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# STRUCTURAL STABILITY OF PAN FIBER UNDER HIGH ELECTRON BEAM RADIATION DOSES

**Eddy S. Pino[1], Clarissa P. Zelinschi de Arruda[2], Luci D. B. Machado[1], Álvaro A. Silva de Carvalho[2], Claudia Giovedi[2]**

[1] Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
eddy132@yahoo.com.br

[2] Laboratório de Caracterização de Materiais – Depto. de Tecnologia do Combustível – Centro Tecnológico da Marinha em São Paulo - CTMSP
Av. Prof. Lineu Prestes, 2468
05508-900 São Paulo, SP
giovedi@ctmsp.mar.mil.br

## ABSTRACT

Fiber-reinforced composite are an important class of engineering material. A relevant task of composite technology in order to produce materials for structures of high mechanical performance is to obtain the best carbon fiber. One of the main ways to produce carbon fibers of high Young`s modulus and tensile strength is to use as starting material polyacrylonitrile (PAN) fibers which after a rigorous and carefully thermal process become carbon fibers. Since some chemical modifications produced in the thermal treatment can be induced by ionizing radiation, the aim of this paper is to evaluate the effect of high electron beam (EB) doses on a commercial PAN fiber in order to evaluate the use of this technology as an alternative treatment to improve the properties and characteristics of the produced carbon fiber. The doses applied were: 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 MGy. The irradiation effects induced on the PAN fiber were evaluated by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and termogravimetry (TG). FTIR obtained data have shown that the main functional groups remain practically unchanged in the non-irradiated and irradiated samples. The single DSC exothermic peak obtained for non-irradiated sample, becomes a double peak after the irradiation, presenting lower initial and higher final temperatures for exothermic DSC curves. The enthalpy involved in the chemical reaction decreases for irradiated samples as compared with the non-irradiated PAN fiber. TG data have shown that irradiated samples start a decomposition process at lower temperatures compared to the non-irradiated sample.

## 1. INTRODUCTION

Carbon fibers are used as reinforcement material associated to epoxy matrices in high performance composites, which have different industrial and nuclear technology applications [1]. Carbon fibers of high Young`s modulus and tensile strength used for structures of high physical and mechanical performance are produced using as starting material polyacrylonitrile (PAN) precursors. These PAN homopolymer fibers are usually modified by suitable comonomers during the polymerization step. The main physical and mechanical characteristics of PAN precursors are: low stabilization temperature, extremely oriented molecular structure, light mass, inert biological and chemical properties and high corrosion resistance [2].

The conventional thermal process to obtain a carbon fiber from PAN precursors requires an oxidative stabilization stage and thereafter a carbonization process carried out in inert atmosphere at temperatures of about 2000 $^{o}$C. Since some chemical modifications produced in the thermal treatment also can be induced by ionizing radiation, this process can be use as an alternative technology to improve the physical and mechanical properties of the resulting carbon fiber [3].

The action of electron beam (EB) radiation on polymeric materials promotes mainly two processes: (a) cross-linking, that is the formation of chemical links between molecular chains, and (b) degradation or scission of polymeric chains, which destroys its molecular structure. These chemical transformations result in changes in the physical and mechanical properties of the polymers. Although these effects occur simultaneously, one plays a dominating role depending on the chemical structure of the polymer, radiation dose and overall experimental conditions [4].

The aim of this paper was to evaluate the changes induced by high EB doses on a commercial PAN fiber in order to evaluate the possibility to use this technology as an alternative process to improve the properties and characteristics of the produced carbon fiber.

## 2. EXPERIMENTAL

### 2.1. Samples

Commercial polyacrylonitrile fiber used as carbon fiber precursor was studied in this work.

### 2.2 EB irradiations

EB irradiations were carried out at the IPEN-CTR facilities using a 1.5 MeV and 37.5 kW Dynamitron Electron Accelerator model JOB-188. The irradiation conditions were: energy 0.569 MeV, electron-current 3.26 mA and dose rate 22.4 kGy $s^{-1}$. The overall doses were: 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 MGy. All the irradiations were carried out in air.

