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Surface Characteristics of Activated Carbons Obtained by Pyrolysis of Plasma Pretreated PET

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Activated carbon materials have been prepared by pyrolysis of plasma pretreated recycled PET. The obtained carbon materials have been texturally characterized by N₂ (77 K) and CO₂ (273 K) adsorption. Atomic force microscopy (AFM) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) have been used to analyze the surface of the treated precursors. Carbon materials obtained by He, N₂, and CO₂ plasma pretreatments (4 min) of the precursor and subsequent pyrolysis have shown a higher adsorption capacity than the corresponding chars (untreated pyrolysed PET). This effect seems to be related to the elimination by the plasma treatments of low-molecular-weight products in the precursor, which are responsible for the formation of amorphous carbon deposits during the carbonization that blocks the porosity. Longer periods of treatment (15 min) do not favor the opening of the microporosity because cross-linking reactions in the precursor producing high molecular weight deposits prevail. The development of porosity is less relevant if oxygen plasma is used, as a considerable amount of oxygen functionalities are also formed. These groups can decompose during pyrolysis producing the above-mentioned amorphous carbon deposits. The textural characteristics of the carbon materials obtained after 4 min of plasma treatment on the precursor are very similar to those obtained after 4 h of CO₂ (1073 K) activation of the same char. Therefore, this method can be an alternative to avoid the burnoff and high energy cost of the activation step.

Introduction

The preparation of activated carbons is frequently carried out by pyrolysis of lignocelulosic precursors. The process involves heat treatment of the raw material in an inert atmosphere (usually He, N₂, or Ar) at high temperatures. The products obtained by this type of procedure have a polymodal distribution of pores, particularly in the range of micropores (width ≤ 2 nm) because of the heterogeneous structure of the precursor. This range of microporosity is particularly important in the adsorption and catalytic behavior of active carbons. Narrow micropore size distributions can be obtained if a precursor with an ordered and homogeneous molecular structure is used as the raw material. Organic polymers have this type of structure which make them very suitable to produce carbon materials with narrow micropore distributions. Among them, many organic polymers and copolymers such as resins of polystyrene sulfonic acid, furfuryl alcohol, phenol formaldehyde, acetone–furfural, or furfuryl alcohol–phenol copolymer are used.¹ Nevertheless, these precursors are very expensive, which is a drawback. An alternative to these is to use waste organic polymers. Poly(ethylene terephthalate) (PET) is a major urban polymer waste because it is used for soft drink bottles. Although a significant part of the waste PET is recycled, there is an important amount which is not and it could be used for the preparation of carbon materials.

An important aspect in the preparation of active carbons is the activation process after carbonization of the raw materials.

This is necessary because after carbonization the microporosity is scarcely developed or the porous network has constrictions which partially hinder the adsorption.² For this reason, it is very frequent to activate the char by physical or chemical treatments. The former usually consists of heat treatment of the char at high temperatures under activating agents such as CO₂, water, oxygen, and so forth.² The latter involves treatment of the char with chemical substances such as H₂O₂, (NH₄)₂SO₄, ZnCl₂, H₃PO₄, HNO₃, and so forth and further heat treatment in an inert flow.^{2–4}

In this paper, we report the preparation of activated carbons by carbonization of plasma-treated PET. Plasma treatment prior to pyrolysis can be an alternative to char activation. It is known that an important effect of the physical and chemical activation processes consists of the elimination of the amorphous carbon which is deposited at the entrance of the micropores. The use of plasma treatments prior to carbonization could partially eliminate the volatile matter which is the precursor of the amorphous carbon deposits.

Experimental Section

The raw material for the preparation of the carbon materials was wasted PET from mineral water drinking bottles. The following characteristics were determined in the CIC (University of Granada): glass transition temperature (by DSC) $T_g = 350$ K, degree of crystallinity (from DSC), $X_c = 24\%$, and melting temperature (in a melting point apparatus) $T_m = 523$ K. The carbonization was carried out by flowing nitrogen (100 cm³ min⁻¹) through a tubular furnace (6 cm i.d.) at 800 and 950 °C. The carbonization temperatures were selected on the base

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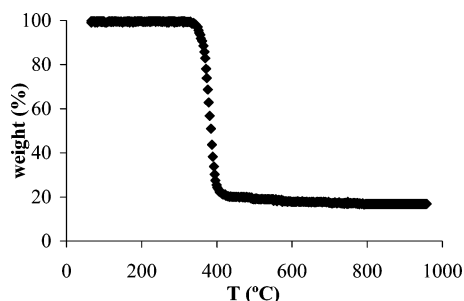


Figure 1. TG profile of PET in nitrogen flow at 5 °C min⁻¹.

of the TGA profile of Figure 1. The heating rate was 5 °C min⁻¹, and the soak time was 1 h. These experimental conditions were used to carbonize PET and plasma-treated PET. The chars obtained from the former are labeled C800 and C950, where the number refers to the pyrolysis temperature. The burnoff in the two cases was 81%.

