Effect of non-oxidative plasma treatments on the surface properties of poly(*p*-phenylene terephthalate) (PPTA) and poly(*p*-phenylene benzobisoxazole) (PBO) fibres as measured by inverse gas chromatography

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Abstract

It has been shown in previous works that the interfacial adhesion in PPTA- and PBO-epoxy composites can be improved by modifying the surface properties of these high-performance fibres upon exposure to non-oxidative plasma treatments. In this work, the effects developed on both types of polymer surface were examined as a function of treatment gas nature (He or N₂) and exposure time (one or four minutes) using inverse gas chromatography at infinite dilution (IGC). From the adsorption of *n*-alkanes, it has been proved that non-oxidative plasma treatments led to energetically heterogeneous surfaces in the case of PPTA, and to low-energy surfaces in the case of PBO. Nevertheless, it was proved with the 1-min plasma treatments (either under helium or under nitrogen) that chemical reactivity was enhanced on the PBO surface. Such a behaviour was ascribed to the presence of low-molecular weight oxidized materials. The mechanisms involved in surface activation of PPTA were not equivalent under He or N₂ exposure. Nitrogen plasma exposure led to a PPTA surface

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that is chemically reactive as a result of polarity enhancement. Helium plasma-treated PPTA surface was characterized by the presence of branched arrangements that intensified the number of chemical contacts onto reactive sites. Finally, for both fibre sets, if the purpose is to enhance the chemical surface reactivity, it makes no sense to increase the plasma exposure time from 1 to 4 min.

Keywords: Inverse gas chromatography (IGC); Zero coverage; High-performance fibres; Non-oxidative plasma treatments; Thermodynamic surface properties

1. INTRODUCTION

Poly(*p*-phenylene terephthalate) (PPTA) and poly(*p*-phenylene benzobisoxazole) (PBO) fibres show outstanding thermal stability [1-5] and specific tensile [6-10] properties that make them suitable reinforcements in high-tech composites. On the other hand, the remarkable chemical stability and smoothness of their surfaces [11-13] limit fibre adhesion to conventional matrices (e.g., epoxy), as shown in previous works [14-15]. In order to improve this adhesion, and thus the stress transfer between the matrix and the fibres, the surface of the fibres needs to be modified.

Cold plasma treatment provides an attractive way of tuning the surface properties of polymers in general and of polymeric fibres in particular [16-20]. Generally speaking, the effects derived from exposure to plasmas are restrained to the uppermost layers of polymeric surfaces, limiting the mechanical damage of the materials [21-24]. Several gases can be used to ignite cold plasmas to treat polymeric fibres, and the obtained results can be very different depending on gas nature. For example, the interfacial adhesion of PPTA and PBO fibres to an epoxy resin, as measured by Raman spectroscopy [25], was substantially improved when using non-oxidative (He or N₂) plasma treatments for just one minute of exposure. Such an

enhancement was superior to that obtained when using an O₂ plasma even after 4 minutes of treatment [1]. In addition, the O₂ plasma treatment of fibres led to an important adsorption of water (and consequent swelling) when exposed to ambient conditions, especially in the case of PPTA [25]. This was not the case when He or N₂ plasma treatments on the same fibres were performed [26].

This work is a follow up of these previous studies and is aimed at better understanding how different plasma treatments affect the surface properties of PPTA and PBO fibres. For that purpose, inverse gas chromatography at infinite dilution (IGC) has been used as a surface characterization technique [27]. IGC studies the interaction between polymeric fibres (adsorbents) and several probes (adsorbates), usually *n*-alkanes and polar molecules, at different temperatures [28-36]. It is important to highlight, on the one hand, the fact that the temperature range of IGC measurements carried out in this study (303-343 K, at 10 K intervals) is very close to the temperature of curing of fibre-epoxy composites (353 K for 24h) studied in previous works [37]. Therefore, surface characterization of PPTA and PBO by IGC can be considered to be representative of fibre properties in the boundary layer exposed when resin curing is performed. On the other hand, IGC measurements were accomplished using approximately one gram of sample (i.e., a macroscopic quantity). For these light fibres of micrometric diameter, the characterisation on a macroscopic scale minimises the possible impact of the structural defects inherent to fibre processing [37-40] on the final properties that are attained.

2. EXPERIMENTAL SECTION

2.1. MATERIALS

Two types of high-performance polymeric fibres were used as starting materials. In the case of PPTA, finish-free Kevlar®-29 fibres were supplied by E.I. DuPont de Nemours. The filament diameter is about 12.1 µm and its specific linear

density is 964 dtex. PBO was used in form of Zylon HM (high-modulus). Fibre yarns were supplied by Toyobo (Japan) with a proprietary finish. The manufacturer filament diameter of Zylon HM is approximately 11.2 μm , and the specific linear density is 545 dtex. Both types of fibres were used as received.