### 2.3 Fourier transform infrared analysis (FTIR)

Samples were prepared with KBr and the measurements were carried out with a spectrophotometer FTIR Nicolet 4700.

### 2.4 Thermal analysis (DSC and TG)

DSC measurements were carried out with a DSC823$^{e}$ from Mettler-Toledo in the temperature range from 25 to 400 ºC at a heating rate of 5 ºC $min^{-1}$ under dynamic nitrogen atmosphere of 50 mL $min^{-1}$ using samples of about 3.5 mg weight set in aluminum crucibles with pierced lid. TG curves were obtained using a TGA/SDTA851$^{e}$ thermobalance from Mettler-Toledo. Sample masses of about 5 mg were set in platinum open crucible and then heated from 25 to 1500 $^{o}$C at 10 ºC $min^{-1}$ under dynamic nitrogen atmosphere of 50 mL $min^{-1}$.

## 3. RESULTS AND DISCUSSION

The ionizing radiation induces significant color changes in the PAN fiber. The original fiber color was white, but this color changes gradually to intense gold-light brown, as a function of the irradiation dose. This color effect is also observed when PAN precursors are submitted to the stabilization oxidative step during the thermal treatment. It was also verified that the PAN fiber shrinks progressively during the irradiation. This behavior is avoided by stretching the PAN fibers before the stabilization thermal process.

Representative FTIR curves for non-irradiated and irradiated with 1.2 MGy samples are shown in Figure 1.

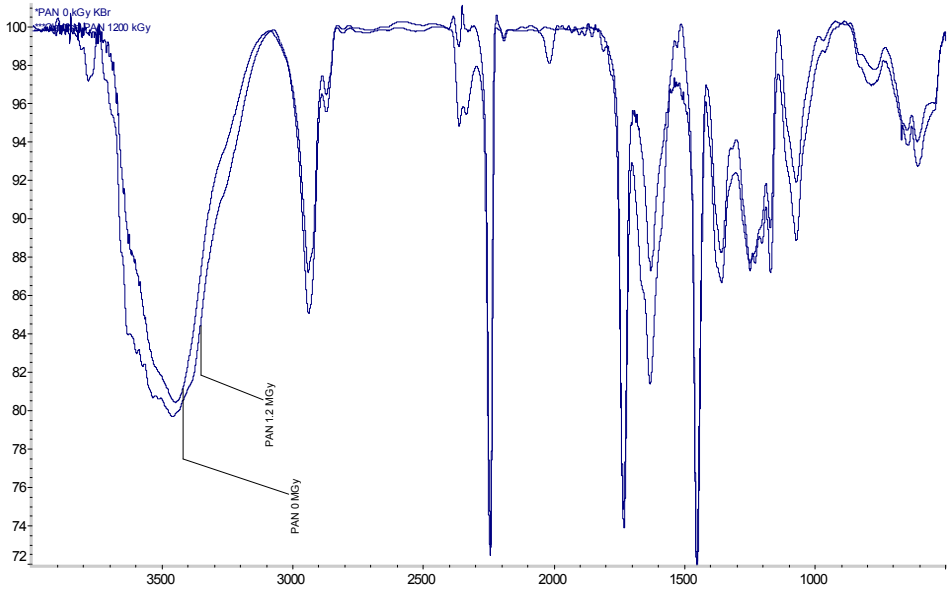


**Figure 1. FTIR curves for PAN fibers non-irradiated and irradiated with 1.2 MGy.**

FTIR data have shown that the main functional groups remain practically unchanged in the non-irradiated and in the irradiated samples. The main groups identified are: aliphatic hydrocarbons, nitriles, carboniles and esters [5]. The presence of aliphatic hydrocarbons and carboniles denotes that the commercial PAN fiber used in this paper contains other comonomers in its composition, besides of acrylonitrile. This is common in PAN fibers used as a precursor to produce carbon fiber by thermal treatment in order to control and promote the stabilization oxidative step.

