

# EFFECT OF OXIDATION ON THE SURFACE PROPERTIES OF POLYETHYLENETEREPHTHALATE (PET) BASED ACTIVATED CARBON

Krisztina László, Katalin Josepovits\*

Department of Physical Chemistry, Budapest University of Technology and Economics  
H-1521 Budapest, Hungary

\*Department of Atomic Physics, Budapest University of Technology and Economics  
H-1521 Budapest, Hungary

## Introduction

The adsorption behavior and the catalytic activity of carbons are basically effected not only by the porosity but also by the chemistry of the surface. This latter can be influenced by introducing hetero atoms, which react practically with the carbon atoms situated at the edges of the turbostratic graphite layers. The hetero atoms like hydrogen, oxygen, nitrogen, halogens, sulfur, phosphorus, etc. form non-stoichiometric stable surface compounds. The oxygen complexes are the most common and most important ones from among these surface groups. O-containing surface groups are formed when activated carbons are treated with various oxidative chemicals.

The oxidation agent, its concentration, the temperature and the time of the treatment influence the chemistry of the surface obtained. However, the oxidative treatment may affect the morphology of the carbon structure as well. The aim of this paper is to reveal the effect of cc nitric acid treatment on both the morphology and the surface chemistry of an activated carbon prepared from polyethyleneterephthalate (PET) by a two-step physical activation procedure.

## Experimental

### Treatment with acid

The preparation of activated carbon from PET and its characterization was published recently [2, 5]. This activated carbon was treated with cc nitric acid at ambient temperature (AT) and at the boiling point (BP) of the carbon – acid suspension for 3 and 6 hours. The acidic samples were then washed with distilled water and extracted in a Soxhlet apparatus until neutral pH was obtained. The air-dried samples were treated in nitrogen flow for 30 min at 700 °C.

The preparation of the carbon samples is listed in Table 1.

### Morphology of the carbons

Nitrogen adsorption/desorption isotherms were measured and evaluated using a Quantachrome Autosorb-1 computer

controlled apparatus. Additionally, the iodine number was measured by the standard method [3].

### Surface chemistry

The Boehm titration method was applied to determine the number of the oxygenated surface groups [4]. The surface chemical composition of the samples was determined by XPS (X-ray Photoelectron Spectroscopy) using an XR3E2 (VG Microtech) twin anode X-ray source and a Clam2 hemispherical electron energy analyzer [5].

## Results and Discussion

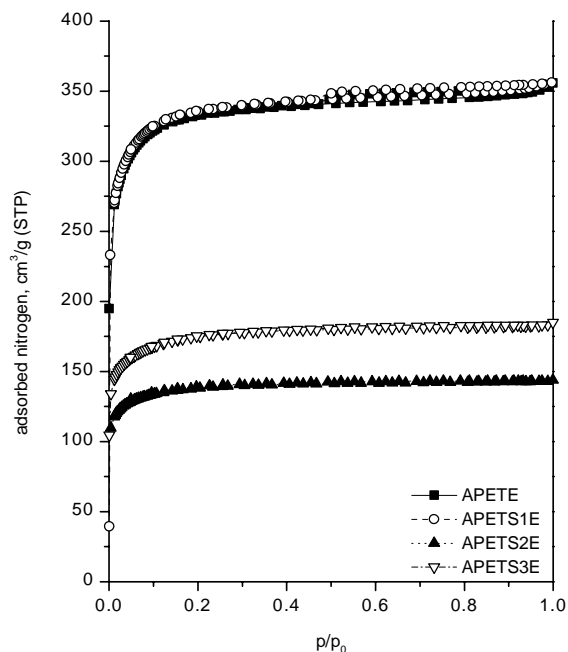


Figure 1. Nitrogen adsorption isotherms of APET carbons treated with cc HNO<sub>3</sub>

The acidic treatment affects both the morphology of the carbon and the chemistry of the surface.