The plasma treatments of PET prior to carbonization were carried out in a microwave apparatus (Technics Plasma GmbH). For this purpose, square pieces (1 × 1 cm) of PET were placed in the chamber and they were outgassed for 5 min to a pressure of less than 0.266 mbar. Then the gas used to produce plasma was admitted up to a pressure of 1.33 mbar and flowed for 5 min. The power supplied to produce the plasma was 200 W, and the PET samples were exposed to this for two periods of time: 4 and 15 min. Four different gases were used as the plasma source: helium, nitrogen, carbon dioxide, and oxygen. The PET samples obtained after the plasma treatments are labeled PA-t, where P refers to the raw material (PET), A is the gas used to produce plasma, and t is the period of plasma treatment (4 or 15 min). After the plasma treatments, the PET samples were carbonized at the experimental conditions already described. The carbons so obtained are labeled PA-t-XXX, where P, A, and t have the same meaning as before and XXX is the carbonization temperature (800 or 950 °C). For instance, the sample labeled PHe-15 refers to the PET sample obtained after helium plasma treatment for 15 min, whereas the name PHe-15-800 refers to the carbon obtained after carbonization of PHe-15 at 800 °C. As it will be explained in the Results and Discussion section, a separate experiment was carried out with two of the PET samples which were treated with nitrogen plasma. After the treatment, they were washed with an 2-propanol-cyclohexane mixture, dried, and then carbonized at 800 °C.

The modifications induced on the PET by the plasma treatments were studied by atomic force microscopy (AFM) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). AFM experiments were carried out in the tapping mode of operation under ambient conditions with a Nanoscope Multimode IIIa, from Digital Instruments. Rectangular cantilevers with a spring constant of ~40 Nm⁻¹ and resonance frequencies around 250 kHz were employed. The nominal tip radius of curvature of these probes was 5–10 nm. To reduce sample disturbance to a minimum and track the sample surface topography accurately, scanning was performed under light tapping conditions, that is, with a set-point to free amplitude ratio of about⁵ 0.9.

DRIFTS spectra of PET samples were obtained in a Nicolet Magna IR560 spectrometer using a high-sensitivity MCT/A detector. Spectra shown are the result of co-adding 400 interferograms obtained at a resolution of 2 cm⁻¹. The textural characteristics of the chars were determined by nitrogen and carbon dioxide adsorption at 77 and 273 K, respectively. The

TABLE 1: Textural Characteristics of the Samples Obtained by Carbonization of PET (C800 and C950) and by Carbonization of Helium Plasma-Treated PET

| | N ₂ adsorption | | CO ₂ adsorption | |
|------------|--|--|--|---|
| | W_{01} (cm ³ g ⁻¹) | S_{N_2} (m ² g ⁻¹) | W_{02} (cm ³ g ⁻¹) | S_{CO_2} (m ² g ⁻¹) |
| C800 | 0.040 ± 0.002 | 60 ± 6 | 0.230 ± 0.005 | 656 ± 13 |
| PHe-4-800 | 0.190 ± 0.001 | 441 ± 11 | 0.250 ± 0.003 | 712 ± 7 |
| PHe-15-800 | 0.130 ± 0.001 | 301 ± 5 | 0.210 ± 0.003 | 577 ± 7 |
| C950 | 0.050 ± 0.001 | 142 ± 8 | 0.240 ± 0.005 | 686 ± 13 |
| PHe-4-950 | 0.100 ± 0.001 | 228 ± 3 | 0.250 ± 0.003 | 715 ± 8 |
| PHe-15-950 | 0.100 ± 0.001 | 219 ± 1 | 0.240 ± 0.002 | 669 ± 5 |

experimental setup is a standard glass-made volumetric apparatus which allows us to measure the nitrogen adsorption up to a relative pressure $P/P_o = 1$. The carbon dioxide adsorption can be measured up to a relative pressure $P/P_o = 0.03$. Before the adsorption measurements, the samples were outgassed at 140 °C under dynamic vacuum (10⁻⁵ mbar) overnight.

Results and Discussion

The textural characteristics obtained from the adsorption isotherms of the C800 and C950 and of the samples pretreated with helium plasma are collected in Table 1. W_{01} is the volume of pores accessible to nitrogen as obtained by using the Dubinin–Radushkevich (DR) equation, and S_{N_2} is the surface area obtained by applying the BET equation to the nitrogen adsorption data. W_{02} and S_{CO_2} are the micropore volume and the surface area determined by the DR equation applied to the carbon dioxide adsorption isotherms. The BET equation was applied in the usual range, $P/P_o = 0–0.1$, while the DR was used in the range the data fit a straight line which depends on the porous network.

The textural characteristics of the chars C800 and C950 have been already reported⁶ although they are included in Table 1 to help the discussion. It is relevant from these data that for these two chars the adsorption volumes and the surface areas measured by CO₂ adsorption (W_{02} and S_{CO_2}) are much larger than those measured by nitrogen adsorption (W_{01} and S_{N_2}). This means that carbonization at 800 and 950 °C produces a micropores network having constrictions which partially hinder the nitrogen access.^{6,7} Nevertheless, carbon dioxide can access this porosity because it is adsorbed at higher temperature than nitrogen (273 and 77 K, respectively). As a consequence, the kinetic energy of the former is much larger in such a way that it can overcome those constrictions.

The nitrogen adsorption isotherms of the samples obtained by carbonization of helium plasma-treated PET at 800 °C (PHe-4-800 and PHe-15-800) are compared with that of the char C800, in Figure 2a. The same comparison for the samples carbonized at 950 °C is shown in Figure 2b. It is observed that the treatment of PET with helium plasma for 4 min produces a large increase in the nitrogen adsorption capacity, W_{01} , of sample PHe-4-800 compared with the char C800. This increase is less relevant when the plasma treatment extends up to 15 min (sample PHe-15-800). When the carbonization temperature is higher (950 °C), an increase in nitrogen adsorption of the samples obtained by pretreatment with helium plasma is also evident, although smaller than at 800 °C. Nevertheless, the effect of the period of plasma treatment (4 or 15 min) on nitrogen adsorption is negligible for the samples carbonized at 950 °C.

