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EVALUATION OF KINETIC PARAMETERS OF PAN FIBER MODIFIED BY ELECTRON BEAM RADIATION

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ABSTRACT

Carbon fibers used for structural application are about 90% based on polyacrylonitrile (PAN) precursors due to their physical and mechanical properties. The thermal process is the conventional way to obtain a carbon fiber from PAN precursors. However, the use of ionizing radiation is given as an alternative technology to improve the physical and mechanical properties of the resulting carbon fiber. The aim of this paper was to obtain kinetic parameters (activation energy, conversion and isoconversion data) from DSC curves of PAN fibers irradiated with electron beam (EB) at different doses using the software Model Free Kinetics. The EB irradiation doses applied were: 0.2; 0.4; 0.6; 0.8; 1.0 and 1.2 MGy. The effect of ionizing radiation was evaluated by the thermal behavior of PAN precursors studied by Differential Scanning Calorimetry (DSC), which presents an exothermic peak in the range of 200°C to 400°C, depending on the experimental conditions of the DSC measurements. The obtained results showed that non-irradiated PAN fiber needs higher temperatures or longer reaction times to reach the same conversion degrees of the irradiated PAN fibers. Among the irradiated fibers, the reaction times decrease as a function of the radiation dose applied. However, the most important changes were observed for doses up to 0.4 MGy. The experimental results indicate that the EB radiation induces modification in the PAN fibers, which became them more liable in the oxidation process.

1. INTRODUCTION

Carbon fibers with high Young`s modulus and tensile strength, used for structural purposes, are made from polyacrylonitrile (PAN) based precursors [1]. The conventional thermal process to produce carbon fibers from PAN fibers involves three thermal steps: the first one is the stabilization step carried out in air at about 220 °C, the second one, the carbonization step, carried out in inert atmosphere at about 1000 °C, and the graphitization at about 2000 °C. The radiation process is given, in literature, as an alternative technology to the thermal process in order to improve the physical and mechanical properties of the resulting carbon fiber [2].

DSC curves of PAN precursors presented an exothermic peak between 200-400 ^{o}C, depending on the comonomer composition, the molecular weight of the PAN precursor polymer, the polymerization reaction and the alternative treatments used during its processing [3].

The kinetic of a chemical reaction can be studied using DSC and thermogravimetry (TG) measured parameters by means of a special software developed for this end [4]. In this way, the software Model Free Kinetics can be applied using the measured DSC parameters obtained at different heating rates in order to determine the reaction conversion at different isothermal temperatures or heating rates [5]. Model Free Kinetics is based on the realization that the function of conversion degree α, and the activation energy indeed depend on the reaction conversion, but that they are always the same at a particular conversion degree, independent of the heating rate used. Because of this, they can be calculated from several measurements carried out at different heating rates.

The aim of this paper was to obtain kinetic parameters, such as activation energy, conversion and isoconversion data of PAN fibers irradiated with electron beam (EB) at different doses using DSC obtained parameters at different heating rates.

2. EXPERIMENTAL

2.1. Samples

In this work, commercial polyacrylonitrile PAN fiber applied as carbon fiber precursor was studied.

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. 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. The EB irradiation was carried out in air.

2.3 Differential Scanning Calorimetry

DSC measurements were carried out on a DSC823^{e} from Mettler-Toledo. Sample masses of about 4 mg were set in aluminum crucible with pierced lid and then heated from 25 to 400 ^{o}C at heating rates of: 5, 10 and 15 ^{o}C min^{-1}, under dynamic nitrogen atmosphere of 50 mL min^{-1}. Model Free Kinetics (MFK) software was used for DSC experimental data of each sample to obtain kinetic parameters related to them. The activation energy, conversion and isoconversion data were obtained for each studied sample. The samples were rigorously prepared using the same procedure in order to assure the best reproducibility data.

3. RESULTS AND DISCUSSION

DSC curves of non-irradiated PAN fibers exhibit a sharp exothermic peak between 220 ^{o}C and 320 ^{o}C depending on the heating rate used. This peak corresponds to dehydrogenation, oxidation, cross-linking and mainly cyclization reactions. These last two reactions are responsible for the nitrile group oligomerization and represent the most important step in the conversion of PAN precursors to carbon fibers [6]. DSC curves obtained for irradiated fibers showed the enlargement of the temperature range for the exothermic peak as a function of the radiation dose. After the irradiation, the single peak obtained for non-irradiated samples becomes a double peak, resulting in lower initial peak temperatures and higher final peak temperatures for the exothermic DSC curve.

Previously to the application of the MFK software used to obtain kinetic parameters, it was checked out the variation of reaction enthalpies at heating rates from 2.5 to 40 $^{o}C\ min^{-1}$ in order to verify if the enthalpy values remain constant. It was observed that in the range of 2.5 to 10 $^{o}C\ min^{-1}$ the enthalpy values, for all studied samples, were constant to within ±5%, so, this heating rate interval was used for the application of the software. Figure 1 shows the curves obtained for non-irradiated and irradiated with 1.2 MGy samples at different heating rates: 2.5, 5 and 10 $^{o}C\ min^{-1}$ to illustrate the observed behavior.

