

THERMAL ANNEALING METHODS FOR THE RESTRUCTURING OF DISORDERED CARBON MATERIALS

B. Apicella*, **A. Tregrossi***, **V. Mennella****, **A. Ciajolo ***, **C. Russo***

apicella@irc.cnr.it

* Istituto di Ricerche sulla Combustione - C.N.R.,
P.le Tecchio 80, 80135 Napoli, Italy

** Istituto Nazionale di Astrofisica – INAF,
Salita Moiarriello, 16 80131, Napoli, Italy

Abstract

The structural analysis of carbons formed by thermally-induced annealing of an anisotropic carbon as naphthalene pitch is presented in this work. Naphthalene pitch has been heated in a furnace in mild conditions (low pressure and temperature ≤ 1000 °C). The carbonization/ graphitization process has been found to occur at a different extent in dependence of the experimental conditions employed for the annealing.

Introduction

The wide class of disordered carbon materials originating from natural (coal, cellulose, etc.) and synthetic sources (pyrolytic carbon, pitches, etc.) constitutes a carbon feedstock sufficiently flexible to be tailored into sundry graphenic nanocarbons by a bottom-up transformation process such as thermally induced annealing. Structural transformations toward nanocarbons of different properties relevant for practical usage (fibers, composites and opto-electronic devices) can be tuned by a suitable choice of the parent carbon nanostructure and annealing conditions [1]. Therefore, a challenging question of the current research is the development of processes less expensive possible from cheap starting materials, which leads to materials with the required properties. To this regard the anisotropic character of a carbon material as the 100% mesophase synthetic Naphthalene Pitch, provided by Mitsubishi Gas Chemical Company [2] (labeled raw-NP), render it a good candidate for graphitization. Hence, in the present work raw-NP has been employed to study the structural transformations occurring under thermal treatment in mild conditions (low pressure and temperature ≤ 1000 °C).

The raw-NP has been extensively characterized by an array of analytical techniques in two recent papers [3,4]. Mass spectrometric analysis of the raw-NP therein reported showed a continuous mass sequence ranging from m/z 150 to about 2000 and no significant presence of low molecular weight (MW) (<400 Da) aromatic species. This finding was confirmed by size exclusion chromatography (SEC) analysis which, however, showed a MW range extending to higher MW(up to 3000 Da), with respect to the mass spectrometric analysis. Indeed, SEC analysis

appeared to be more reliable for the MW determination of pitch samples, even though some drawbacks related to the use of calibrants should be considered.

With regard to the spectroscopic analysis, UV–vis, FT-IR and fluorescence spectroscopic methods highlighted the presence of rylene polycyclic aromatic hydrocarbons (PAH) moieties bridged and/or substituted with alkyl groups and naphthenic rings in NP aromatic structure. The assessment of raw-NP chemical structure is of concern for the present study as the high MW and thermal reactivity of its alkyl-substituted aromatic components can favor intramolecular pyrolytic/polycondensation reactions during heating treatment.

Experimental

Raw-NP samples have been weighted and put into a crucible in a furnace operating under vacuum (at about 10^{-6} mbar). The thermal annealing has been performed in different operative conditions in terms of temperature and time spans as reported in Table 1.

Table 1- Upper fraction percentage for each temperature and time span employed.

T (°C)	t (h)	% upper fraction
200	3	0.4
300	3	19.1
500	0.5	15.9
500	2	17.9
500	3	17.1
500	4	17.8
600	3	19.3
800	3	16.9
1000	2	13.0
1000	3	11.0

At the end of each heating cycle, part of the loaded material was found to be deposited on the top of the annealing reactor. The percentage of this “upper fraction” is reported in the Table 1. It was also noteworthy that for $T > 500^\circ\text{C}$ the “upper fraction” was not completely soluble in dichloromethane (DCM). Therefore the condensed material has been filtered for separating the insoluble part (this fraction was below 15% of the “upper fraction) which was dissolved in N-methyl pyrrolidone (NMP) and analysed separately. The “carbonized” material left inside the crucible constitutes the “bottom fraction”. It was insoluble both in DCM and in NMP and therefore was analysed in solid phase.

The array of the characterization techniques applied on upper and bottom fraction includes thermogravimetry, elemental analysis, X-Ray diffraction, UV-Visible absorption and Raman spectroscopy. Details on each analytical technique are reported in [3,4].

Results and discussion

The percentage of “upper fraction” (Tab.1) formed in the annealing treatment of NP accounts for a rather constant value (16-19%) of the raw carbon in the range 300-800 °C, independently from the annealing time. Only at 1000°C it sharply decreases up to about 11%. Up to 500°C the upper fraction is constituted only by species which are completely soluble in DCM, whereas after 500°C, a little fraction insoluble in DCM, is also present, as reported in the experimental section. This finding suggests that also the upper fraction condensed on the top of the reactor undergoes a mild thermal treatment, which anyway occurs in a lower temperature range with respect to that experienced by the bottom fraction. Thus, a carbonization process at a different extent occurs to both upper and bottom fractions of carbon materials in dependence of the starting material, the temperature and the time span of the annealing. The two carbonization processes have been studied separately with the techniques more suitable to the different chemical-physical characteristics of the two fractions.