Surface treatments were carried out in a plasma reactor (Technics Plasma, model 200-G), using two different gases, He and N_2 (both 99.999% pure), for igniting the plasma. The experimental procedure was the same as that reported previously for oxygen plasma-treated PPTA and PBO fibres []. The operating conditions inside the resonant chamber were kept at 70 W power and 1 mbar pressure. The samples were disposed in the same place inside the discharge cavity in order to achieve reproducible results. The polymer fibres were plasma-treated for either one or four minutes.

PPTA and PBO fibre samples were coded with K and Z letters, respectively. Plasma-treated fibres were labelled adding He or N, depending on the treatment gas (He or N_2 , respectively) to K and Z characters. Finally, the number (1 or 4) attached to the end represents the plasma exposure time (in min) (e.g., KN1 is PPTA exposed to a nitrogen plasma for one minute).

2.2. ADSORPTION MEASUREMENTS AND PROPERTIES

Adsorption measurements by IGC were carried out as reported in previous works [,.]. Briefly, continuous plasma-treated fibre yarns (~ 1.0 g) were packed into approximately 480 mm long passivated nickel columns (2.4 mm i.d., approx. 40.0 % of packing degree). Small amounts of vapours (0.1-1.0 μL) of *n*-alkanes ($\text{C}_7\text{--C}_{12}$, >99% pure) and polar probes with different acid-base properties (benzene, nitromethane, acetonitrile, pyridine, acetone, *t*-butyl alcohol, ethyl acetate and tetrahydrofuran) were injected at the same time as methane (used as marker) into the filled column. Polar probes were denoted as follows: Bz for benzene, NM for nitromethane, ACN for acetonitrile, Py for pyridine, Ket for acetone, *t*-BuOH for *tert*-butyl alcohol, Ethyl Ac for

ethyl acetate and THF for tetrahydrofuran. All these liquids were of purity >99.0%. The acid or basic nature of the polar molecules was ranked according to the acceptor (AN) and donor (DN) number method [41,42], respectively. Table 1 lists the values corresponding to the polar probes used in this work according to reported data [-44].

Adsorption studies at infinite dilution were carried out at intervals of 10 K within the 303–343 K temperature range. At least five injections of each probe molecule were carried out at each tested temperature.

Retention times (t_R) and net retention volumes (V_N) were calculated for the different probes at different temperatures. V_N is defined as:

$$V_N = (t_R - t_m) \cdot F \quad (1)$$

where, F is the flow rate and t_m is the gas hold-up time (i.e. determined from methane elution). From these two fundamental values, several thermodynamic magnitudes of adsorption were calculated [1]: standard free energy of adsorption (ΔG_a^0), standard enthalpy of adsorption (ΔH_a^0) (or its equivalent, the standard heat of adsorption, $q_d^0 = -\Delta H_a^0$), standard entropy of adsorption (ΔS_a^0) and dispersive component of the free surface energy (γ_s^D). Specific (i.e. ΔG_a^p and ΔH_a^p) adsorption parameters were also obtained.

The method proposed by Donnet et al. [45], which considers the molecular polarizability of polar probes to reliably describe the specific interactions onto surfaces [1], has been used.

2.3. CHEMICAL CHARACTERIZATION BY DRIFTS

Diffuse reflectance Fourier transform infrared (DRIFTS) spectra were collected with a Nicolet Magna IR 560 spectrometer equipped with a high-sensitivity MCT/A detector using an accessory for diffuse reflectance. Different portions of freshly plasma-treated fibres were tested in the 4000-700 cm^{-1} spectral range. Spectra were obtained as a result of coadding 200 interferograms with a resolution of 4 cm^{-1} .

3. RESULTS

The elution peaks for *n*-alkanes from plasma-treated PPTA and PBO fibres were symmetrical for all tested *n*-alkanes; moreover, their maxima did not depend on the injected amount. This means that adsorption took place in the Henry's law regime [46,47], thus warranting the reliability of the adsorption thermodynamic magnitudes determined from these peaks.

For all studied *n*-alkane-adsorbent systems, a linear behaviour was obtained in the $(-\Delta G_a^0/T)$ vs $(1/T)$ plots as shown, for example, in Fig. 1 for *n*-nonane onto He plasma-treated PPTA and PBO fibres. The slopes of these curves give the differential heat of adsorption [48]. Table 2 collects q_d^0 data. The standard entropy of adsorption of *n*-alkanes $(-\Delta S_a^0)$ can be then calculated straightforwardly from ΔG_a^0 and q_d^0 data. Values of $-\Delta S_a^0$ are depicted in Fig. 2.

As it was found for the same polymeric fibres treated in an oxygen plasma [49], the absolute values of q_d^0 and $-\Delta S_a^0$ increased proportionally with increasing length of the *n*-alkane molecule, except in a few cases (see Table 2 and Fig. 2). Values of the differential heat of adsorption of the *n*-alkanes on KN1 fibres were slightly smaller than for the starting material, K (Table 2). This situation is also observed for the adsorption of *n*-nonane and *n*-dodecane onto ZHe1 and ZN1, which is slightly less exothermic than on the untreated fibre, Z (Table 2). Moreover, for the *n*-alkanes adsorbed on all the PBO samples, $q_d^0 < -\Delta H_{liq}^a$ (liquefaction heat), the opposite ($q_d^0 \geq -\Delta H_{liq}^a$) occurring in the case of PPTA fibres (Table 2). This means that the interaction of *n*-alkanes with PBO surfaces is weak. In previous works, such a behaviour was ascribed to a low concentration of high-energy sites (e.g. micropores and/or mesopores) and / or to the fact that adsorption takes place on the external surface of PBO [48]. In the case of the untreated fibre, this type of behaviour was related to the presence of contaminant substances [50].