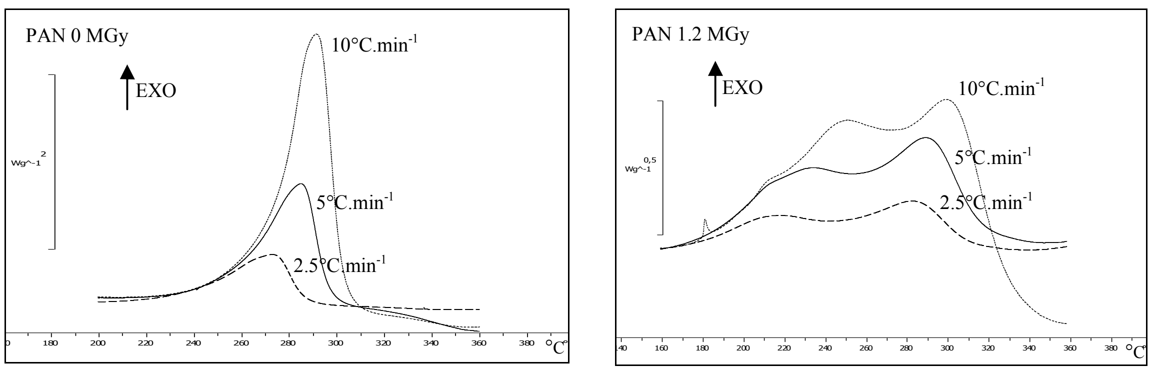

Figure 1: DSC curves for PAN 0 MGy e 1.2 MGy at different heating rates (2.5, 5 and 10^{o} C min^{-1}).

From these DSC curves, for each studied sample, it was obtained the correspondent activation energy curve as a function of α, and the conversion and isoconversion tables and plots by MFK. Figure 2 shows the curves of activation energy as a function of α obtained by the MFK software for non-irradiated and irradiated with 1.2 MGy samples.

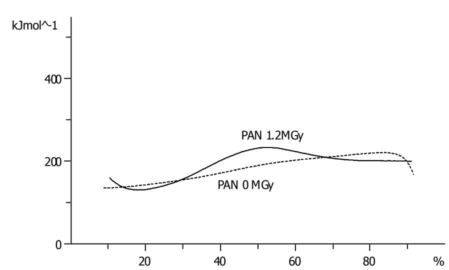

Figure 2: Activation energy as a function of α obtained by MFK for PAN 0 MGy e 1.2 MGy.

Figure 2 shows that there is a gradual change in the activation energy curves as a function of α in the interval of radiation dose applied. These curves became sharper with the increase of the radiation dose. From activation energy curves as a function of α, it was possible to obtain data for conversion and isoconversion reaction.

The results show that non-irradiated PAN fiber needs higher temperature or bigger reaction time to reach the same conversion degree of the irradiated PAN fibers. Among the irradiated fibers, the reaction times decrease as a function of the radiation dose applied. However, the most important changes were observed for doses up to 0.4 MGy.

The validation of kinetic data was checked by means of isothermal experiments carried out by DSC using the conditions calculated by MFK. The experimental conditions and the obtained results are shown in Table 1.

Table 1: Experimental data from DSC simulated isothermal experiments based on MFK data.

Sample	Isotherm Temperature [ºC]	Isotherm Time [minutes]	$-\Delta H_{MFK}$ [J g^{-1}]	$-\Delta H_{exp.}$ [J g^{-1}]	Deviation [%]
0 MGy	233	50	248	262	+6
0.2 MGy	227	50	248	256	+3
0.4 MGy	225	50	237	257	+8
0.6 MGy	222	50	239	257	+7
0.8 MGy	224	50	232	236	+2
1.0 MGy	221	50	217	200	-8
1.2 MGy	217	100	217	189	-3

Table 1 shows that the deviation obtained comparing the enthalpy values from the conversion and isoconversion tables calculated by MFK to the experimental values from isothermal experiments were lower than ±10%. This confirms the usefulness of the MFK software in the evaluation of the kinetic behavior.

4. CONCLUSIONS

DSC curves obtained for all irradiated fibers showed the enlargement of the temperature range for the exothermic peak as a function of the radiation dose. This peak corresponds to dehydrogenation, oxidation, cross-linking and mainly cyclization reactions. Cross-linking and cyclization are responsible for the nitrile group oligomerization and represent the most important step in the conversion of PAN precursors to carbon fibers. Then, the enlargement of the temperature range and the changes observed in activation energy curves as a function of α show that the irradiation process can be useful, in the future, to improve the characteristics of the carbon fibers produced from PAN precursors. The obtained results in the experiments carried out based in the parameters calculated by MFK confirmed that kinetic data obtained by DSC measurements are an important tool to evaluate the modifications induced by ionizing radiation on PAN fibers thermal behavior.

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