The comparison of the CO₂ adsorption isotherms for the same samples is shown in Figure 3. The helium plasma pretreatments do not produce differences on the carbon dioxide adsorption,

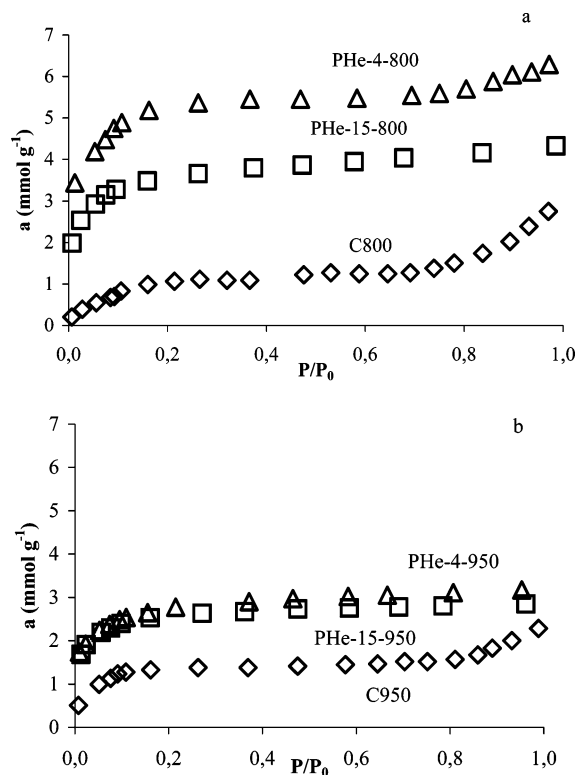


Figure 2. Nitrogen adsorption isotherms of carbons obtained after direct carbonization of PET, C800, and C950 and of carbons obtained from PET pretreated with helium plasma for 4 min. Temperature of carbonization: (a) 800 and (b) 950 °C.

as the isotherms are almost coincident, in contrast to the differences in nitrogen adsorption shown in Figure 2.

As can be expected from these isotherms, the helium plasma treatments prior to carbonization produce an important increase in W_{01} and S_{N_2} in all cases (Table 1). This is more relevant when the heat treatment is carried out at 800 °C. Moreover, the highest increase is obtained at this temperature when the period of plasma treatment is 4 min. When the pyrolysis is carried out at 950 °C, there is also an increase in the textural characteristics, W_{01} and S_{N_2} , but the influence of the period of plasma treatment (4 or 15 min) seems to be irrelevant (samples PHe-4-950 and PHe-15-950). Nevertheless, the effect of the helium plasma treatment (samples PHe-4-800, PHe-15-800, PHe-4-950, and PHe-15-950) in the textural characteristics measured by CO₂ adsorption (W_{02} and S_{CO_2}) seems to be negligible if those characteristics are compared with those of the chars, C800 and C950. Therefore, N₂ adsorption parameters become closer to those measured by CO₂ adsorption. This means that the consequence of the plasma treatment prior to the carbonization is the partial elimination of the constrictions which appear in the micropore networks of C800 and C950. These constrictions are produced by amorphous carbon deposits formed by low-molecular-weight products degradation during the carbonization process.^{6,8} Thus, it is likely that the elimination of the constrictions of samples pretreated with helium plasma is due to the fact that this treatment removes in part these low-molecular-weight materials.^{9–13} This effect is particularly relevant at small periods of helium plasma treatment (4 min). Nevertheless, at larger periods (15 min) of helium plasma treatment, cross-linking reactions appear.^{9,13–16} As a consequence, the treatment at these larger periods results in the elimination of the low-molecular-weight materials and also in the production of higher molecular-weight products (by cross-linking) which are deposited on the surface of PET and which can also be a source of amorphous

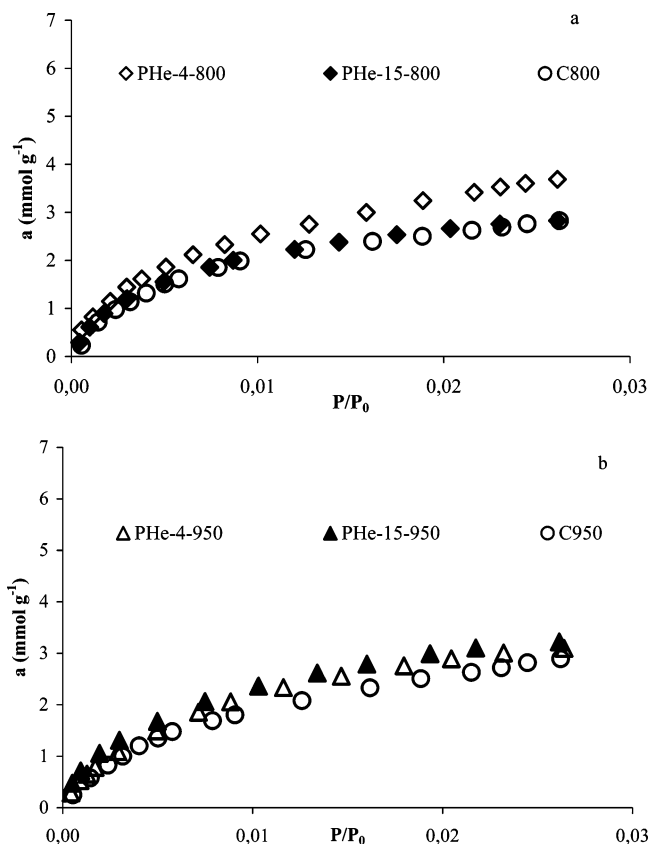


Figure 3. Carbon dioxide adsorption isotherms of samples obtained from direct carbonization of PET (C800 and C950) and from PET pretreated with helium plasma and heat treated at (a) 800 and (b) 950 °C.