Figure 1 illustrates the progressive increase of aromatic moieties extension with temperature increase for both the volatile upper fraction (by UV-visible absorption, in DCM solution) and the residual bottom fraction (by Raman, in solid phase).

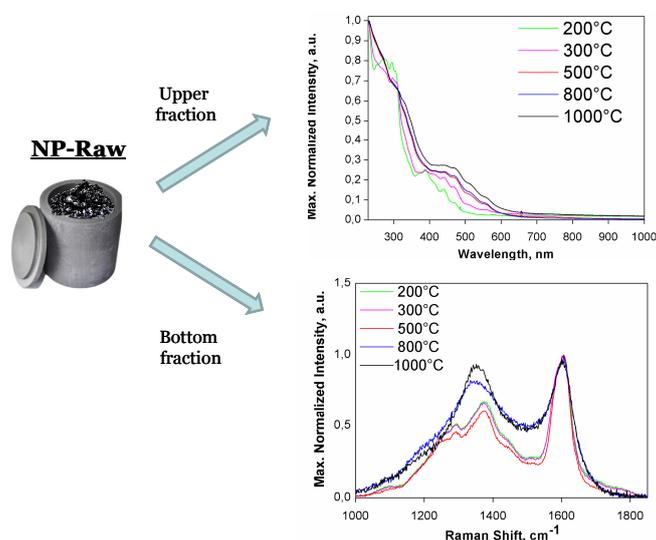


Figure 1. Height normalized UV-vis absorption spectra (top) of the volatile upper fraction and height normalized Raman spectra (bottom) of the bottom residual fraction from NP heating at constant time span (3h) and different temperatures .

A fine spectral structure in the wavelength range 200–400 nm, indicating the presence of small PAH molecules (up to three condensed rings) can be observed only for the sample treated at 200°. For higher temperatures, however, and in particular for $T \geq 500^\circ\text{C}$, the spectral absorption appears shifted at greater

wavelengths (400–600 nm, i.e. in the visible region), indicating the formation of heavier molecules.

The Raman spectra of the residual bottom fraction, also reported in Fig. 1, show a gradual decrease of the fluorescence background intensity with the temperature, demonstrating the gradual hydrogen decrease resulting from the aromatization and condensation of the molecules during the heat treatment. At low temperatures, $< 500^{\circ}\text{C}$, Raman spectra are similar to those recorded for the raw-NP [5]. In particular, the samples treated up to 500°C show a fine structure in the D-peak region ($1200\text{--}1480\text{ cm}^{-1}$), typical of molecular structures, and a sharp G-peak at 1600 cm^{-1} . This means that the thermal treatment up to 500°C keeps on the aromatic structure similar to that of the pre-existing pitch. Instead, a neat change of the Raman features, with respect to the raw-NP sample, can be observed at $T > 500^{\circ}\text{C}$, with the disappearance of the fine structure in the D-peak and the I(D)/I(G) ratio increase. These two features are symptoms of the fact that the NP is going towards higher order and the broad background between D and G peaks also indicates the formation of a structure typical of a complex solid carbonaceous material. It was noticed that the bottom samples obtained at different time span (not reported) present a very similar behavior.

The thermogravimetric profiles in air of bottom fractions, reported in Figure 2, shows that the thermal annealing leads to a decrease of reactivity toward oxygen as temperature rises.

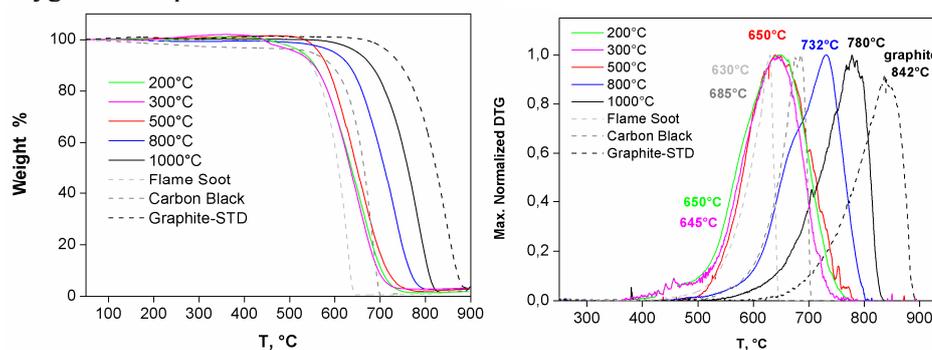


Figure 2. Thermogravimetric profiles of raw-NP, bottom fractions at different annealing temperatures and reference compounds (left side). Weight normalized DTG profiles of the same samples (right side).