The standard entropy of adsorption increases linearly (in absolute value) with increasing chain length from C8 to C12 on plasma-treated PPTA fibres, except for KN1 and KHe4 samples (Fig. 2). The behaviour of *n*-heptane slightly deviates from that trend. In the case of PBO, linearity is observed between C9 and C11. Moreover, adsorption of *n*-nonane onto ZHe1 sample renders values of $|\Delta S_a^0| < |\Delta S_{th}^0|$, where $-\Delta S_{th}^0$ are the values predicted by a theoretical estimation based on de Boer's model [49].

Fig. 3 shows the values of the dispersive component of the surface free energy for the different fibre samples at different temperatures (303-343 K). In the case of PPTA, there was a ~10% reduction in γ_s^D following plasma treatments except for sample KHe1, where the decrease was more pronounced (i.e. ~20%, see Fig. 3a). The decrease in γ_s^D suggests that the degree of molecular alignment of the PPTA chains has diminished upon plasma treatments. Accordingly, it may be assumed that the He plasma treatment for 1 min disrupts the semi-rigidity of the PPTA chains (at the upper layers) to a slightly higher extent than for the rest of PPTA plasma-treated fibres. Helium plasma treatment contributes to the formation of radicals [50-52]. The fact that γ_s^D increased for KHe4 in respect to KHe1 suggests that cross-linking reactions have taken place from radicals formed during the first minute of treatment (either between neighbouring polymer segments or with species present in the chamber discharge) [-].

Concerning PBO fibres and according to Figure 3b, the differences detected for γ_s^D between untreated and plasma-treated surfaces are not significant (i.e. within about 2%). Furthermore, the values of γ_s^D depicted in Fig. 3b are not typical of highly-crystalline polymers [1,53]. In the case of the untreated PBO fibre, whose crystallinity degree exceeds 90% [54], such a behaviour was related to the presence of contaminants onto PBO fibre surface [1].

Additional information related to the surface acid-base properties was obtained from the first momentum of peaks that were obtained working at extremely low polar probe concentrations to diminish the peak asymmetry associated with the so-called “slow kinetic processes” [55,56]. As described elsewhere [], $-\Delta G_a^p$ values were determined by the Donnet et al.’s method []. In this way, the slope of the $(-\Delta G_a^p/T)$ vs $(1/T)$ plots is the specific contribution to the standard enthalpy of adsorption (i.e. $-\Delta H_a^p$). Accordingly, $-\Delta G_a^p$ and $-\Delta H_a^p$ data obtained for polar probes are listed in Tables 3 and 4, respectively. Additionally, to simplify the analysis of this large set of data, $(-\Delta G_a^p)$ values of polar probes were graphically depicted in the Supporting Information (Fig. S1) for a given temperature, as specified in the plots. Blank spaces detected for plasma-treated PBO fibres in Table 3 are a result of the fast elution of polar probes at the tested temperature. This means that adsorbate-adsorbent interactions are weak, likely due to the presence of low-energy sites.

In previous studies [] it was concluded that it is not easy to ascertain the absolute acidic or basic nature of fresh PPTA and PBO polymeric surfaces based only on donor and acceptor numbers (Table 1), due to the simultaneous presence of slightly acidic and basic sites on their surfaces (Tables 3 and 4). Due to this singularity, several properties related to structural characteristics of molecules have been also listed in Table 1 [57,58,59].

In the case of 1 min plasma-treated PPTA fibres, $-\Delta G_a^p$ values were enhanced or practically kept unmodified over the temperature range under consideration, except for ACN and NM on KN1 (Table 3). However, the values of $-\Delta H_a^p$ were strongly dependent on the type of gas used to ignite the plasma. Thus, they increased following N_2 plasma exposure and, except in the cases of NM and THF, they decreased for KHe1 (Table 4). In particular, similar results were obtained for NM between KHe1 and K (Table 4). Concerning THF, $-\Delta H_a^p$ data were principally increased in the case of 1 min plasma treatments (by ~15% for KHe1 and ~55% for

KN1). This suggests that the number/strength of the specific interactions (determined from $-\Delta H_a^p$) is enhanced upon N_2 plasma treatment.