carbon during the carbonization. For this reason, after 15 min of helium plasma treatment, the increase in S_{N_2} and W_{01} (samples PHe-15-800 and PHe-15-950) is less relevant than after 4 min of plasma treatment. As already commented on the base of the adsorption isotherms (Figure 2), the effect of the pretreatment is less important when the carbonization is carried out at 950 °C than at 800 °C. In fact, the increase in W_{01} and S_{N_2} is smaller when the pyrolysis is carried out at 950 °C (samples PHe-4-950 and PHe-15-950) which is probably due to the partial shrinkage of the porous network at this higher temperature.^{7,17,18}

AFM micrographs can give some insight on the effect of helium plasma treatment on PET. This can be seen in the AFM micrographs in Figure 4. The surface of the original PET is rather smooth, although at nanometer scale has a granular topography with no particular spatial arrangement (Figure 4a).

After 4 min of helium plasma treatment, the surface consists of two layers (see the $2 \times 2 \mu\text{m}$ magnification of Figure 4b), each one having the morphology of relatively large nodules (see $400 \times 400 \text{ nm}$ magnification of Figure 4b). Following 15 min of treatment (Figure 4c), the surface structure of the PET changes to one consisting of a network of particles connected to each other by thin strands (see the $500 \times 500 \text{ nm}$ magnification of Figure 4c). Thus, the AFM micrographs seem to support the above hypothesis on the effect of the He plasma treatment on the surface of PET: at a small time period of treatment, it produces the etching of the surface by bond breaking, which results in the formation of nodules on the surface and the release of volatile degradation products (low-molecular-weight materials). Nevertheless, at a larger time period of plasma treatment, the sputtered polymer fragments are cross-linked and re-deposited on the surface of PET. AFM

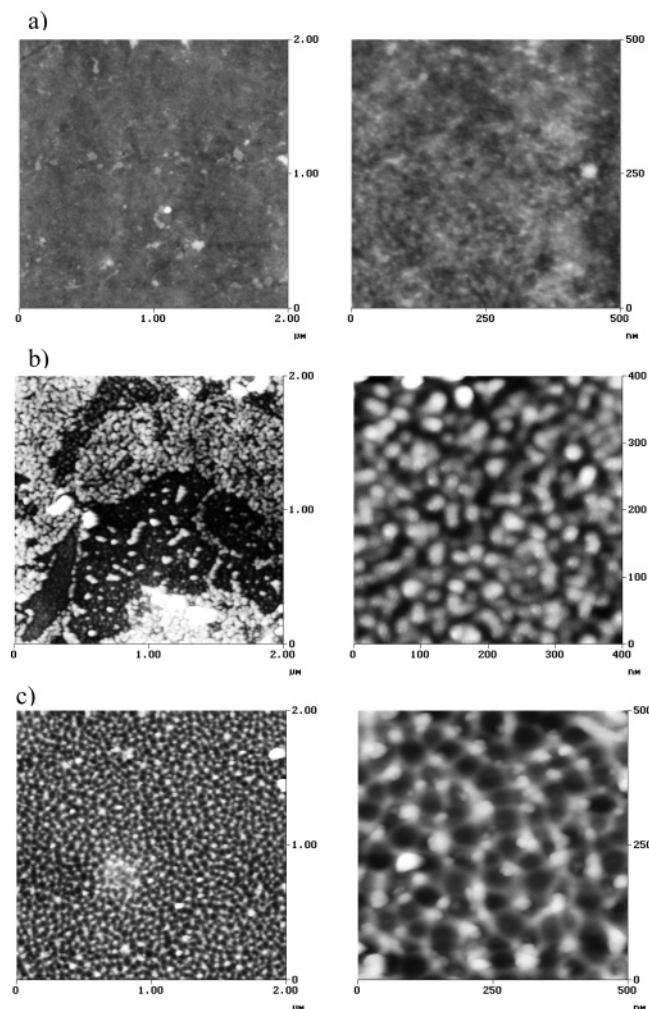


Figure 4. AFM micrographs: (a) PET, (b) PHe-4, and (c) PHe-15.

TABLE 2: Textural Characteristics of the Samples Obtained after Nitrogen, Carbon Dioxide, and Oxygen Plasma Pretreatment, and Further Carbonization at 800 and 950 °C