The thermal behavior of the studied PAN fibers was evaluated by DSC and TG. Figure 2 presents representative DSC curves for some of the studied samples.

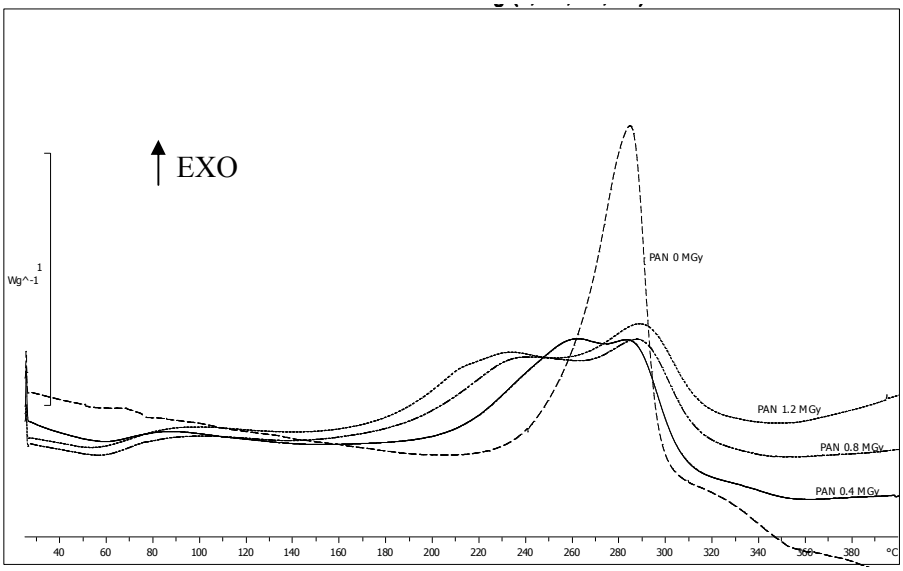


**Figure 2. DSC curves for PAN fibers non-irradiated and irradiated with 0.4, 0.8 and 1.2 MGy.**

In Figure 2, the exothermic curves show that, the irradiation process, produced significant changes on the thermal behavior of PAN fibers. DSC curve for non-irradiated sample presents a single peak. After the irradiation, the curves present a double peak, resulting in a lower initial peak temperature and a higher final peak temperature for the exothermic curve. The decrease of the initial peak temperature indicates that he EB irradiation produces new specimens which need less energy to react. By the other hand, the cross-linking effect induced by EB radiation promoted the increase of the final peak temperature. These two effects are induced simultaneously always that a polymeric material is under irradiation. However, one plays a dominating role depending on the chemical structure of the polymer, radiation dose and overall experimental conditions. The parameters of the DSC obtained curves are listed in Table 1. The values correspond to an average of five measurements carried out on each sample.

**Table 1. Experimental data obtained from DSC curves for non-irradiated and irradiated PAN fiber at different doses.**

| Sample | $T_{ip}$ [°C] | $T_p$ [°C] | $T_{fp}$ [°C] | $-\Delta H$ [J $g^{-1}$] |
|---|---|---|---|---|
| 0 MGy | 195 | 283 | 314 | 520 |
| 0.2 MGy | 164 | 277 | 325 | 498 |
| 0.4 MGy | 150 | 282 | 325 | 475 |
| 0.6 MGy | 140 | 285 | 334 | 471 |
| 0.8 MGy | 137 | 287 | 340 | 474 |
| 1.0 MGy | 145 | 288 | 340 | 434 |
| 1.2 MGy | 149 | 288 | 344 | 433 |

$T_{ip}$: initial peak temperature; $T_p$: peak temperature; $T_{fp}$: final peak temperature; $\Delta H$: enthalpy.