All the heat-treated samples have a burn-off temperature above that of the raw-NP, as better seen from the DTG profiles reported in the right side of Fig.2. The burnoff temperature increases as the annealing temperature increases and a neat change is noticeable for samples at $T > 500^{\circ}\text{C}$. The residual bottom fractions obtained at $T \leq 500^{\circ}\text{C}$ present burn-off temperatures typical of low-hydrogenated disordered carbons, intermediate between a mature flame soot ($T_{\text{burnoff}} = 630^{\circ}\text{C}$) and a commercial carbon black ($T_{\text{burnoff}} = 685^{\circ}\text{C}$). By contrast, the bottom fraction formed at 1000°C shows a thermal behavior which is next to that of graphite

($T_{\text{burnoff}}(\text{Graphite}) = 842^{\circ}\text{C}$). The increase in the burn-off temperature indicates that the material is changing its structure and that alkylated branches of the NP structure are gradually disappearing within the structure which is going towards a more ordered and mainly aromatic one. No significant effect of the time span increase on the TG profiles (not reported) has been found.

The changes in the structure of the solids are further clarified by the elemental analysis and XRD spectroscopy.

H/C ratios obtained from the elemental analysis of the bottom fractions are reported in the left part of Figure 3. It is possible to observe that the hydrogen content is similar to that of Raw-NP for CS at 200°C and 300°C heating temperatures and it dramatically changes when temperature increases from 300°C to 500°C , while it gets closer to zero for the sample treated at 1000°C , approaching typical values of a carbon black, showing that the carbonization process occurred at a large extent at these temperatures.

The application of XRD to the characterization of carbon materials gives information about the crystalline arrangement of the investigated materials. From the right side of Figure 3, where XRD spectra of the raw-NP and bottom fractions are reported, it can be noticed that thermally treated NP samples are characterized by two broad signals at $2\theta = 26^{\circ}$ and 42° . They correspond to the diffraction of the [002] and [100] crystalline planes, which are typical of graphene layers.

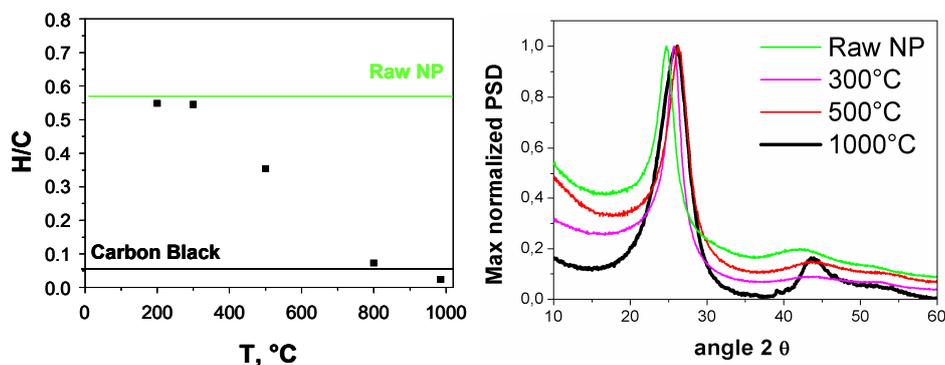


Figure 3. H/C ratio of raw-NP, carbon black and bottom fractions at different annealing temperatures. Height normalized XRD spectra of raw-NP and some selected bottom fractions.

In particular, the peak at $2\theta = 26^{\circ}$ corresponds to the reflection in the [002] plane from the parallel layers of carbon atoms, while the peak at $2\theta = 42^{\circ}$ corresponds to the reflection in the [100] plane from the two-dimensional flat sheets of condensed aromatic hydrocarbons [6] and, in general, the lower is the [100] peak intensity, the lower is the quality of the carbon nanomaterial produced.

The change of order and disorder degree of these materials can also be detected following the broadening of the peaks: the broader is the peak, the more is

disorder. Moreover, a broad background due to the presence of a γ -band of an aliphatic contribution at $2\theta = 20^\circ$ (indicating the presence of an amorphous phase) is also present. It can be noted that both the broadness of the peaks and the aliphatic background largely decrease with the increasing of the annealing temperature. In particular, the peak at 42° , which is simply a bump in the Raw-pitch and at low annealing temperature, becomes more pronounced, up to become really a neat peak at 1000°C . These findings are better observable from Table 2, where the intensity ratio of peaks at [100] and [002] are reported.

Table 2- Intensity ratio of peaks at [100] and [002]

Sample	I [100]/I[002]
raw-NP	0.023
200°C	0.023
300°C	0.023
500°C	0.037
600°C	0.039
800°C	0.070
1000°C	0.160

Final remarks

Carbonization and/or graphitization processes of carbon materials as a naphthalene pitch have been carried out in mild conditions ($T \leq 1000^\circ\text{C}$) and low pressure environment ($P \leq 10\text{E-}6$ mbar). The structural transformations occur at a different extent to both upper and bottom fractions produced, in dependence of the temperature and the time span of the annealing process. The structural features of the two (volatile and residual) fractions have been studied with the techniques more adapt to their different chemical-physical characteristics.

The maximum transformation of the raw pitch needed a temperature of 1000°C but with a time span of only thirty minutes. Further analytical work will be carried out for verifying the occurrence of carbonization and/or graphitization.

Acknowledgments

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