| | N ₂ adsorption | | CO ₂ adsorption | |
|--------------------------|--|--|--|---|
| | W_{01} (cm ³ g ⁻¹) | S_{N_2} (m ² g ⁻¹) | W_{02} (cm ³ g ⁻¹) | S_{CO_2} (m ² g ⁻¹) |
| PN ₂ -4-800 | 0.230 ± 0.001 | 575 ± 10 | 0.230 ± 0.007 | 652 ± 18 |
| PN ₂ -15-800 | 0.150 ± 0.000 | 342 ± 2 | 0.200 ± 0.001 | 549 ± 4 |
| PN ₂ -4-950 | 0.120 ± 0.000 | 288 ± 2 | 0.250 ± 0.005 | 701 ± 13 |
| PN ₂ -15-950 | 0.100 ± 0.000 | 233 ± 1 | 0.230 ± 0.002 | 655 ± 4 |
| PCO ₂ -4-800 | 0.230 ± 0.000 | 526 ± 3 | 0.210 ± 0.002 | 594 ± 6 |
| PCO ₂ -15-800 | 0.130 ± 0.001 | 283 ± 2 | 0.200 ± 0.002 | 552 ± 6 |
| PCO ₂ -4-950 | 0.090 ± 0.001 | 216 ± 1 | 0.230 ± 0.002 | 638 ± 5 |
| PCO ₂ -15-950 | 0.080 ± 0.001 | 185 ± 1 | 0.230 ± 0.003 | 653 ± 8 |
| PO ₂ -4-800 | 0.080 ± 0.000 | 176 ± 1 | 0.230 ± 0.002 | 650 ± 5 |
| PO ₂ -15-800 | 0.050 ± 0.001 | 117 ± 1 | 0.220 ± 0.003 | 606 ± 9 |
| PO ₂ -4-950 | 0.080 ± 0.001 | 193 ± 3 | 0.190 ± 0.001 | 542 ± 4 |
| PO ₂ -15-950 | 0.050 ± 0.001 | 111 ± 1 | 0.200 ± 0.003 | 571 ± 8 |

analysis of the changes produced by He plasma on the surface of polymers has been already reported.¹⁹

The textural properties of the samples obtained by pretreatments with nitrogen or carbon dioxide plasmas and further carbonization are shown in Table 2. A similar trend to that found for samples pretreated with He plasma (Table 1) is apparent, that is, an increase in W_{01} and S_{N_2} which is particularly relevant at 4 min of plasma treatment (nitrogen or carbon dioxide) and at 800 °C. Moreover, the textural properties measured by CO₂

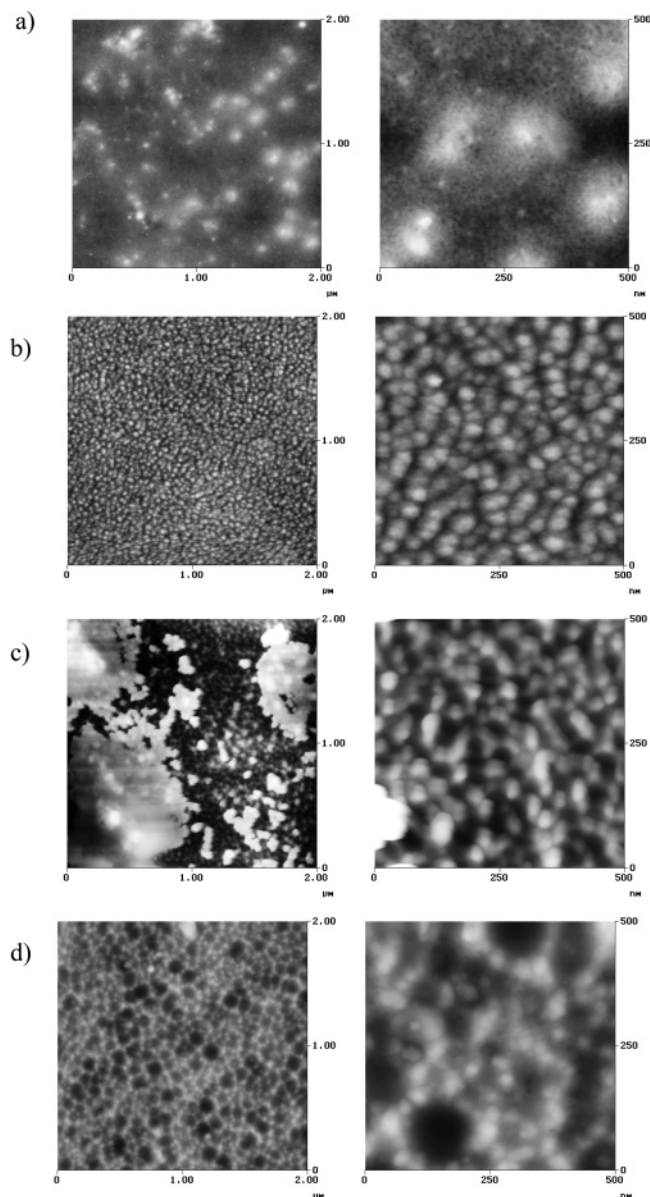


Figure 5. AFM micrographs of PET after plasma treatments: (a) PN₂-4, (b) PN₂-15, (c) PCO₂-4, and (d) PCO₂-15.

adsorption are almost the same for all the samples and very close to the original chars, C800 and C950 (Table 1).

Thus, it is plausible to think that both plasmas act in a similar way to helium plasma. This can be seen in Figure 5 which shows the micrographs of PET after being treated with N₂ and CO₂ plasmas. After exposure to N₂ plasma for 4 min (Figure 5a), bumps of about 100 nm wide, not observed on the fresh PET (Figure 3a), are developed. Nitrogen plasma treatment after 15 min (Figure 5b) changes more drastically the polymer surface and is now made up of a close-packed arrangement of hillocks. The CO₂ plasma treatment for 4 min produces featureless patches on top of a granular morphology (bright and dark area of Figure 5c (2 × 2 μm)). The underlying grains are quite compactly arranged, as can be seen in the 500 × 500 nm magnification of Figure 5c. The sample treated for 15 min (Figure 5d) presents a network of aggregated globular features (20–40 nm wide) which are round with a great number of holes about 50–10 nm in diameter (see the 500 × 500 nm magnification of Figure 5d). Therefore, AFM micrographs seem to support the above hypothesis on the effect of these plasmas on the surface of PET.

