WATER-BASED SIZING DEVELOPMENT: INVESTIGATION OF THE SELF-ASSEMBLY OF NANOSCALE BIO-INSPIRED ADHESIVE PROMOTERS DEDICATED TO HIGH-PERFORMANCE COMPOSITES

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Abstract

This contribution addresses an innovative methodology for the development of water-based sizing, containing nanomaterials adhesive promoter dedicated to the surface treatment of carbon fiber, using bio-inspired dopamine molecules. Based on the supramolecular assembly of coatings obtained by adsorption and self-assembly of selected macromolecules onto solid surfaces, sizing formulations were developed via the film-making of thin polymer coatings, having tailored microstructures and properties and containing nanoscale adhesive promoters. Indeed, taking advantage of the organization of molecules arise from electrostatic interactions, polyelectrolytes were used to control the growth of polydopamine nanoparticles. The use of nano polydopamine in sizing formulation paves the way for the compatibilization and adhesion promotion at the interface of high-performance composites using their ability to attach to all kinds of materials under wet conditions. Sulfonated-poly(etheretherketone) (PEEK) was synthesized and used to control the nanomaterials size to tune sizing formulation development for high-performance applications. It is shown that a polyelectrolyte based on PEEK, can be used to manage the growth of the nano polydopamine materials efficiently. It is proved that these nanomaterials could be used to the development of high-performance water-based sizing for the surface treatment of carbon-based materials.

1. Introduction

The development of new composite materials by the use of innovative and environmentally-friendly methodologies or the use of recyclable constituents is a research area of spectacular success [1-2]. Incidentally, it is assumed that fiber-matrix interface is the key to reach high-performance in composites [3]. Interestingly, one of the challenges linked to composite's breakthrough relates to the fiber-matrix interface compatibilization, adhesion promotion, aging and improvement of damage tolerance. In this context, the properties of carbon fiber reinforced-matrix composites depend on the interphase properties which are directly induced by the structural arrangements of its constituents and the interfacial layer during the composites fabrication [4-5]. Regarding the replacement of thermoset polymer matrix by recyclable thermoplastics, an insufficient number of interfacial layer (including sizing formulation) via environmentally-friendly methodologies has been reported so far [6]. For this reason, research works were focused on the development of environmentally-friendly sizing applied via water-based processes for compatibilization and adhesion promotion at the interfacial layer of thermostable and high-performance composite materials [7].

Inspired by mussels and their capability to adhere to any kinds of substrates under wet conditions, the development of "polydopamine" (PDA) coatings emerged as bio-inspired coatings for an efficient adhesion promotion [8]. Despite its several advantages, very well described in the literature [9], PDA and its procedure deposition present some drawbacks link to the thickness of the coatings, the duration of the surface treatment and the intrinsic mechanical properties of the resulted-film. A significant challenge needs to be addressed to make this compatibilization and adhesion promotion partner a key pillar in the formulation of water-based sizing dedicated to composite applications. Our team has demonstrated that a PDA-based coating at the pitch-based carbon fiber surface, used as reinforcement material of a PEEK-composites, acted as a transcrystallinity and adhesive promoter [7]. As above-mentioned, the principal drawback of these surface treatments was the duration of the dipping. The best results were obtained with a 24 hours surface treatment duration.

In that sense, the development of a sizing formulation applying via water-based procedure in a one-step process and containing adhesive promoter such as nano polydopamine could lead to virtually promoting the fiber/matrix interface quality.

Oxidative effective strategies inducing PDA coating have been extensively studied [10], and very recently, the possibility to obtain a stable suspension of PDA has been highlighted [11]. These stable PDA-materials solutions pave the way to the development of stable suspension in water-based solutions of nano polydopamine. In this framework and inspired by the layer-by-layer (LBL) assembly via electrostatic interaction, our efforts were focused on the control of the polydopamine growth in water-based solutions using polyelectrolytes for composites applications. Indeed, the LBL technique relies upon the deposition of an oppositely charged polyelectrolyte to a previously adsorbed one, hence modifying the surface properties. Relevant reviews have been published recently detailing the LBL technique [12-13]. An 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 [14], complementary stereoregular polymers [15] and nanomaterials [16] justifying their use with polydopamine (PDA).