The nitrogen adsorption isotherms in Fig. 1 show, that the carbons obtained are highly microporous. The adsorption

**Table 1.** Preparation of the modified APET carbons

| Sample  | Treatment applied                                 |         |   |   |
|---------|---|---------|---|---|
|         | treatment with cc HNO <sub>3</sub><br>temperature | time    | extraction with<br>distilled water <sup>c</sup> | additional heat<br>treatment <sup>d</sup> |
| APETE   | –   | –       | +   | –   |
| APETS1E | AT <sup>a</sup>                                   | 6 hours | +   | +   |
| APETS2E | BP <sup>b</sup>                                   | 6 hours | +   | +   |
| APETS3E | BP  | 3 hours | +   | +   |

<sup>a</sup> at ambient temperature, < 40 °C

<sup>b</sup> at the boiling point of the carbon – acid suspension

<sup>c</sup> extraction in a Soxhlet apparatus until neutral pH

<sup>d</sup> in a rotary quartz reactor, at 700 °C, 30 min, 25 l/h N<sub>2</sub> flow

**Table 2.** Analysis of the nitrogen adsorption/desorption isotherms

| Sample  | Specific surface area<br>(BET)<br>m <sup>2</sup> /g | Iodine<br>number<br>mg/g | V <sub>tot</sub><br>cm <sup>3</sup> /g | V <sub>MP</sub><br>cm <sup>3</sup> /g | S <sub>ext</sub><br>m <sup>2</sup> /g | L <sub>0</sub><br>nm |
|---------|---|--------------------------|--|---------------------------------------|---------------------------------------|----------------------|
| APETE   | 1215  | 1059                     | 0.540                                  | 0.35383                               | 49.2                                  | 1.88                 |
| APETS1E | 1217  | 972                      | 0.551                                  | 0.44305                               | 30.9                                  | 1.54                 |
| APETS2E | 496   | 170                      | 0.221                                  | 0.25220                               | 14.5                                  | 1.00                 |
| APETS3E | 636   | 368                      | 0.286                                  | 0.21383                               | 14.0                                  | 1.08                 |

**Table 3.** Selected data of the surface analysis (Boehm titration, XPS)

| Sample  | Functional group, μmol/g |            |         |        |       |        |        | O/C<br>atomic %** |
|---------|--------------------------|------------|---------|--------|-------|--------|--------|-------------------|
|         |                          | Acidic*    |         |        |       | Basic* | Total* |                   |
|         |                          | carboxylic | lactone | phenol | total |        |        |                   |
| APETE   | μmol/g                   | 4.9        | 13.3    | 130.1  | 148.3 | 375.5  | 523.8  | 11.0              |
|         | mmol/m <sup>2</sup>      | 4.0        | 11.0    | 107.1  | 122.1 | 309.1  | 431.2  |                   |
| APETS1E | μmol/g                   | 17.7       | 69.5    | 207.1  | 294.3 | 336.4  | 630.7  | 11.2              |
|         | mmol/m <sup>2</sup>      | 14.5       | 57.1    | 170.2  | 241.8 | 276.4  | 518.2  |                   |
| APETS2E | μmol/g                   | 27.1       | 32.7    | 103.1  | 162.9 | 433.1  | 596.0  | 10.4              |
|         | mmol/m <sup>2</sup>      | 54.6       | 65.9    | 207.9  | 328.4 | 873.2  | 1201.6 |                   |
| APETS3E | μmol/g                   | 19.6       | 60.9    | 85.6   | 166.1 | 416.6  | 582.7  | 8.9               |
|         | mmol/m <sup>2</sup>      | 30.8       | 95.8    | 134.6  | 261.2 | 655.0  | 916.2  |                   |

\* from the Boehm titration

\*\* from the XPS analysis

isotherms of APETE and APETS1E samples are very similar showing high microporosity and a narrow hysteresis loop. From the shape of these isotherms it can be deduced that the acidic treatment at ambient temperature has no remarkable effect upon the porosity of the sample. The treatments at elevated temperature lead to adsorption isotherms of Type I, typically characteristic to microporous carbons. The disappearance of the mesopore region may be concluded from the pore size distribution curves as well (not shown here). The BET surface area, total pore volume ( $V_{tot}$ ), MP micropore volume ( $V_{MP}$ ), external surface area ( $S_{ext}$ ) and the micropore width ( $L_0$ ) calculated according to Stoeckli [6] are reported in Table 2.

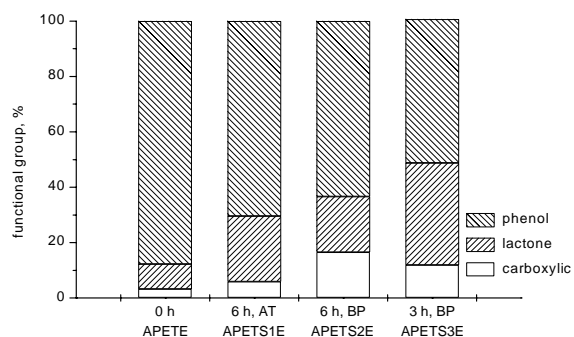
The results of the Boehm titration is collected in Table 3. Surface concentration ( $\text{mmol/m}^2$ ) of the functional groups was derived from the combination of the Boehm titration data and the BET surface area. The relative distribution of the acidic functional groups is illustrated in Fig. 2.