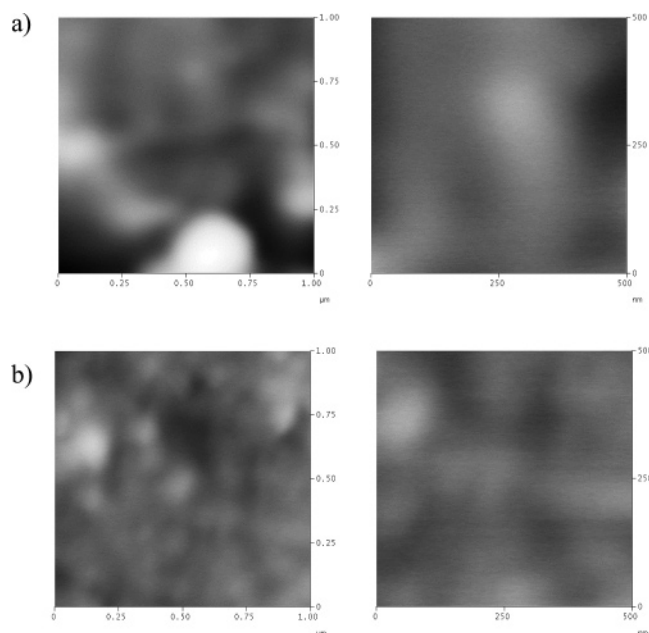


Figure 6. AFM micrographs of PN₂-4 after washing with a cyclohexane/2-propanol 1:1 mixture for (a) 15 min and (b) 4 h.

TABLE 3: Effect of the Elimination of the Deposits Produced by Nitrogen Plasma Pretreatment for 4 min on the Textural Characteristics of the Carbons

| | N ₂ adsorption | | CO ₂ adsorption | |
|---|--|--|--|---|
| | W_{01} (cm ³ g ⁻¹) | S_{N_2} (m ² g ⁻¹) | W_{02} (cm ³ g ⁻¹) | S_{CO_2} (m ² g ⁻¹) |
| PN ₂ -4-800 | 0.230 ± 0.001 | 575 ± 10 | 0.230 ± 0.007 | 652 ± 18 |
| PN ₂ -4-800 (washed 15 min) | 0.210 ± 0.000 | 501 ± 9 | 0.230 ± 0.002 | 633 ± 6 |
| PN ₂ -4-800 (washed 4 h) | 0.190 ± 0.001 | 484 ± 6 | 0.230 ± 0.005 | 633 ± 13 |

These effects can be summarized as follows: (i) when the period of treatment is 4 min, the main process is the elimination of volatile products, which produce the pore constrictions if they are present on the PET when it is heat treated, and the partial re-deposition of polymer fragments, and (ii) at 15 min of treatment, cross-linking reactions prevail producing high-molecular-weight deposits which do not favor the opening of the microporosity because they also produce carbon deposits by carbonization. To check if the deposits produced by the plasma treatments have a substantial effect on the textural characteristics of the carbon materials, two samples of PET pretreated with nitrogen plasma for 4 and 15 min (PN₂-4 and PN₂-15) were selected. First, the sample pretreated for 4 min (PN₂-4) was washed with a cyclohexane/2-propanol 1:1 mixture before pyrolysis at 800 °C. It has been reported^{20–22} that this mixture washing eliminates the globular features produced by plasma treatment. The washing procedure was carried out using an ultrasonic device for two periods of time: 15 min and 4 h. After the samples were washed, they were dried at 110 °C and then heat treated in nitrogen flow at 800 °C. The textural characteristics of the samples so obtained were measured in the usual way, and the results are collected in Table 3.

The results of the washing process on the surface of PET can be seen in the micrographs of Figure 6.

The comparison of these micrographs with those of plasma-treated PET for 4 min (Figure 5a) shows that most of the deposits on PET have been eliminated by washing. The textural characteristics (Table 3) of the sample heat treated at 800 °C after washing, PN₂-4-800 (washed 15 min), are very close to

TABLE 4: Effect of the Elimination of the Deposits Produced by Nitrogen Plasma Pretreatment for 15 min on the Textural Characteristics of the Carbons

| | N ₂ adsorption | | CO ₂ adsorption | |
|-------------------------------------|--|--|--|---|
| | W_{01} (cm ³ g ⁻¹) | S_{N_2} (m ² g ⁻¹) | W_{02} (cm ³ g ⁻¹) | S_{CO_2} (m ² g ⁻¹) |
| PN ₂ -4-800 | 0.230 ± 0.001 | 575 ± 10 | 0.230 ± 0.007 | 652 ± 18 |
| PN ₂ -15-800 | 0.150 ± 0.000 | 342 ± 2 | 0.200 ± 0.001 | 549 ± 4 |
| PN ₂ -15-800 (washed) | 0.240 ± 0.001 | 526 ± 3 | 0.220 ± 0.002 | 631 ± 5 |

those of PN₂-4-800, with W_{01} and S_{N_2} being a bit smaller for the former. When the washing procedure is extended up to 4 h, some new modifications seem to appear on the PET (Figure 6b) which should be produced by the cyclohexane/2-propanol mixture. As a consequence, the textural characteristics of the sample after the heat treatment, PN₂-4-800 (washed 4 h), measured by nitrogen adsorption have a small decrease. In the two cases, the textural characteristics measured by CO₂ adsorption do not change and the values of W_{01} and S_{N_2} are far from those expected if the deposits on the PET after 4 min of treatment played a role in the carbonization process. Therefore, these data suggest that the deposits on the PET produced by 4 min of plasma treatment are not relevant on the textural characteristics of the samples obtained by further heat treatment which are determined by the elimination of low-molecular-weight materials. This seems to support the above conclusion about the effect of the 4 min plasma treatment on the textural characteristics of the carbons.