Going now to the 4-min plasma treatments of PPTA, one sees much more significant differences between KHe4 and KN4 samples. For KHe4, both $-\Delta G_a^p$ and $-\Delta H_a^p$ have considerably decreased regarding the untreated material (Tables 3 and 4). Particularly, the $-\Delta G_a^p$ values decreased by almost 50% in respect to those for untreated K (Table 3). This suggests that relevant chemical (as deduced from $-\Delta H_a^p$) and nanostructural (based on $-\Delta G_a^p$) modifications have taken place at the outermost layers of the fibres. Concerning KN4 sample, the specific chemical interaction parameter $-\Delta H_a^p$ increased in respect to fresh K by 40% for THF, by 23% for NM, by 14% for ACN and by 7% for *t* BuOH. In the case of Ket, no enhancement in $-\Delta H_a^p$ could be detected (Table 4). However, $-\Delta G_a^p$ increased in respect to K for Ethyl ac, *t*-BuOH, Ket and THF, whereas it decreased for Py, ACN and NM probes (Table 3).

In the case of the PBO plasma-treated fibres, no increase in $-\Delta G_a^p$ was detected following the shortest plasma exposures (either under He or under N_2) in the tested temperature range, except for Py on both samples (Table 3). Additionally, the sequence of $-\Delta G_a^p$ values for polar probes on ZHe1 and ZN1 was practically the same as that found for Z surface (ACN > NM > THF > Ethyl Ac $\approx$ *t*-BuOH > Bz). However, as deduced from $-\Delta H_a^p$ values (Table 4), interactions of polar probes were substantially favoured (by >25%) on ZHe1 and more moderately (by ~15%), on ZN1. This evidences the presence of reactive sites on both ZHe1 and ZN1 surfaces. Based on these trends, it may be concluded that the accessibility of polar probes onto specific adsorption sites of ZHe1 and ZN1 is hindered since $-\Delta G_a^p$ has not increased under infinite dilution, except for Py on both surfaces.

For the longest plasma treatments (in either He or N_2), $-\Delta G_a^p$ only increased for Py by more than 7% on ZHe4 and by 25% on ZN4 (Table 3) in regard to the fresh

material. For the rest of polar probes, $-\Delta G_a^p$ decreased moderately (by not more than 10%) in respect to Z sample (Table 3). On the other hand, $-\Delta H_a^p$ values obtained for NM (medium acid) and Py (medium base) have not decreased in respect to Z (Table 4), thus evidencing the presence of chemically reactive sites on both ZHe4 and ZN4 surfaces.

4. DISCUSSION

4.1. PPTA fibres

The IGC results for *n*-alkane adsorption on PPTA at infinite dilution are characteristic of heterogeneous surfaces []. When the number of adsorbate molecules is low, *n*-alkane adsorption takes place preferentially on high-energy sites, contributing to a proportional increase of q_d^0 and $-\Delta S_a^0$ as the carbon chain length increases [,60]. For the biggest studied *n*-alkane (i.e., C12), no proportional increase in q_d^0 and $-\Delta S_a^0$ was observed regarding the previous hydrocarbon in the series (C11) (Table 2 and Fig. 2a). This may be ascribed to size-exclusion phenomena []. The presence of micropores with dimensions comparable to the molecular dimensions of the tested *n*-alkanes would enhance q_d^0 and $-\Delta S_a^0$ values in a systematic way, except for C12.

Based on the specific interaction determined from $-\Delta H_a^p$ (Table 4), the shorter He plasma exposure favoured the interaction of KHe1 with THF probe (medium base, Table 1) by about 15%, while no significant enhancement of $-\Delta H_a^p$ could be noticed for NM (medium acid, Table 1) on KHe1. However, from the point of view of thermodynamics ($-\Delta G_a^p$), it may be confirmed that the entropic component favoured specific interactions of NM (by 12%) and *t*-BuOH (by 20%) with KHe1 (Table 3). NM and *t*-BuOH are classified as medium and strong acids, respectively (Table 1). Concerning Ket and Ethyl ac interactions, it is observed that these two amphoteric

molecules have a similar value of DN (~ 71 kJ/mol, Table 1) although $-\Delta G_a^D$ was increased to a slightly greater extent for Ethyl ac (Table 3). This behaviour could be related to AN, that is higher in the case of Ket (10.45 vs 6.27 of Ethyl ac, Table 1). Nonetheless, it was verified an increase of $-\Delta G_a^D$ for Bz on KHe1, in which case AN (0.71) is higher than DN (0.42). According to these results, it is difficult to establish the acidic or basic character of KHe1 merely based on the donor and acceptor numbers listed in Table 1. But in relative terms to K surface, it may be concluded, from THF interaction (medium base), that under the shorter He plasma exposure the number of acid sites have increased on KHe1 surface (Table 4). Likewise, as deduced from *t*-BuOH (strongly acid), NM (medium acid) and Bz (acid) probes, the access to basic sites of KHe1 was favoured from thermodynamic point of view (Table 3). This means that interactions of *t*-BuOH, NM and Bz with KHe1 were multiplied owing to the entropic component. In other words, the access to basic sites of KHe1 was favoured by surface conformation as tested under infinite dilution.