The O/C atomic ratio in the surface layers was derived from the XPS curves (Table 3). After the linear base line was subtracted, the curve-fitting was performed assuming a Gaussian peak shape. Five peaks were identified by the deconvolution of the typically asymmetric  $C_{1s}$  spectrum: graphitic carbon (Peak I, BE=283.7 - 283.8 eV), carbon present in phenolic, alcohol or ether groups (Peak II, BE=284.8 - 285.2 eV), carbonyl or quinone groups (Peak III, BE=286.2 - 286.5 eV), carboxyl or ester groups (Peak IV, BE= 287.9 - 288.3 eV), and shake-up satellite peaks due to  $\pi - \pi^*$  transitions in aromatic systems (Peak V, BE=289.1 - 289.9 eV) [7]. The  $O_{1s}$  spectra reveal the presence of three peaks. Peak I (530.0 - 530.9 eV) corresponds to C=O groups (ketone, lactone, carbonyl), Peak II (BE=532.0 - 532.5 eV) to carbonyl oxygen atoms in esters, carboxylic anhydrides and oxygen atoms in hydroxyls or ethers and Peak III (BE=533.6 - 534.0 eV) to the oxygen atoms in carboxyl groups [7]. The distribution of the surface functionalities in the upper (ca. 10 nm) layer of the samples, resulted from the XPS analysis is shown in Figs. 3a and 3b.

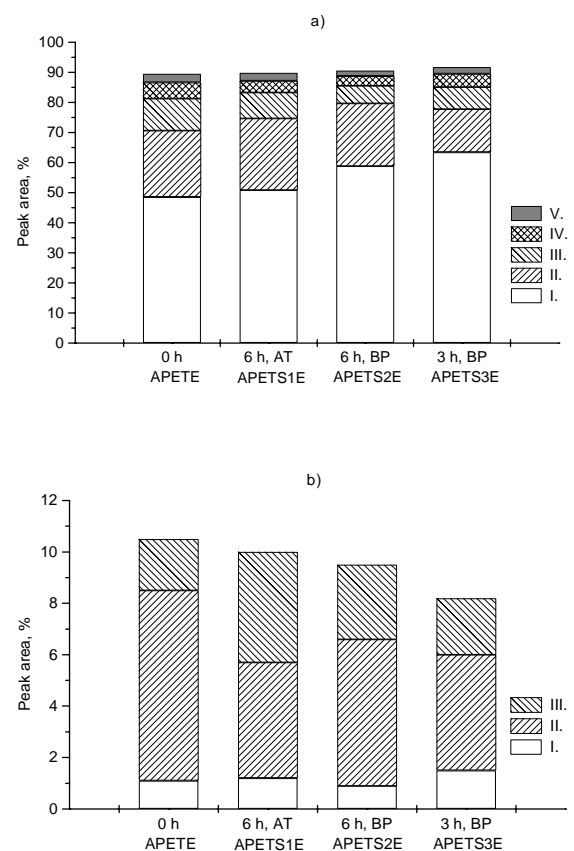
### Morphology

The treatment at the lower temperature has practically no influence on the surface area and the micropore volume, only a slight reduction of the external surface and the mean micropore width was experienced. The effect is more significant at elevated temperature. Already the 3-hour treatment diminishes the surface area and the micropore volume about to the half of the original values, and these parameters are further reduced during the extended treatment. However, the extended treatment has practically no influence onto the external surface area and the mean micropore width.

Probably only part of the amorphous part „dissolves” in the acid at ambient temperature. The graphitic part is also



**Figure 2.** Relative distribution of the functional groups on the cc  $\text{HNO}_3$  treated APET carbons derived from the Boehm titration. AT: treated at ambient temperature, BP: treated at the boiling point of the carbon/acid suspension



**Figure 3.** XPS analysis of APET carbons treated with cc  $\text{HNO}_3$ ; a): from  $C_{1s}$  spectra; b): from  $O_{1s}$  spectra

involved in the high temperature treatment: graphitic layers are removed during the BP treatment. Small angle X-ray scattering experiments performed recently (to be published soon) indicate a concurrent rearrangement in the microcrystalline region.

