Surface modification of high-performance polymeric fibers by an oxygen plasma. A comparative study of poly(*p*-phenylene terephthalamide) and poly(*p*-phenylene benzobisoxazole)

K. Tamargo-Martínez *, A. Martínez-Alonso, S. Villar-Rodil, J.I. Paredes, M.A. Montes-Morán, J.M.D. Tascón

Instituto Nacional del Carbón, INCAR-CSIC, Apartado 73, 33080 Oviedo, Spain

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ABSTRACT

Poly(*p*-phenylene terephthalamide) (PPTA) and poly(*p*-phenylene benzobisoxazole) (PBO) fibers were exposed to an oxygen plasma under equivalent conditions. The resulting changes in the surface properties of PPTA and PBO were comparatively investigated using inverse gas chromatography (IGC) and atomic force microscopy (AFM). Both non-polar (*n*-alkanes) and polar probes of different acid–base characteristics were used in IGC adsorption experiments. Following plasma exposure, size-exclusion phenomena, probably associated to the formation of pores (nanoroughness), were detected with the largest *n*-alkanes (C_9 and C_{10}). From the adsorption of polar probes, an increase in the number or strength of the acidic and basic sites present at the fiber surfaces following plasma treatment was detected. The effects of the oxygen plasma treatments were similar for PPTA and PBO. In both cases, oxygen plasma introduces polar groups onto the surfaces, involving an increase in the degree of surface nanoroughness. AFM measurements evidenced substantial changes in the surface morphology at the nanometer scale, especially after plasma exposure for a long time. For the PBO fibers, the outermost layer – contaminant substances – was removed thanks to the plasma treatment, which indicates that this agent had a surface cleaning effect.

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1. Introduction

Poly(*p*-phenylene benzobisoxazole) (PBO) has deserved considerable attention in both basic and applied areas of research on high-performance materials [1–8]. PBO belongs to the new class of high-performance rigid-rod materials. The repeat chemical structure is as follows:
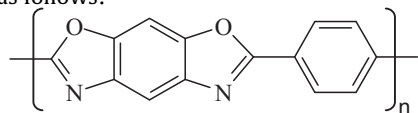
This chemical structure confers to PBO an excellent thermal stability [9], chemical resistance and specific stiffness and strength [10]. Therefore, PBO provides great potential applications such as reinforcing fibers for composites (FRC). Nevertheless, PBO fiber-reinforced composites generally show a poor interfacial adhesion between untreated fibers and matrix resin [11], due to the inert nature of the PBO fiber. In consequence, as the load transfer through the interface is related to the interfacial interactions, it is necessary to improve the interfacial bonding or adhesion by increasing either the number of interactions or the bond strength. In this sense, several surface modification methods have been proposed for some polymeric fiber materials, including chemical (electrolytic oxidation, coupling agents) [12,13,15–20], or plasma treatments [14,21]. One peculiar advantage of the low-pressure plasma treatment is that it can be used to modify the chemical and physical states of a surface without altering the bulk fiber properties [22].

Therefore, the knowledge of the fiber surface energetics is essential for the specific design of interfaces since the adhesion is determined by chemical and physical structures of both, fiber and matrix. Inverse gas chromatography (IGC) at infinite dilution is a straightforward and very sensitive technique for the thermodynamic characterization of polymer surfaces [23] since it is versatile, robust, user-friendly and inexpensive. In a previous work, a number of differently solvent-scoured commercial PBO fiber samples have been studied using IGC [24] in order to establish the efficiency of the different cleaning solvents and determine the thermodynamic properties of the pristine PBO surface.

In this work, the effects of oxygen plasma treatment on the surface characteristics of PBO fibers were investigated through the study of their interaction with both non-polar and polar probe molecules using IGC. For comparison, samples of oxygen plasma-

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* Corresponding author. Tel.: +34 985119090; fax: +34 985297662.
  E-mail address: katia@incar.csic.es (K. Tamargo-Martínez).

Table 1
Sample codes.

Plasma treatment conditions			Fibers	
Power	Gas	Time	PPTA	PBO
70 W	O_2	1 min	KO 1	ZO 1
		4 min	KO 4	ZO 4

treated poly(p-phenylene terephthalamide) (PPTA) fibers were prepared and characterized under identical experimental conditions. The results obtained with PPTA are taken as a reference since some previous knowledge is available on the surface thermodynamics of this material [25]. As a complementary technique, atomic force microscopy (AFM) was employed to monitor the changes in surface structure induced by the oxygen plasma treatments on both polymeric fibers. The objective was to determine whether there is a relationship between topographic properties of the fiber surfaces and the thermodynamic magnitudes determined by IGC.

2. Experimental

2.1. Materials

Two types of polymeric fibers have been used as starting materials for this work.

PPTA: Finish-free Kevlar®-29 fibers – supplied by E.I. DuPont de Nemours, which were used as received (referred as sample K). The yarn is made of 1000 filaments of ∼12.1 μm diameter and the specific linear density is 964 dtex.

PBO: Zylon® HM fiber yarn – supplied by Toyobo (referred as sample Z). The manufacturer filament diameter was ∼11.2 μm and the specific linear density of the yarns was 545 dtex.