The second washed PET sample was that pretreated with nitrogen plasma for 15 min (PN₂-15). The effect on the surface was similar to that of sample PN₂-4 after 15 min of washing, shown in Figure 6, that is, the washing process eliminated the deposits. After the heat treatment at 800 °C, the carbon sample, PN₂-15-800 (washed), was characterized and the results are collected in Table 4 together with those of the sample plasma treated for 4 min. For comparison, the values of the original sample plasma treated for 15 min and carbonized at 800 °C, PN₂-15-800, are also collected in the same table.

The most relevant feature is that the carbonization of the washed PET at 800 °C produces a carbon, PN₂-15-800 (washed), which has a volume and surface area, W_{01} and S_{N_2} , clearly larger than these of PN₂-15-800. Moreover those values are now very close to that of the sample PN₂-4-800. This supports the above hypothesis in relation to the role of the high-molecular-weight products (cross-linked deposits) produced by the plasma treatment for 15 min on the PET, that is, these can partially evolve as carbon deposits during the heat treatment process which partially hinders the nitrogen adsorption. For this reason, when these deposits are eliminated before the heat treatment, the textural characteristics of the carbon are very close to those of the sample obtained by plasma pretreatment for 4 min and further carbonization.

The textural characteristics of the carbons obtained by oxygen plasma pretreatment and further carbonization are also collected in Table 2. The effect of this plasma in the nitrogen-measured textural characteristics (W_{01} and S_{N_2}) is less relevant than that of the other plasmas and similar with regard to CO₂ characterization, W_{02} and S_{CO_2} . This means that the effect of the oxygen plasma on the elimination of porous constrictions is less important than that of the other plasmas. The changes produced by oxygen plasma on the PET are shown in the AFM micrographs of Figure 7.

After 4 min of plasma treatment, the surface presents a network of aggregated globular features which are round with

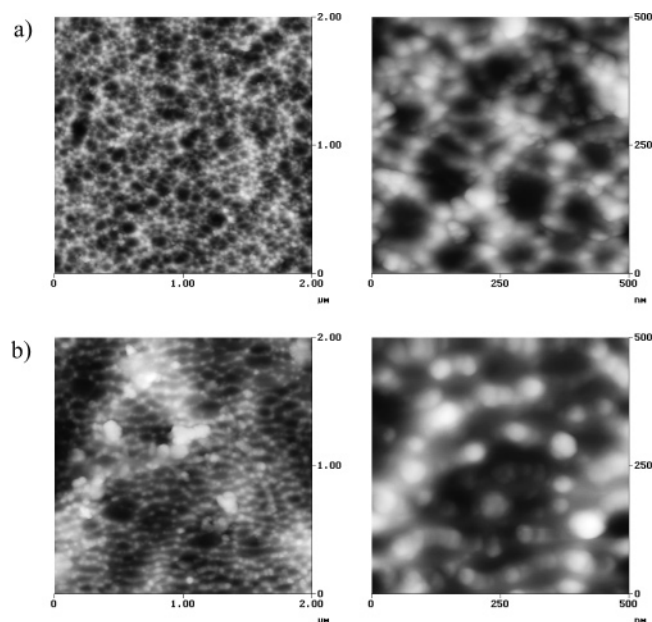


Figure 7. AFM micrographs of oxygen plasma-treated PET: (a) PO₂-4 and (b) PO₂-15.

a great number of holes about 50–100 nm in size. After 15 min of treatment, the features appear more isolated from each other and the holes are now less evident and somewhat elongated. Similar modification to these have been already reported for PET and other polymers treated with oxygen plasma.²⁰ These are attributed to “polymer chain scission produces oxidized low-molecular-weight materials, which rearranges to form small globules in order to minimize polar surface energy”.²⁰

Although there are clear differences between the micrographs of oxygen plasma-treated PET and those of the other plasmas (Figures 5 and 7), it could be expected that the effect of the deposits in the textural characteristics of the carbons should be similar. As oxygen pretreated samples present different textural characteristics (Table 2), it is plausible to think that there is another factor which can condition those properties. Some insight on this issue can be drawn from DRIFTS spectra in Figure 8. This shows the spectra of PET and also of the PET samples treated with oxygen and carbon dioxide plasmas for 15 min, PO₂-15 and PCO₂-15. The PET spectrum has been already reported and the bands assignments are in the literature.^{23–27} The spectrum of PET treated with oxygen plasma is similar to that of untreated PET. Nevertheless, the band at 1740 cm⁻¹ corresponding to the stretching of carbonyl groups sharpened and increased its intensity in relation to the bands of ester groups (1300 and 1140 cm⁻¹). Also the shoulder at 1829 cm⁻¹ has red shifted to 1819 cm⁻¹, which may arise from C=O stretching vibrations of new oxygen functionalities (anhydride and lactone type). The peak at 3340 cm⁻¹ stemming from terminal hydroxyl groups has broadened and increased its intensity following the plasma treatment, reflecting a larger proportion of such functionalities. Also the bands in the region 3050–3100 cm⁻¹ corresponding to the stretching vibrations in unsaturated compounds are modified which can be related to the degradation of the polymer. Thus, it is likely that oxygen plasma treatment breaks the polymer chains, in agreement with AFM micrographs, but also introduces oxygen-containing functional groups. The introduction of oxygen groups by oxygen plasma treatment on the surface of PET has already been reported in the literature.^{20,28,29} Moreover, this is also in