Thus, this contribution aims at focusing on (i) the synthesis of a polyelectrolyte from a thermostable and high-performance thermoplastic polymer namely PEEK, (ii) the control of the growth of polydopamine in polyelectrolyte solutions based on PEEK, and (iii) the surface treatment of carbon fiber with such preliminary sizing formulation. We assume that this environmentally-friendly methodology is an innovative challenge that allows the possibility to enhance fiber-matrix interfacial layer quality and propose innovative surface treatment solutions for high-performance applications.

2. Materials and Methods

2.1. Materials

2.1.1. Poly(etheretherketone). One thermostable thermoplastic polymer was used in this study to synthesize a polyelectrolyte compatible with high-performance applications. An unreinforced and uncharged poly(etheretherketone) (PEEK) was supplied in the form of a fine powder (PEEK 150XF) by Victrex.

2.1.2. Silicon wafers. Silicon wafers (type <100>) are purchased from Si-Mat. Surface deposits are performed on the polished side of silicon wafers pieces. Before surface treatments, silicon pieces were cleaned in a three-step process: (i) ultrasonic stirring in HellmanexTM III dilution (2 vol-% in deionized water) for 30 min at 50°C, (ii) flushing the polished side by a flow of deionized-water during a few seconds, (iii) drying in a flow of nitrogen.

2.1.3. Carbon fiber.

The high performance GRANOC yarn pitch-based carbon fibres YSH-50A-60Z produced by Nippon Graphite Fiber Corporation. Based on the supplier datasheet, this is a 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. The fibre is not sized (CF-Z) and used as-received.

2.1.4. Chemicals.

All chemicals were used as received. Tris(hydroxymethyl)aminomethane (THAM) (product n°: T4661, CAS: 77-86-1), dopamine hydrochloride (product n°: H8502, CAS: 62-31-7), were supplied by Sigma Aldrich. Hydrochloric acid 37% (product n°: X942, CAS: 7647-01-0) and sulphuric acid 95-98% (product n°: X944, CAS: 7664-98-9) were supplied by Carl Roth.

2.2. Methods

2.2.1. Synthesis of sulfonated-poly(etheretherketone) (S-PEEK).

The electrophilic aromatic sulfonation of the PEEK polymer was performed via the post-sulfonation method, according to the protocol used by Huang et al. [17]. The PEEK powder was dried in an oven at 120°C during 5h as recommended by the supplier. 5 g of PEEK were dissolved in 95 mL of concentrated sulfuric acid (H2SO4, 95-97wt.%, ACS) into a three-necked round bottom flask and stirred at room temperature for 1h30. Then,the solution was heated at 70°C from 2.5h to 24h. The S-PEEK polymer was slowly precipitated in ice-cold ultrapure water (18.2 MΩ.cm, 25°C). Then, the S-PEEK strands were washed thoroughly with ultrapure water until neutrality and dried at 80 °C overnight in a vacuum oven.

2.2.2. Sulfonation Degree calculation using nuclear magnetic resonance (NMR).

^{1}H nuclear magnetic resonance (NMR) spectra were obtained using an Avance III HD 600 NMR spectrometer from Bruker operating at a ^{1}H resonance frequency of 600 MHz and using a commercial double channel probe. Liquid NMR was performed with SPEEK samples dissolved in DMSO. For ^{1}H-NMR 64k complex data points were acquired using a 30° pulse and a relaxation delay of 1 second. Spectra were processed using 0.3 Hz exponential multiplication and single zerofilling. The degree of sulfonation was determined using the following equation.

$$SD\ (\%) = \left(1 - \frac{A_{H_F}}{A_{H_{AA'}}}\right) x\ 100$$

where A_{HF} the area of signal of 4 protons if non sulfonated unit and $A_{AA'}$ the area of signal of 8 protons of the other units.