From Table 1, it is possible to observe the occurrence of an enlargement of the temperature range for the exothermic peak as a function of the radiation dose. However, the effect is most severe for the initial peak temperature. For the non-irradiated fiber, the difference between the initial and final peak temperature is 119 $^{o}$C, and this difference increases to 175 $^{o}$C for the PAN fiber irradiated with 0.4 MGy. The maximum difference was registered for the PAN fiber irradiated with 0.8 MGy and it reaches the value of 203 $^{o}$C. For higher doses the value remains around 195$^{o}$C. The reduction observed for the initial temperature of the exothermic reaction is important because it reduces the entropic relaxation of molecules, which translate into an improvement of the tensile properties of the resulting carbon fiber [6].

Table 1 also shows that the enthalpy involved in the reaction decreases progressively as a function of the radiation dose. The global decrease is about 20% for the sample irradiated with 1.2 MGy compared to the non-irradiated PAN fiber. This behavior also shows the occurrence of modifications in the PAN fiber, induced by the ionizing radiation, probably due to the generation of new specimens which need less energy to react.

TG curves presented in Figure 3 also show the occurrence of structural changes induced by ionizing radiation in the PAN fiber.

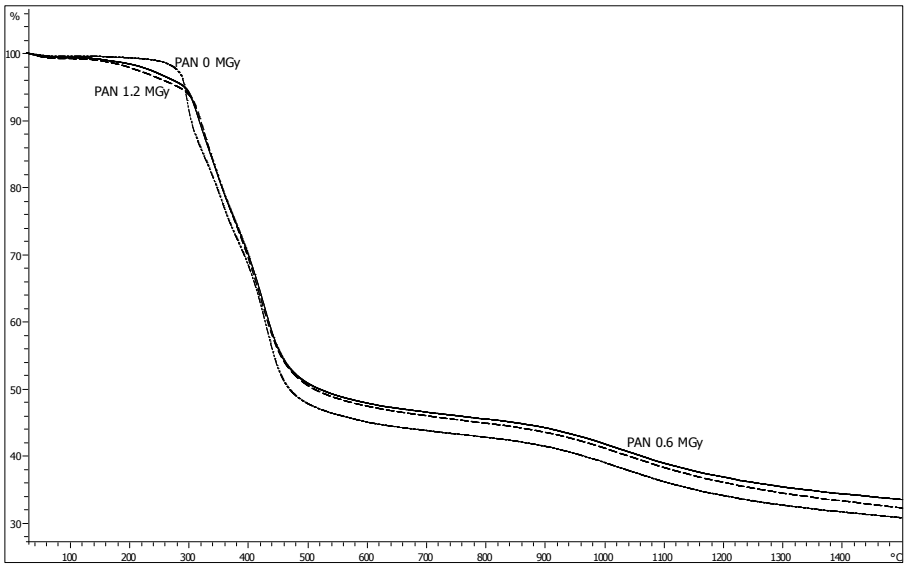


**Figure 3. TG curves for PAN fibers non-irradiated and irradiated with 0.6 and 1.2 MGy.**

The main difference observed in TG curves is in the initial decomposition temperature: irradiated samples start the decomposition process about 60 $^{o}$C lower than for the non-irradiated sample. The thermal behavior at high temperatures is in all cases similar. An important difference is observed in the loss mass: irradiated samples react producing more residues, and the difference is about 4 %. These facts also show that the ionizing radiation induced the formation of new specimens which react in a different way producing different kinds and amount of residues.

## 4. CONCLUSIONS

FTIR results shows that the main functional groups present in non-irradiated samples remain practically unchanged after the irradiation process, independently of the radiation dose applied. However, the thermal behavior studied by DSC presented significant changes for the exothermic peak: a split, an enlargement of the temperature range and a decrease of the associated enthalpy. These results indicate the possibility that the irradiation process, in the studied conditions, promoted in the PAN fiber both scission and cross-linking of the polymeric chains without destructing the basic structure. These observations are supported by TG data which show that irradiated samples start its decomposition process at lower temperature compared to the non-irradiated sample, but the global thermal behavior is very similar.

The enlargement of the temperature range verified for DSC curves shows that, in the future, the EB irradiation processing can be associated to a thermal treatment in order to reduce the energy spent in this process and produce carbon fiber with better mechanical properties.

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