As concerns surface structure, the 1-min He plasma treatment of PPTA fibres brought about a surface with γ_s^D values that are 20% lower than those for the starting material (Fig. 3a). This suggests that the structural semi-rigidity of PPTA polymer chains in the untreated material has been disrupted either as a result of a decrease in the number of inter-chain interactions (i.e., a reduction of hydrogen bonds and/or van der Waals forces) and/or due to bond breaking along the polymer skeleton [-]. He plasmas emit VUV light, which promotes more energetic metastable species than the rest of noble gases [61], having enough energy to dissociate C-C and C-H polymeric bonds [62]. In this way, free radicals formed in the plasma could participate in chain-transfer regrouping and/or be stabilised with highly active species previously detached (small molecules and/or low-molecular-weight fragments) either via cross-linking and branching processes or after exposure to air when the treatment concludes [.,]. In this sense, rounded and narrow (10-40 nm) features detected by AFM (Fig. 4-b.1) on

KHe1 surface have been assigned to branched nanostructures []. Likewise, Fig. 6 reveals that surface functionalization took place on KHe1 since the XPS O/C and N/C atomic ratios have been enhanced in respect to K. Then, it is feasible to think that chemical and topographic transformations underwent by PPTA fibre under the shorter He plasma exposure have contributed to the proliferation of contacts to polar probes (Fig. 4-b.1). Therefore, IGC and AFM measurements support the idea that the 1-min He plasma exposure will favour the fibre-epoxy matrix adhesion through chemical and physical interactions.

Longer He plasma exposure (KHe4 sample) resulted in an increase in γ_s^D in respect to KHe1 (Fig. 3a), as well as an important reduction of the specific interactions (Tables 3 and 4). Concurrently, qualitative changes were detected by infrared spectroscopy. Taking as reference the band associated to C=C stretching vibrations (i.e. 1615 cm^{-1}), the relative intensities of bands centred at 1652 , 1538 and 1274 cm^{-1} (known as amide I, amide II and amide III, respectively) have diminished for KHe4 (Fig. 5). Particularly, there exists a significant degree of overlap around amide II and amide III modes. This means that these peaks could be not well resolved in comparison to the rest of plasma-treated PPTA fibres (Fig. 5). Likewise, the band centred at 1406 cm^{-1} , which is related to C-C stretching and contraction of the carbon-carbon bonds of the benzene ring (i.e. ring breathing mode) is broadened to some degree. These spectroscopic modifications occur in parallel with the loss of surface heteroatoms as deduced from XPS measurements. Specifically, the O/C and N/C atomic ratios decreased when the time of exposure to a helium plasma increased from one to four minutes (Fig. 6) [.,63], thus suggesting the loss of oxygen and nitrogen functionalities. This can be associated with the loss of amide groups detected by DRIFTS. From a mechanistic point of view, the kinetics of removal processes in a He plasma is slightly faster than the kinetics of branching. The progressive removal of chemically active functionalities would justify the important decrease of the chemical

affinity in KHe4 in comparison with KHe1 (Table 4). Indeed, it was observed that the average diameter of K fibres decreased by about 0.3 μm under the longer helium exposure []. In addition, it was identified by AFM the presence on KHe4 surface of clear stripes aligned along fibre axis in coexistence with occasional globular shapes (Fig. 4-b.2). This evidences that rounded and narrow domains developed on KHe1 have diminished between one and four minutes of treatment (Fig. 4, compare parts b.1 and b.2). Secondly, the anisotropy inherent to the starting material is manifestly observable on KHe4 surface (Fig. 4, compare parts a and b.2). This difference between the effects of one and four minute treatments may be justified considering that removal processes are faster than branching ones.

Fig. 6 shows that the O/C and N/C atomic ratios were practically the same for both KHe1 and KN1 surfaces although the evolution of adsorption properties was not similar. In particular, it was evidenced that q_d^0 values on KN1 were slightly lower than those obtained for K and KHe1 (Table 2). As concerns polar probes, specific interactions (measured in terms of $-\Delta H_a^p$) were particularly favoured on KN1 for THF (by 55%), followed by NM (by 18%), Ket (by 14%), ACN (by 9%) and *t*-BuOH (by 4.3%). However, based on $-\Delta G_a^p$ results (Table 3), *t*-BuOH interactions were intensified (by 15%) upon the shorter nitrogen plasma exposure over the temperature range under consideration while in the case of THF, Ket, Ethyl ac, and NM, variations of $-\Delta G_a^p$ were barely detected ($\leq 5\%$) from 313 K on (Table 3). Unlike *t*-BuOH (strong acid), it seems that the access of NM (medium acid), Ket (amphoteric) and THF (medium base) probes to reactive sites is less favoured from the entropic point of view.