The discrepancy between the BET surface and the iodine number indicates a molecular sieve effect affected by both the temperature and the time of the treatment. The surface area derived from the iodine number (1 mg adsorbed iodine roughly equals 1 m<sup>2</sup>) is only 87 and 80 % of the BET surface in the case of the APETE and APETS1E samples, respectively. This ratio falls back to 58 and 34%, when boiling acid is applied for 3 and 6 hrs, respectively. Therefore, the L<sub>0</sub> values mean rather an average size than a uniform pore width.

### *Surface chemistry*

Unlike the surface area and the pore structure, the chemistry of the surface is definitely affected already by the low temperature treatment. The amount of the surface acidic groups doubles, and that of the basic groups is only slightly depressed. The relative amount of the carboxylic and lactone groups is increased and the ratio of the phenolic group is lowered, according to the Boehm titration (Table 3, Fig. 2). The O/C atomic ratio as well as Peaks I and V in the C<sub>1s</sub> spectrum and Peak 1 in the O<sub>1s</sub> spectrum are not affected during this treatment (Figure 3). At the boiling point of the suspension the same treatment practically triples the surface concentration of both acidic and basic groups. The concentration of all the acidic species increases. The relative amount of the carboxylic and lactone groups increases, however, the phenol is the most dominant group on the APETS2 surface. The O/C ratio is not influenced. The proportion of Peak I in the C<sub>1s</sub> significantly increases, while all the other functional groups deconvoluted in the C<sub>1s</sub> spectrum fall back as compared either to the original sample or APETS1.

When the treatment at the boiling point was reduced to 3 hrs, the concentration of both the acidic and basic groups falls back, however, the acidic groups exhibit different distributions depending on the time of the treatment. The lactone group shows the highest concentration in this carbon. In this case the O/C ratio decreases as well and Peak 1 in the C<sub>1s</sub> spectrum reaches as high as 63.5 %. The total concentration of the functional groups increases as the time of the boiling point treatment increases, but not proportionally. The acidic and basic groups show different rates.

The temperature of the treatment has a more expressed influence on the chemistry of the surface, than the time of the treatment. The discrepancies between Boehm titration and XPS results trace back to the limited depth of the XPS analysis, and indicates that the chemistry of the upper layer might be different from that of the "bulk".

## **Conclusion**

The treatment of the PET based activated carbon with cc nitric acid resulted in a significant modification in the morphology and the surface chemistry of the carbon. Both the temperature and the time of the treatment may have a significant influence. The room temperature treatment does not affect significantly the surface area and porosity of the sample, but changes the chemistry of the surface. The nitric acid treatment performed at the boiling point dramatically decreases the surface area and modify the pore structure. The surface concentration and the distribution of the O-containing functional groups is affected by both the temperature and the time of the treatment. The BP treatment results in a more intensive change in the surface chemistry. The effect of the temperature is stronger than that of the duration of the treatment.

## **Acknowledgements**

This research was supported by the Hungarian National Research Fund (OTKA, grant No. T 025581). The experimental work of Ms. Emese Fülöp and Mr. György Bosznai is gratefully acknowledged. K. L. wish to express her appreciation to Ms. E. Csibi for the technical support.

## **References**

- [1] Bóta A, László K, Nagy LG, Copitzky T. Comparative study of active carbons from different precursors. *Langmuir* 1997;13:6502-6509.
- [2] László K, Bóta A, Nagy LG. Comparative Adsorption Study on Carbons from Polymer Precursors. *Carbon* 2000; 38:1965-1976
- [3] NORIT Testing Methods, Special Publication
- [4] Boehm HP. In: Eley DD, Pines H, Weisz PB editors, *Advances in Catalysis*, vol. 16, New York: Academic, 1966:179-274.
- [5] László K, Tombácz E, Josepovits K. Effect of Activation on the Surface Chemistry of Carbons from Polymer Precursors. *Carbon*, in press
- [6] Stoeckli F, Daguerre E, Guillot A. The development of micropore volumes and widths during physical activation of various precursors. *Carbon* 1999; 37:2075-2077
- [7] Biniak S, Szymanski G, Siedlewski J, Swiatkowski A. The characterization of activated carbons with oxygen and nitrogen surface groups. *Carbon* 1997;35:1799-1810