2.2.3. Synthesis of polydopamine in buffer/polyelectrolyte solutions.

Ultrapure water (18.2 MΩ.cm, 25°C) used in all experiments (except for fiber 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.

Dopamine hydrochloride at 2 mg/mL was dissolved in a 50 mM tris(hydroxymethyl)aminomethane (THAM)/HCl buffer solution (pH = 8.5) containing the polyelectrolyte in the presence of dissolved O_2 acting as an oxidant. Indeed, SPEEK at 2 mg/mL were dissolved in the THAM buffer solution before adding the dopamine hydrochloride. The time t=0 is defined by the dissolution of the dopamine hydrochloride in the buffer.

2.2.4. D.L.S: Dynamic Light Scattering.

Dynamic light scattering (DLS) measurements were performed at different time intervals to estimate the hydrodynamic size (hydrodynamic diameter based on the diffusion of the particles in ultrapure water) of the PDA nanoparticles in the presence of polyelectrolytes as a function of the polyelectrolyte concentration, and oxidation duration. Additionally, visual observations of the solutions in term of color change have been performed accordingly.

2.2.5. Carbon fiber surface treatment.

Carbon fibers were immersed in polyelectrolyte solutions containing the stabilized-nano polydopamine during 10 s, and rinsed with water before any further use and characterization. Concerning surface deposit onto silicon wafers substrates (without any surface preparation), drops of the nano polydopamine mixtures were deposited onto the silicon wafers substrate and dried at room temperature.

2.2.6. 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 fiber surface, the surface treatment deposition quality and the nano dopamine particles topography. 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).

2.2.7. X-ray photoelectron spectroscopy analysis.

X-ray photoelectron spectroscopy (XPS) analyses of the carbon fibers were performed with a Hemispherical Energy Analyser SPECS (PHOIBOS 150) using a monochromatic source AlKα (1486.74 eV) as the incident radiation. Scans were collected from 0 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) by fixing the full-width-at-half-maximum (FWHM) using XPSCASA software, except for the C-C sp^2 for which the spectrum was fitted allowing some variation of the FWHM. The analytic depth of the XPS method was estimated to be 10 nm.

3. Results and Discussions

Sulfonation of the PEEK polymer was performed at 70°C to obtain SPEEK for the preparation of polyelectrolyte solutions. Figure 1 presents the time dependence of the sulfonation degree (SD) of the SPEEK. The sulfonation reaction achieves, as expected, a higher SD after about 24 hours. This material was dissolved in hot water and used for the preparation of the PEEK-based polyelectrolyte solutions.