Nitrogen-plasma treatments typically promote surface functionalisation either by reactions with species present in the discharge chamber (i.e. emitted from feed gas or previously detached such as small molecules or low-molecular-weight fragments) and/or as a result of breaking of several bonds so that the polymeric chain is not fully

disrupted and long-lived radicals are stabilized in contact with air [64]. In this last sense, AFM investigations demonstrated that the anisotropy inherent to the pristine PPTA fibre is preserved to a slightly greater extent on KN1 than on KHe1 (Fig. 4, parts a and c.1) []. A rupture of several bonds along the backbone chain so that the polymer skeleton is predominately retained would justify the anisotropy detected by AFM on KN1 (Fig. 4, part c.1) []. Secondly, the stabilization of long-lived radicals in contact with air may also contribute to the increases in the XPS O/C and N/C atomic ratios in respect to K surface (Fig. 6). Thirdly, the fact that oxygen and/or nitrogen may be bonded to sp^2 carbon atoms means that reactive groups (i.e. heteroatoms bonded to sp^2 carbon) cannot freely rotate. This could justify that THF (medium base), NM (medium acid), and Ket (amphoteric) interactions on KN1 were not so favoured from an entropic point of view (as deduced from Tables 3 and 4). Based on Table 1, in the cases of NM, Ket and THF, the rotational movement of functional group (i.e. $-NO_2$, $-CO-$ and half-chair conformation, respectively) is partially constrained as a result of the chemical conformation of these probes. However, the C-O bond of *t*-BuOH can freely rotate favouring polar interactions on KN1. The fact that Bz interaction was not diminished on KN1 reinforces this assumption since π - π interactions were a priori unaffected from a thermodynamic point of view (Table 3). Finally, the fact that q_d^0 values of *n*-alkanes on KN1 surface were slightly smaller than for K (Table 2) indicates that *n*-alkanes conformation (i.e. chain conformation) on KN1 is energetically less stable than on K sample. In other words, the formation of functionalised unsaturated bonds (i.e. polar bonds) would justify the conformational modifications detected on KN1 surface in respect to K sample. On the other hand, the presence of polar bonds (i.e. polarity) on KN1 surface would justify the improvement of the chemical affinity in respect to K (Table 4).

For the longer nitrogen plasma treatment, it was proved that the increase underwent by $-\Delta H_a^0$ (40%) in the case of THF (medium base) was reduced until 6% in

terms of $-\Delta G_a^p$ (Table 3). For *t*-BuOH (strong acid), the opposite trend was detected. That is to say, $-\Delta H_a^p$ was slightly enhanced (by 7%) while $-\Delta G_a^p$ was intensified at least by 25% in respect to K surface. On the contrary, the specific interactions with ACN (amphoteric), NM (medium acid) and Py (medium base) were thermodynamically disfavoured (Table 3), although $-\Delta H_a^p$ values had been slightly enhanced (at least for ACN and NM, see Table 4). On the other hand, it may be deduced that the lower or practically equal chemical affinity of THF (medium base), Ket (amphoteric) and Ethyl ac (amphoteric) on KN4 in respect to KN1 (Table 4) has been thermodynamically compensated (Table 3) by the entropic term. Particularly for THF, specific interactions on reactive sites of KN4 were even more favoured than in the case of KN1 in relation to K (Tables 3 and 4). In summary, the access of ACN (amphoteric) and NM (medium acid) onto reactive sites of KN4 was not entropically favoured unlike the rest of polar probes. Accordingly, it was proved by AFM that, between one and four minutes, the nitrogen plasma promoted a slight loss of anisotropy and generated quite an isotropic dotted surface (Fig 4, parts c.1 and c.2). The presence of such rounded structural domains on KN4 could be responsible for the thermodynamic behaviour described in the previous paragraph. Finally, comparing results of $-\Delta H_a^p$ between KN1 and KN4 (Table 4), it is proved that while *t*-BuOH (strong acid) and NM (medium acid) interactions have been barely enhanced (by 1.2 and 1.3 kJ/mol, respectively), the decrease detected for THF (medium base), was more substantial (4.1 kJ/mol). This means that, in relative terms, the electron-donor capacity of KN4 seems to be slightly higher than that of KN1. In this sense, exposure to a nitrogen plasma generated surfaces on which the N/C and O/C ratios have raised as a function of treatment time (Fig. 6). The surface functionalization on KN4 could be assigned to alcohol and amine groups since they are usually considered as common nucleophile functionalities. The fact that the electron-donor capacity of KN4 was increased in respect to KN1 (in

relative terms) could be a drawback for the adhesion to an epoxy resin due to the nucleophilic character of the hardener used as curing agent [,,].

4.2. PBO fibres

The evolution of the thermodynamic parameters obtained from the adsorption at infinite dilution of *n*-alkanes and polar probes on PBO fibres, was similar for both He and N₂ plasma-treated fibres when compared to the untreated material (Z). Also, the effect of the treatment time (1 or 4 min) is almost negligible. Moreover, as Figure S2 displays, no significant modification has been detected in the spectral range [1720-720] cm⁻¹.

