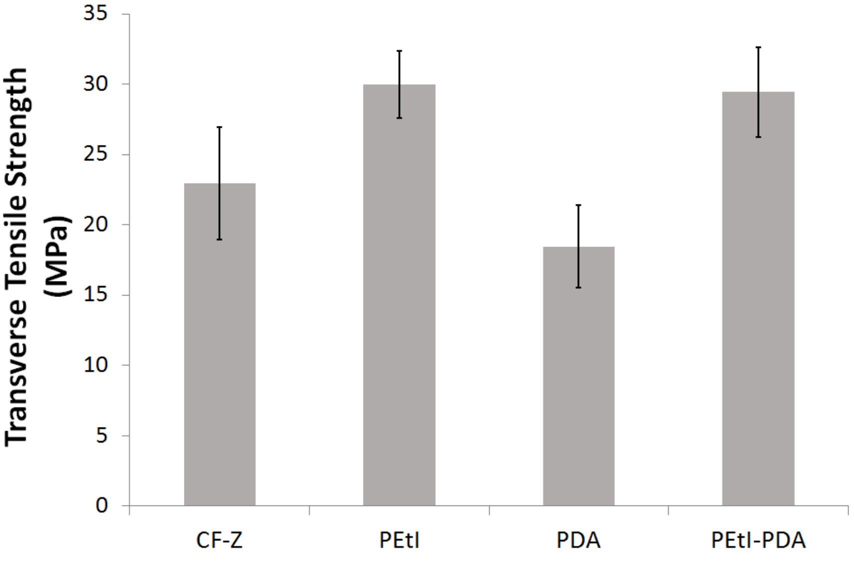

Figure 4. Transverse tensile strength of PEEK composites reinforced with the 4 studied carbon fibres.

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3. Conclusions

This study showed an innovative methodology for fibre-matrix interface compatibilization and adhesion promotion through interphase transcrystallinity which succeeded in incorporating polyelectrolyte and a mussel-inspired adhesive promoter into a thin self-assembling coating by water-based sizing procedure. Carbon fibre surface have been modified and higher crystallinity has been measured by XRD measurements. We assumed that these surface modifications induce a higher quantity of nucleation sites thanks to π-stacking interactions. Higher performance in terms of fibre/matrix compatibilization and mechanical properties of the composites in the transverse direction have been obtained. Hence these treatements processed by environmentally friendly methodology are promising for high performance composites for replacement of the traditionnal thermoset based sizings.

References

[1] A.M. Díez-Pascual, B. Ashrafi, M. Nakkakh, J.M. González-Domínguez, A. Johnston, B. Simard, M.T. Martínez, M.A. Gómez-Fatou. Influence of carbon nanotubes on the thermal, electrical and mechanical properties of PEEK/glass fiber laminates. *Carbon,* 49:2817-2833, 2011.

[2] S.F. Bartolucci, G. Mago, F.T. Fisher, E. Troiano, D.M. Kalyon. Unusual fracture surface morphology of fatigued carbon nanofiber/PEEK composites. *Carbon,* 50:2347-2374, 2012.

[3] A.M. Díez-Pascual, M. Nakkakh, M.A. Gómez, C. Marco, G. Ellis, M.T. Martínez, A. Ansón, J.M. González-Domínguez, Y. Martínez-Rubi, B. Simard. Development and characterization of PEEK/carbon nanotube composites. *Carbon,* 47:3079-3090, 2009.

[4] J. Flöck, K. Friedrich, Q. Yuan. On the friction and wear behavior of PAN- and pitch-carbon fiber reinforced PEEK composites. *Wear,* 225-229, 304-311, 1999.

[5] M. Guvendiren, P.B. Messersmith, K.R. Shull. Self-assembly and adhesion of DOPA-modified methacrylic triblock hydrogels. *Biomacromolecules,* 9:122-128, 2008.

[6] H. Lee, S.M. Dellatore, W.M. Miller, P.B. Messersmith. Mussel-inspired surface chemistry for multifunctional coatings. *Science,* 318:426-430, 2007.

[7] E. Kharlampieva, V. Kozlovskaya, S.A. Sukhishvili. Layer-by-Layer hydrogen-bonded polymer films: from fundamentals to applications. *Advanced Materials*, 21, 2053-3065, 2009.

[8] G. Crevecoeur, G. Groeninckx, Binary blends of PEEK and poly(ether imide). Miscibility, crystallization behavior, and semicrystalline morphology. *Macromolecules,* 24:1190-1195, 1991.

[9] J.E. Harris, L.M. Robeson. Miscible blends of poly(aryl ether ketone)s and polyetherimides. *Journal of applied science,* 35:1877-1891, 1988.

[10] A. Martin, D. Pietras-Ozga, P. Ponsaud, C. Kowandy, M. Barczak, B. Defoort, X. Coqueret. Radiation-curing of acrylate composites including carbon fibres: A customized surface modification for improving mechanical performances. *Radiation Physics and Chemistry,* 102:63-68, 2014.

[11] M. Bortolotti, M. Brugnara, C. Della Volpe, S. Siboni. *Journal of Colloid and Interface Science,* 336:285–297, 2009.

[12] [A.V. Franiti, E.M. Cross, R.B. Whitaker, W.W. Adams. Refinement of the structure of PEEK fibre in an orthorhombic unit cell. *Polymer,* 27:861-865, 1986.

[13] S.-L. Gao, J.-K. Kim. Cooling rate influences in carbon fibre/PEEK composites. Part 1. Crystalization and interface adhesion. *Composites: Part A,* 31:517-530, 2000.

[14] N. Ogata, H. Yasumoto, K. Yamasaki, H. Yu, T. Ogihara, T. Yanagawa, K. Yoshida, Y. Yamada. Evaluation of interfacial properties between carbon fibres and semicrystalline thermoplastic matrices in single-fibre composites. *Journal of Material science,* 27:5108-5112, 1992.

[15] K. Naito J.-M. Yang Y. Xu, Y. Kagawa. Enhancing the thermal conductivity of polyacrylonitrile- and pitch-based carbon fibers by grafting carbon nanotubes. *Carbon,* 48:1849-1857, 2010.

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