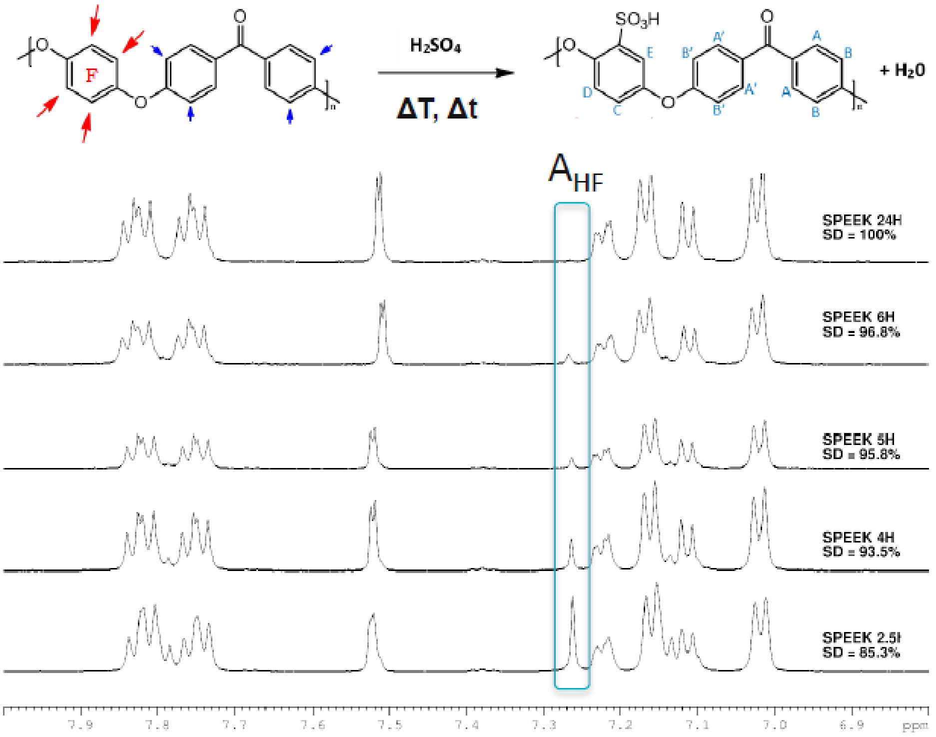

Figure 1. PEEK sulfonation reaction and ^{1}H-NMR of SPEEK as a function of the time of sulfonation.

Surface coatings based on PDA can be prepared in alkaline aqueous solution by oxidant-induced polymerization. After several minutes, the particles size is close to the micrometer (Fig.1 THAM 50 sample). Dark solutions with micrometer scale suspensions and sediments particles confirming the dopamine polymerization and aggregation are obtained. We assume that these aggregates are typically multi-layered stacks of polydopamine self-assembled via supramolecular interaction such as π- π stacking. This uncontrolled growth of these particles assures the prime of the importance of the solution aging when dedicated to surface coating. Moreover, for composite applications such as the interfacial layer improvement, the oxidant-induced polymerization process should be preferred to trigger strong interaction between dissimilar materials such as continuous fibers and a polymer matrix. However, control the growth of PDA particles is imperative for the development of sizing formulations dedicated to high-performance applications.

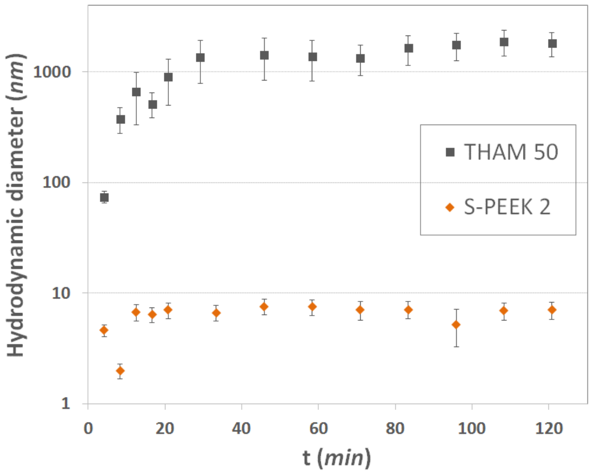

Figure 2. Hydrodynamic diameter of PDA particles (nm) in THAM buffer solution and in 2 mg/mL SPEEK-based polyelectrolyte in the buffer solution as a function of the oxidation duration (min).

Figure 2 presents the growth of PDA particles in a THAM buffer solution with or without SPEEK-based polyelectrolyte as a function of the oxidant-induced polymerization duration. The presence of polyelectrolytes allows obtaining particles of about 10 nm hydrodynamic diameter. This solution and the particle size are very stable and allow treating the surface of carbon fiber.

