KINETIC BEHAVIOR OF IRRADIATED POLYACRYLONITRILE FIBER

Claudia Giovedi [1], Clarissa P. Z. Arruda [1], Ana Claudia V. Carolino [1], Luci D. B. Machado [2], Eddy S. Pino [2]

[1] Centro Tecnológico da Marinha em São Paulo (CTMSP), São Paulo, Brazil, giovedi@ctmsp.mar.mil.br
[2] Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN-SP), São Paulo, Brazil, eddypino132@yahoo.com.br

Abstract

The production of carbon fiber from PAN precursors involves a long and expensive thermal process. However, in the literature, the ionizing radiation is given as an alternative technology to improve the properties of the resulting carbon fiber. The aim of this paper is to obtain kinetic parameters from DSC curves of PAN fibers irradiated with electron beam (EB) at different doses up to 2.0 MGy using the software Model Free Kinetics. The obtained results have shown that non-irradiated PAN fiber needs higher temperatures or longer reaction times to reach the same conversion degrees of the irradiated PAN fibers.

Key-words: polyacrylonitrile, electron beam, kinetic.

1. INTRODUCTION

Carbon fibers are used in a wide variety of applications, such as in the automobile and aeronautic industry, manufacture of medical instruments, and also nuclear technology applications. Nowadays about 90% of available carbon fibers are processed from polyacrylonitrile (PAN) based precursors [1] due to their physical and mechanical properties. The production of carbon fiber from PAN precursors involves a long and expensive thermal process. However, in the literature, the ionizing radiation is given as an alternative technology to improve the properties of the resulting carbon fiber produced from PAN precursors [2].

The thermal behavior of PAN precursors can be studied by Differential Scanning Calorimetry (DSC). DSC curves of PAN precursors present an exothermic peak between 200-400^{o}C depending on different factors, such as comonomer composition and molecular weight of the PAN precursor polymer [3].

The kinetic of a chemical reaction can be studied using DSC measured parameters and applying the software Model Free Kinetics [4]. This software can be applied using the measured DSC parameters obtained at different heating rates in order to determine the reaction conversion at different isothermal temperatures [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 is to obtain kinetic parameters, such as 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.

2. EXPERIMENTAL

2.1. Samples

Commercial polyacrylonitrile fiber applied as carbon fiber precursor was used in this paper.

2.2. EB irradiation conditions

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 EB radiation doses studied were: 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8 and 2.0 MGy. EB irradiations were carried out in air.

2.3. Differential Scanning Calorimetry (DSC)

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°C at heating rates of: 2.5, 5, 10 and 15°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. The kinetic parameters were obtained from DSC curves carried out at different heating rates.

3. RESULTS AND DISCUSSION

Non-irradiated PAN fiber presents a DSC curve with a sharp exothermic peak in the range from 220°C to 320°C depending on the heating rate used. On the other hand, 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 process, DSC curves present a double peak, resulting in lower initial peak temperatures and higher final peak temperatures for the exothermic DSC curve compared to the one obtained for non-irradiated sample.

Initially, it was checked out the variation of reaction enthalpies at heating rates from 2.5 to 40 °C min^{-1} in order to verify if the enthalpy values remain constant. It was observed that in the range of 2.5 to 15°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 MFK. Figure 1 shows the curves obtained for non-irradiated and irradiated with 2.0 MGy samples at different heating rates.