All studied PBO fibre samples rendered q_d^0 values for *n*-alkanes that are very close to the *n*-alkane liquefaction heats ($-\Delta H_{Liq}^a$, Table 2). This behaviour suggests that adsorption of these non-polar probes has taken place on the external surface and/or on the nanostructure []. In this sense, it was demonstrated that q_d^0 and $-\Delta S_a^0$ increased in a linear way with increasing chain length of C9-C11 *n*-alkanes onto plasma-treated PBO fibres (Table 2 and Fig. 2b). This means that each new methyl group contributed in an equivalent way to the adsorbent-adsorbate interaction energy as the *n*-alkane chain size increased [65]. However, this trend was not followed for the adsorption of *n*-octane (C8) and *n*-dodecane (C12). Particularly for *n*-octane, q_d^0 (listed in Table 2) was more favoured (higher absolute value) than that calculated from the linear fit of experimental q_d^0 values (Fig. S3) vs carbon atom number of *n*-alkane (between C9 and C11). As a result, the difference between experimental (C₈) and calculated (C₈^{*}, Table 2) values was higher (in absolute value) by about 4 kJ/mol for helium plasma-treated PBO surfaces (ZHe1 and ZHe4), and by 3 kJ/mol for nitrogen plasma-treated PBO ones (ZN1 y ZN4) (Table 2).

Previous works about functionalized alkanes on graphite [66,67] or mixtures of normal alkanes on hexagonal boron nitride [68] revealed that such molecules lie flat

onto those surfaces. Considering that q_d^0 was more favoured for C8 than expected (Table 2), it is feasible to think that C8 interacts with its energetically more stable rotational isomer (or zig-zag conformation or pleated chain).

Concurrently, the presence of low-molecular-weight oxidized materials (LMWOM) may justify why q_d^0 was practically the same in plasma-treated PBO samples than in the starting material (Table 2). LMWOM are usually made up from highly oxidized functional groups (e.g., carboxyl, carbonyl or hydroxyl) and can be dissolved in polar solvents [69]. Moreover, the fact that q_d^0 data were very similar to $-\Delta H_{liq}^a$ (Table 2) suggests that adsorption interactions took place on external surfaces (i.e., onto LMWOM) [,,]. Accordingly, the formation of PBO plasma-treated surfaces rich in LMWOM would explain: (i), the fact that the O/C atomic ratio of PBO plasma-treated fibres was higher than for the untreated sample (Fig. 6); and (ii), the increase of chemical affinity observed for polar probes onto plasma-treated PBO surfaces (Table 4).

In this last sense, $-\Delta H_a^p$ was noticeably augmented (> 60%) for Bz (acid) and *t*-BuOH (strong acid) on ZHe1 in regard to Z (Table 4). However, the access onto basic sites was apparently hindered from the thermodynamic point of view (Table 3). The increases of $-\Delta G_a^p$ and $-\Delta H_a^p$ underwent by Py (medium base) were more moderate (13 and 20%, respectively) in the tested temperature range (Tables 3 and 4). Based on its chemical structure (Table 1), Py could act by establishing π - π interactions owing to its aromatic nature, or as a nucleophile through the lone pair of electrons of the nitrogen atom. Concerning ZN1 surface, the interaction of Py (medium base) was favoured in terms of both $-\Delta G_a^p$ and $-\Delta H_a^p$ by 14 and 30%, respectively (Tables 3 and 4). Secondly, the increase of $-\Delta H_a^p$ for NM and ACN (Table 4) was more moderate on ZN1 (15%) than on ZHe1 (30%). This means that the number of acid and basic sites (deduced from Py, NM and ACN interactions, Table 3) has raised on ZN1 in respect to Z. Likewise, specific interactions of NM (medium acid)

and ACN (amphoteric) were more intense on ZHe1 than on ZN1 (Table 4). However, the opposite trend was detected for Py (medium base). Accordingly, this behaviour could be justified considering that the number of basic sites is higher on ZHe1 than on ZN1. Despite these differences (detected in terms of $-\Delta H_a^p$, $-\Delta G_a^p$ values corresponding to NM (medium acid), ACN (amphoteric) and Py (medium base) were very similar on both ZHe1 and ZN1 surfaces (Table 3). This means that the entropic component (i.e. surface conformation) determines the access of polar probes onto reactive sites of ZN1.

In this sense, structural differences obtained by AFM disclosed additional information (Fig. 7). ZHe1 surface was characterized by a disrupted arrangement made up of elongated domains along fibre axis. Therefore, the anisotropy inherent to the starting material was partially retained (Fig. 7, compare parts a and b.1) []. Regarding ZN1, prominent globular areas were detected, about 60-80 nm width (Fig. 7, compare parts a and c.1) []. Comparing the IGC results obtained for polar probes on ZHe1 and ZN1 (Tables 3 and 4) leads one to assume that the globular morphology of ZN1 favours the contacts of polar probes on reactive sites of ZN1.