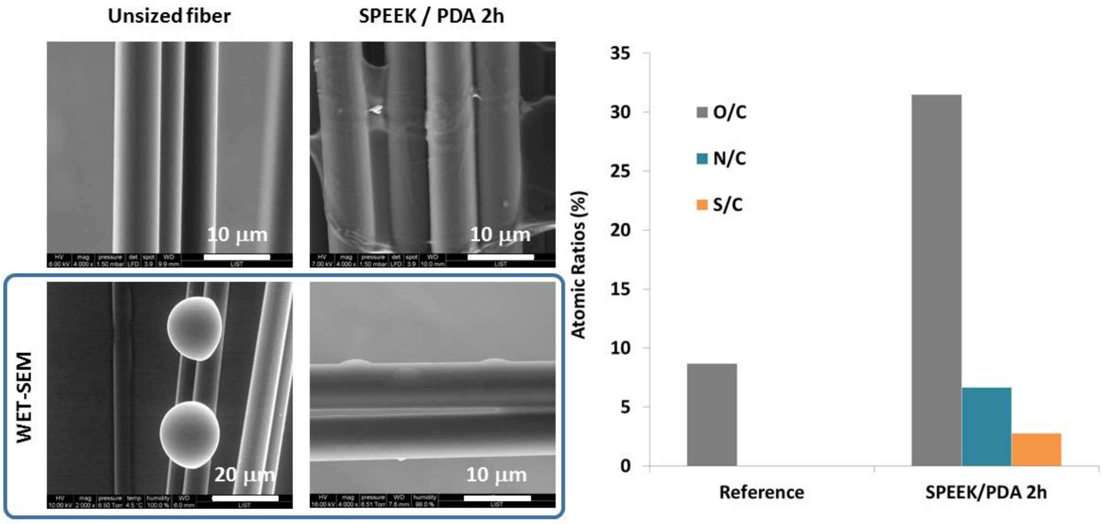

Figure 3. *Left side: SEM observations and WET-SEM experiments on unsized and coated carbon fibers with the SPEEK/PDA-buffer solution. Right side: O/C, N/C and S/C atomic ratios determined at the fibers surface calculated using XPS results.*

The carbon fibers were coated using two hours aged buffer solution containing the SPEEK/PDA partners. Figure 3 presents the SEM observations and WET-SEM experiments performed onto the unsized reference fibers and fibers treated with the abovementioned solutions. Regarding the SEM observations, one can notice the presence of a thin film onto the fiber treated with the SPEEK/PDA partners. This result highlights the film-making property of the SPEEK. Moreover, the surface coating seems to be quite homogeneous and creating a bridge between the monofilaments. Regarding the WET-SEM experiments, the drops growing onto the reference and unsized fiber have olive shape with a very weak contact area between the fiber and the drop. Regarding the treated fiber, they seem to be cover with no possibility to make growth drop onto the surface. This result highlights the modification of the chemical properties of the extreme surface after surface treatment. The XPS results (Fig. 3 right side) confirm the observations with an improvement of the O/C ratio and the identification of N and S atoms onto the fiber. These results demonstrated the possibility to treat carbon fiber with such formulation paving the way to the formulation of sizing for composite materials dedicated to high-performance applications.

4. Conclusions

This study detailed the challenging investigation of the development of bio-inspired and environmentally-friendly sizing formulation dedicated to carbon fiber reinforced high-performance thermoplastic composites. The control of the growth of a bio-inspired adhesive partner, namely polydopamine, was discussed and solutions containing stable nanoparticles of polydopamine were obtained using polyelectrolyte solutions. To this end, sulfonation reaction of a high-performance thermoplastic, poly(ether ether ketone), was performed to develop water-based solution containing a polyelectrolyte compatible with high-performance matrix. Thus, a stable water-based solution containing the SPEEK polyelectrolyte and nanoparticles of PDA was used to treat continuous carbon fiber. The surface chemistry and the quality of the coating were characterized using SEM observations, WET-SEM experiments, and XPS analysis. These characterizations demonstrated the surface modification and the possibility of using such chemistry in sizing. Finally, this methodology appeared to be very interesting and an efficient way to the development of high-performance sizing processable by an industrial process.

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