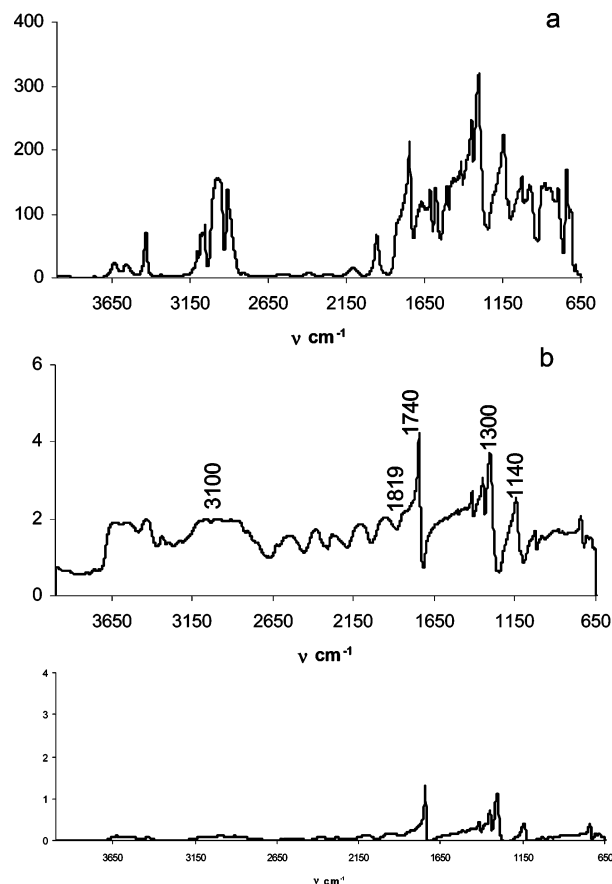


Figure 8. DRIFTS spectra: (a) PET, (b) oxygen plasma-treated PET for 15 min, and (c) carbon dioxide plasma-treated PET for 15 min.

agreement with reported adsorbate–adsorbent specific interactions measured by inverse gas–solid chromatography.³⁰

Cold plasmas consist of a mixture of charged particles (electrons and ions), neutral species, free radicals, and photons.^{9,14,31} In the case of oxygen plasma, atomic radicals are the most abundant. The activation energy of the reaction of these radicals with the polymer chains must be very small. A consequence of this is that, although this plasma produces the etching of the surface and the re-deposition of polymer fragments similar to the other plasmas, an important effect is the partial reaction with the surface which introduces oxygen functionalities on the polymer structure as reported by Greenwood et al.²⁰

Although in the case of CO₂ plasma treatment oxygen atomic radicals can also be present, this effect is less important due to the lower reactivity of this plasma. Therefore, the CO₂ plasma-treated sample has a DRIFTS spectrum (Figure 8) similar to that of the oxygen plasma-treated sample although the intensity of the oxygen functionalities peaks is smaller. In addition, it has been reported that CO₂ plasma treatment of PET does not increase the specific adsorbate–adsorbent interactions²⁷ which means that the oxygen functionalities of the polymer are scarcely modified.

Thus, the main difference between the effect of oxygen plasma treatment and the other plasmas seems to be that the former introduces a considerable amount of oxygen chemical functionalities on the surface of the polymer. Therefore, these functionalities should be responsible for the low increase in *W*₀₁ and *S*_{N₂} of the carbons obtained by pretreatment with oxygen plasma before the carbonization if they are compared with the samples pretreated with the other plasmas. It is likely that the oxygen groups evolve as carbon monoxide, particularly at high

temperatures of the thermal treatment used for the preparation of the carbons. At these high temperatures, carbon monoxide undergoes disproportionation.³² This produces carbon dioxide and carbon deposits which should be responsible for the porous constrictions found in those samples (Table 2).

It is remarkable that the carbon materials obtained after 4 min of plasma pretreatment present adsorption capacities very similar to those of activated carbon materials obtained after 4 h of CO₂ activation (1073 K) of the same chars⁶ and very close to those obtained after 8 h. Therefore, the microwave plasma pretreatment offers an interesting option for mild activation of this kind of material. In comparison with CO₂ activation, plasma pretreatments are cleaner, energetically less demanding, and present higher yields, as burnoff degrees during CO₂ activation of these materials are in the range 10–20%.

Conclusions

Short periods (4 min) of plasma (He, N₂, and CO₂) pretreatment of the PET precursor and subsequent pyrolysis (1073 K) have shown to produce carbon materials with higher nitrogen adsorption capacity than the untreated pyrolysed PET, while textural parameters related to CO₂ adsorption at 273 K are not modified. The effect of the plasmas seems to be related to the elimination of volatile matter in the precursor, which can be a source of amorphous carbon deposits during the carbonization step. If longer periods of plasma treatments are employed, cross-linking reactions producing high-molecular-weight deposits start to occur. These deposits evolve forming amorphous carbon during the carbonization, which decrease the accessibility to the porosity. At higher carbonization temperatures (1223 K), shrinking of the porosity makes the effect of the pretreatments less important. Oxygen plasma behavior is somewhat different as it also introduces a considerable amount of oxygen functionalities which act as a source of amorphous carbon during the pyrolysis step. The nitrogen adsorption capacities of samples prepared using plasma pretreated PET are very close to those obtained after 4–8 h of CO₂ activation of the same char. Therefore, it can be a suitable method to avoid the activation process, which can be expensive and material-consuming.

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