For PPTA and PBO fibers, the average molecular weight is very similar each other. It is of the order of 20,000–40,000 depending on the processing parameters which are unknown in our case.

Plasma treatments were carried out in a plasma processor, Technics Plasma 200-G. An oxygen (99.9990% pure) gas flow was introduced so as to maintain a pressure of 1.0 mbar inside the reaction chamber. Fresh PPTA and PBO were treated at 70 W of microwave (2.45 GHz) plasma power, during one or 4 min, respectively. Reference codes for the plasma-treated samples are given in Table 1.

2.2. Methods

2.2.1. Thermodynamic parameters and adsorption measurements

The fundamental parameter measured by IGC is the net retention volume V_N defined as the volume of carrier gas required to elute a given zone of solute vapor [26]. This parameter is estimated, for a given probe, from the measured retention time, t_R:

$$V_N = (t_R - t_m) \cdot F \tag{1}$$

where F is the flow rate and t_m is the gas hold-up time.

V_N is directly related to the partition coefficient for the solute surface K_s [27] according to Eq. (2):

$$V_N = K_s A \tag{2}$$

where A is the total surface area of the stationary phase. If the adsorption experiments are carried out under very low adsorbate concentration, i.e., in the limit of infinite dilution, the interactions between adsorbate molecules are negligible and the adsorption is described by Henry's law and K_s is then directly proportional to the Henry's constant [27]. The previous equation is valid as long as the bulk absorption of the probe in the stationary phase is negligible

[26]. Thermodynamic functions of the adsorption process at infinite dilution can be thus calculated from K_s [28]:

$$\Delta G_a^0 = RT \ln V_N = RT \ln \left(K_s \frac{p_{s,g}}{\pi_s} \right) \tag{3}$$

$$q_d^0 = \left[\frac{\partial(\Delta G_a^0/T)}{\partial(1/T)} \right]_p = \left[\frac{\partial(\ln K_s)}{\partial(1/T)} \right]_p \tag{4}$$

where $p_{s,g}$ is a reference pressure having a value of 1 atm (101 kN m^{-2}) and π_s is the two-dimensional pressure of the adsorbed state, 0.338 mN m^{-1} [29]. From the adsorption standard free energies and standard enthalpies, adsorption entropies can be calculated straightforwardly according to Eq. (5):

$$-\Delta S_a^0 = \frac{q_d^0 - \Delta G_a^0}{T} \tag{5}$$

Selection of the probes to be used in IGC studies of solid surfaces depends on the type of information that should be gathered. In the case of high performance fibers, it is interesting to determine parameters related to their surface microstructure, such as textural and energetic parameters. Also, information related to their surface chemistry, i.e., acid–base properties is of key relevance.

For the first purpose, there is a well-established experimental procedure consisting of the elution of linear n-alkanes through the stationary phase. According to the early concepts of Riddle and Fowkes on the nature of the interaction at interfaces, n-alkanes are only capable of dispersive interactions [30]. Based on this, Dorris and Gray [31] proposed a calculation method in which the difference in the free energy of adsorption of two n-alkanes with succeeding values of $n(-\Delta G_a^{CH_2})$ was used to calculate the dispersive component of the surface free energy of the stationary phase, γ_s^D:

$$\gamma_s^D = \frac{1}{4N_A^2 a_{CH_2}^2} \frac{(-\Delta G_a^{CH_2})^2}{\gamma CH_2} \tag{6}$$

where N_A is Avogadro number, a_{CH_2} is the area of a methylene group (0.06 nm^2) [31], and γ_{CH_2} is the surface tension of ideal liquid polyethylene; the latter parameter is computed as a function of temperature as follows:

$$\gamma_{CH_2}[mJ/m^2] = 35.600 - 0.058[T(\circ C) - 20] \tag{7}$$

where T is the temperature in °C.

On the other hand, if polar probes are injected into the column instead of n-alkanes, the adsorption of the adsorbate molecules on the stationary phase involves not only dispersive but also specific interactions [32–35]. Thus, $-\Delta G_a^0$ is assumed to be the sum of two independent contributions accounting for both types of molecular interaction:

$$\Delta G_a^0 = \Delta G_a^D + \Delta G_a^p \tag{8}$$

The additional contribution $-\Delta G_a^p$ can be estimated in different ways by the elution of polar probes (at infinite dilution conditions) covering a wide range of acid–base character. The method proposed by Donnet et al. [36], which takes into account the molecular polarizability of the different adsorbates, seems to be particularly reliable with regard to the specific (acid–base) interactions on relatively high energetic surfaces. According to such method, the dispersive component of the free energy of interaction of any probe with a surface at infinite dilution conditions can be, at a first approximation, estimated from a simplified version of the London equation:

$$-\Delta G_a^0 = K(h\nu_s)^{1/2}\alpha_s \cdot (h\nu_L)^{1/2}\alpha_L + C \tag{9}$$

where K and C are constants, h is the Planck's constant, ν_s and ν_L are characteristic electronic frequencies corresponding to solid (S)