THERMAL ANALYTICAL EVALUATION ON POLYACRYLONITRILE FIBER IRRADIATED WITH ELECTRON BEAM AT HIGH DOSES

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Abstract

Polyacrylonitrile (PAN) fiber is the most important precursor to obtain carbon fiber. EB radiation induces structural changes in PAN fibers improving the properties of resulting carbon fibers. Therefore, the aim of this paper was to evaluate the thermal behavior of a PAN irradiated up to 2.0 MGy. The evaluations were made by DSC and TG. FTIR data have shown that the PAN structure remains unchanged after irradiation. DSC data have shown that the exothermic reaction occurs at a higher temperature interval with a lower energy. TG evaluations have shown that PAN fibers, at highest dose, presented no drastic degradation.

Key-words: polyacrylonitrile, electron beam, thermal behavior.

1. INTRODUCTION

Carbon fibers are used as reinforcement material associated to epoxy matrices in high performance composites. The major structural applications are in aeronautic, automotive, and also nuclear technology applications [1]. Carbon fibers with high tensile strength and modulus used are produced using polyacrylonitrile (PAN) precursors. These PAN homo-polymer fibers are usually modified by suitable co-monomers during the polymerization step [2].

The conventional process to obtain a carbon fiber from PAN is a long and expensive thermal process. Since some chemical and structural changes 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].

EB radiation induces on polymers mostly two effects: cross-linking and degradation. Although these effects occur simultaneously, one plays a dominating role depending mainly on their chemical structure [4].

Therefore, the aim of this paper was to evaluate the thermal behavior of a PAN irradiated up to 2.0 MGy, and also to evaluate the changes induced on a commercial PAN fiber in order to determine the possibility of using this technology as an alternative process to improve the properties and characteristics of the produced carbon fiber.

2. EXPERIMENTAL

2.1. PAN samples

Commercial polyacrylonitrile PAN fiber used as carbon fiber precursor was studied.

2.2 EB irradiations

EB irradiations were carried out at the CTR-IPEN using the Dynamitron Electron Accelerator model JOB-188, 1.5 MeV and 37.5 kW. The irradiation conditions were: energy 0.569 MeV, electron-current 3.26 mA and dose

rate 22.4 kGy s^{-1}. The doses were: 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8 and 2.0 MGy. All the irradiations were carried out in air.

2.3 Fourier transform infrared analysis (FTIR)

Samples were analyzed as KBr pellets using a FTIR Nicolet 4700 spectrophotometer.

2.4 Thermal analysis (DSC and TG)

Differential scanning calorimetry (DSC) measurements were carried out with a DSC823^e from Mettler-Toledo in the temperature range from 25ºC to 400ºC at a heating rate of 5ºC min^{-1} under dynamic nitrogen atmosphere. Thermogravimetry (TG) experiments were carried out using a TGA/SDTA851^e thermo-balance from Mettler-Toledo.

3. RESULTS AND DISCUSSION

FTIR data have shown that the main functional groups remain practical unchanged in the irradiated samples as compared with non-irradiated samples. The main groups identified are: aliphatic hydrocarbons, nitriles, carboniles and esters [5]. The presence of aliphatic hydrocarbons and carboniles shows that the commercial PAN fiber used in this paper contains other comonomers in its composition, besides of acrylonitrile.

Figure 1 presents representative DSC curves for some of the studied samples.

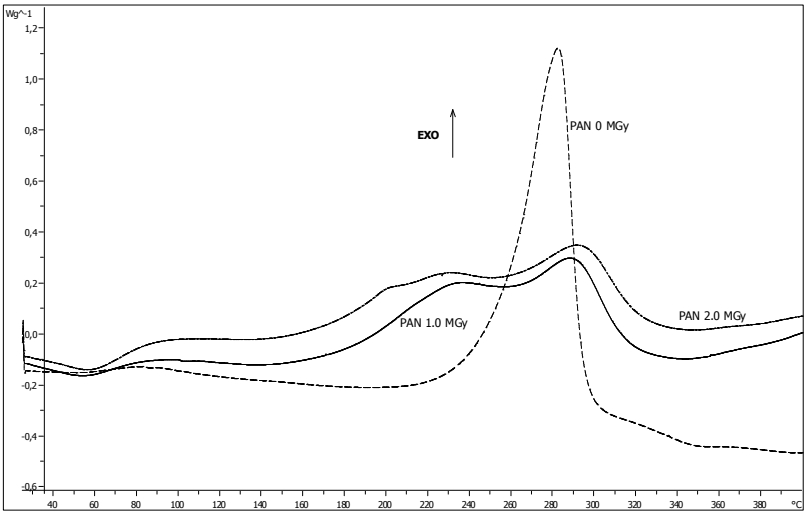

Figure 1. DSC curves for PAN fibers non-irradiated and irradiated at different doses.

In Figure 1, the exothermic curves show that, the EB radiation produced significant changes on the thermal behavior of PAN fibers. DSC curve for non-irradiated sample presents a single peak and 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 radiation produces new

specimens which need less energy to react. In the other hand, the cross-linking effect induced by EB radiation promoted the increase of the final peak temperature.

DSC parameters values for all studied samples are given in Table 1.

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]	-ΔH [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
1.4 MGy	137	288	349	468
1.6 MGy	136	288	347	453
1.8 MGy	133	290	348	430
2.0 MGy	134	291	345	401

T_{ip}: initial peak temperature; T_p: peak temperature; T_{fp}: final peak temperature; Δ*H*: enthalpy.

From Table 1, it was evaluated an enlargement of the temperature range for the exothermic peak as a function of the irradiation dose and this effect is most severe for the initial peak temperature. For the non-irradiated fiber samples, the difference between the initial and final peak temperature is about 119°C, and this difference increases to 175°C for the PAN fiber irradiated at 0.4 MGy. The maximum difference of 203°C was registered for the PAN fiber irradiated at 0.8 MGy. For higher doses the value remains unchanged at about 195°C. The reduction of the initial temperature of the exothermic reaction is important because it reduces the entropic relaxation of molecules, which produce an improvement of the tensile properties for the resulting carbon fiber [6].

Table 1 also shows that the enthalpy decreases progressively as a function of the applied dose, and this decrease is about 20% for the sample irradiated at 1.2 MGy. These radiation modifications probably are due to the generation of new specimens which need less energy to react.

The TG data have shown that decomposition temperature, in irradiated samples, started at about 60 °C lower than for the non-irradiated sample. The thermal behavior at higher temperatures is, in all cases, similar, and the loss mass was in the range of about 4% in the irradiated samples.

4. CONCLUSIONS

FTIR results show that the main functional groups present in non-irradiated samples remain practical unchanged after the irradiation, independently of the radiation dose. However, the thermal behavior studied by DSC presented significant changes for the exothermic peaks obtained for irradiated samples, and 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 some degree of both scission and cross-linking of the polymeric chains without destructing the basic chemical structure. These observations are supported by TG data which have shown that irradiated samples start its decomposition process at lower temperature compared to the non-irradiated sample, a similar thermal behavior at higher temperatures, and also a small difference in the loss mass without a drastic of degradation, even at the highest dose of 2.0 MGy.

The enlargement of the temperature range verified in the DSC curves have shown that the EB radiation processing can be associated to a thermal treatment in order to reduce the energy spent in thermal treatment processes, producing carbon fiber with better mechanical properties.

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