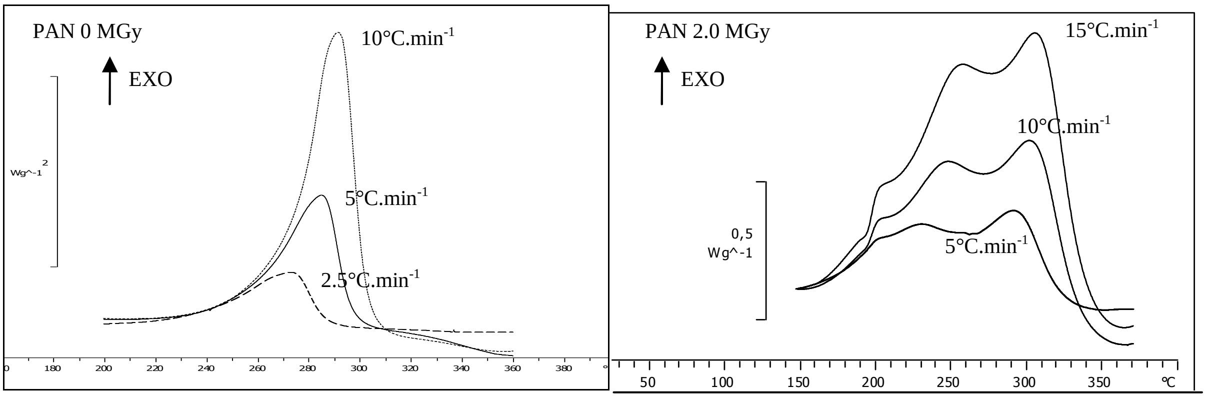

Figure 1: DSC curves for PAN 0 MGy and 2.0 MGy at different heating rates.

From DSC curves at different heating rates, 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 samples at different doses.

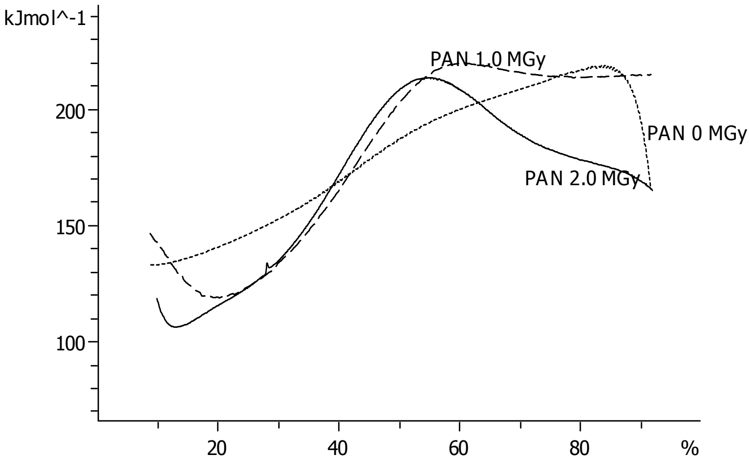

Figure 2: Activation energy as a function of α obtained by MFK for PAN fibers non-irradiated and irradiated at 1.0 and 2.0 MGy.

Figure 2 shows that the profile of the activation energy curve as a function of the conversion degree for the samples irradiated at different doses changes considerably.

Based on the results calculated by MFK, isothermal experiments were carried out by DSC in order to check the obtained results. The experimental conditions and the obtained results are shown in Table 1. The experimental and predict by MFK values present deviation within ±10%, which is in a good agreement for this kind of study.

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

Sample	Isotherm Temp. [ºC]	Time [minutes]	- ΔH_{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
1.4 MGy	212	50	230	262	+12
1.6 MGy	216	50	239	243	+2
1.8 MGy	220	50	216	215	-0.4
2.0 MGy	212	50	207	234	+11

4. CONCLUSION

The obtained results have shown 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. Significant changes have been observed in the profile of the activation energy curve as a function of the conversion degree for the samples irradiated at different doses.

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 to improve the characteristics of the carbon fibers produced from PAN precursors. The obtained experimental data and the data 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 and its thermal behavior.

ACKNOWLEDGEMENTS

The authors acknowledge FAPESP and CNPq for financial support, the CTR-IPEN for the use of the radiation infrastructure and the CTMSP for the permission granted to publish this paper.

REFERENCES

[1] BANSAL, R.C.; DONNET, J. B. Fibers. Marcel Dekker Inc., New York, 1994.

[2] TURI, E.A. Thermal Characterization of Polymeric Materials. Academic Press, Orlando, p. 776-779, 1981.

[3] CATTA PRETA, I. F.; SAKATA, S. K.; GARCIA, G.; ZIMMERMANN, J. P.; GALEMBECK, F.; GIOVEDI, C. Thermal behavior of polyacrylonitrile polymers synthesized under different conditions and comonomer compositions. **Journal of Thermal Analysis and Calorimetry**, v. 87, p. 657-659, 2007.

[4] VYAZOVKIN, S.; GORYACHKO, V. Potentialities of software for kinetic processing of thermoanalytical data by the isoconversion method. **Thermochimica Acta**, v. 194, p. 221-230, 1992.

[5] BROWN, M. E. Some kinetic aspects of thermal analysis. **Journal of Thermal Analysis and Calorimetry**, v. 49, p. 17-32, 1997.