Increasing the exposure time from 1 to 4 min under either He or N₂ plasma for PBO fibres, no enhancement of specific adsorption parameters was found except for Py that increased under nitrogen exposure (Table 3). For both plasmas, this trend is accompanied by a slight decrease of oxygen functionalities and an increase of nitrogen ones (Fig. 6). However, the trend described for ZN1 *vs* ZHe1 (i.e. the proportion of acid sites being slightly higher on ZN1 than on ZHe1) is also detected between ZN4 *vs* ZHe4 surfaces. This statement is based on NM (medium acid) and Py (medium base) interactions. The chemical affinity of Py was practically equal on both ZHe4 and ZN4 surfaces (~20.7 kJ/mol, Table 4). However, whereas a slight increment took place for NM on ZHe4 in respect to Z, no increase was noticed on ZN4 (Table 4). AFM revealed the existence of continuous arrangements (stripes) well

aligned along the fibre axis on ZHe4 (Fig. 7, part b.2). One could also notice the presence of disrupted structural domains with different shapes (spherical, rounded or asymmetric) in ZHe4. In particular, one may observe in Fig 7-b.2 the splitting of one longitudinal structure into two. The width of both irregular shapes and linear arrangements (determined in transversal direction with respect to the fibre axis) oscillated between 20-150 nm. Cross-linking reactions between polymer surface and low-molecular weight oxidized materials and/or small molecules previously detached in the discharge chamber would justify the detection of the asymmetrical structures found on ZHe4. In the particular case of ZN4, AFM evidenced the proliferation of rounded shapes [] whose dimensions were narrower than on ZN1 by almost one order of magnitude (Fig. 7, compare parts c.1 and c.2). In this sense, previous investigations demonstrated that surface functionalization on ZN4 was related to rigid crosslinked structures where nitrogen species are forming part of polycondensed systems [].

In summary, AFM investigations support the development of structural domains with a preferential orientation along fibre axis under He plasma treatments and with globular or rounded arrangements under N₂ ones.

5. CONCLUSIONS

IGC measurements have shown that non-oxidative plasma treatments (either under He or under N₂) gave place to energetically heterogeneous surfaces in the case of PPTA. High-energy sites were detected on plasma-treated PPTA fibres, but not on plasma-treated PBO fibres. This was ascribed to the presence, in the latter materials, of low-molecular weight oxidized materials that contributed, in general, to enhance the chemical affinity of polar probes. Likewise, the acid character was slightly higher for both nitrogen plasma-treated PBO surfaces than for the respective helium plasma-treated ones. The 1-min exposure to both He and N₂ plasmas contributed to generate reactive PPTA surfaces. In the case of KN1 sample, surface activation was improved

owing to an increase of surface polarity. Concerning KHe1, the globular morphology detected on the surface seems to have promoted the interactions of polar probes on reactive sites (under infinite dilution). For the longer exposure time (4 min), no surface activation could be detected on KHe4 as a result of the removal of polymeric material at the uppermost layers. The longer nitrogen plasma treatment produced a slightly more basic surface in comparison to KN1.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge financial support from the European Union – project Growth GRD-CT-2002-00747, from the 3rd PRI Asturias – project PB-EXP01-06–, from the Spanish MEC –project CTQ2005-09105-c04-02– and from the CSIC–PIE –project 201880E048. Special thanks are due to Toyobo (Japan) and DuPont de Nemours Int. (Switzerland) for supplying the PBO and PPTA samples, respectively.

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510 FIGURE CAPTIONS

511 **Figure 1.** Variation of $(\Delta G_a^0/T)$ with $(1/T)$ for the adsorption of *n*-nonane on helium plasma-
512 treated PPTA (a) and PBO (b) fibres. Data for K and Z samples (taken from [27] and [29],
513 respectively) are included as reference. The slopes of the linear fits correspond to the differential
514 heats of adsorption ($R^2 > 0.9997$).

515 **Figure 2.** Standard entropies of adsorption ($-\Delta S_a^0$) of *n*-alkanes on the different PPTA (a) and
516 PBO (b) samples and standard entropy of adsorption ($-\Delta S_{th}^0$, at 303 K) calculated according to
517 de Boer's model [49]. Data for K and Z samples were taken from [27] and [29], respectively.

518 **Figure 3.** Values of γ_s^D of plasma-treated PPTA (a) and PBO (b) samples, at different temperatures.
519 Data for K [27] and Z [29] are also included as reference. Values at 293 K (red arrow) were obtained by
520 extrapolation of data measured in the temperature range [303–343] K.

521 **Figure 4.** AFM micrographs ($1 \times 1 \mu m^2$ areas) of fresh K (a), KHe1 (b.1), KHe4 (b.2), KN1 (c.1) and KN4
522 (c.2) PPTA fibres.

523 **Figure 5.** DRIFTS spectra of fresh (K) and plasma-treated PPTA (KHe1, KHe4, KN1 and KN4) fibres.

524 **Figure 6.** O/C and N/C atomic ratios corresponding to XPS data previously reported for PPTA (left)
525 [22,25,63] and PBO (right) [23,24,29,63] fibres. Kth and Zth are theoretical atomic ratios that have been
526 calculated from their respective monomeric units.

527 **Figure 7.** AFM micrographs ($1 \times 1 \mu m^2$ areas) of fresh Z (a), ZHe1 (b.1), ZHe4 (b.2), ZN1 (c.1) and ZN4
528 (c.2) PBO fibres.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7