Advanced stabilization of PAN fibers for fabrication of carbon fibers by e-beam irradiation

Joon-Pyo Jeun [a,b], Du-Young Kim [a], Hye-Kyoung Shin [a], Jung-Ki Park [b], Phil-Hyun Kang [a*]
[a]*Research Division for Industry & Environment, Korea Atomic Energy Research Institute, 1266 Sinjeong-dong, Jeongeup-si, Jeollabuk-do 580-185, Korea*
[b]*Department of Chemical & Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 291 Deahak-ro, Yuseong-gu 305-701, Korea*
[*]*Corresponding author: phkang@kaeri.re.kr*

1. Introduction

In recent years, the carbon fiber industry has been growing rapidly to meet the demand from efferent industries such as aerospace, military, turbine blades, light weight cylinders and pressure vessels [1].

Generally, carbon fibers are manufactured by a controlled pyrolysis of stabilized precursor fiber such as polyacrylonitrile (PAN). In the stabilization step, the linear PAN molecules are first converted to cyclic structure. However, cyclization is a very complicated process and there are still differences of opinion on the reaction mechanisms [2-5].

Photo-induced crosslinking and stabilization of PAN via ion beam, X-ray, gamma ray and UV irradiation has been reported in the literature [6-8]. However, the process required a long stabilization time.

In this work, a new and highly effective method of pretreatment PAN precursor fiber was described. The effect of the e-beam on the stabilization process of the fibers was investigated using differential scanning calorimeter (DSC) and X-ray diffraction (XRD) measurement.

2. Experimental

2.1 Material

PAN fiber was purchased from Anshan East Asia Carbon Fiber Co., Ltd, China. Additional details on the characteristics of the fiber can be found in the technical documents.

2.2 Stabilization

PAN fibers were stabilized with an e-beam accelerator. The accelerating voltage was 1.14 MeV with a beam current of 30 mA. The samples were irradiated at room temperature in an air atmosphere.

2.3 Characterization

DSC experiments were carried out on a DSC Q100 instrument. Calefactive scans were conducted over a temperature range of 40-350°C. All measurements were carried out at a heating rate of 10°C /min under an air atmosphere.

The XRD patterns of the e-beam-induced stabilized PAN fibers were used to determine the stabilized structures. XRD measurements were performed on a RIGAKU, D/MAX-2500 with Cu Kα radiation generated at 40 kV and 30 mA. The samples were prepared by compressing the randomly aligned short fibers into thin discs. The scanning speed was 6°/min with a scanning step of 0.02°.

The tensile strength tests were carried out on single fiber- samples using the ISO 11566 standard procedure. The test apparatus consisted of an Instron 5569 tensile tester equipped with a load cell of 2.5 N. At least 30 tensile tests were performed on each fiber type and the results were then averaged.

3. Results and Discussion

The PAN precursor fiber exhibited a sharp single exothermic peak, whereas the stabilized PAN fibers by e-beam irradiation showed a doublet exothermic peak as shown in Fig. 1. The first exothermic peak at the lower temperature mainly corresponds to the cyclization reactions. This peak gradually shifted to a lower temperature with increasing radiation dose, as the heat evolved significantly decreased. The second peak is attributed to the oxidation reactions, which are always controlled by the diffusion rate of oxygen, generally occurring behind cyclization reaction. As a result, we could conclude that stabilization by e-beam irradiation decreased the activated energy for thermal reactions of stabilized PAN fibers by changing into their cyclized structure with increasing radiation dose

The X-ray diffraction patterns of the original PAN fiber and the stabilized PAN fibers at a varying radiation doses was shown in Fig. 2. The original PAN fiber produced a strong diffraction peak centered at 16~17°2Θ, while a weak diffraction peak was centered at 2Θ=29.3° prior to stabilization by e-beam irradiation. These two peaks correspond to the (100) and (110) crystallographic planes of the original PAN fiber. The intensities of the two original peaks for e-beam-induced stabilized PAN fibers are weaker than those of PAN precursor fiber. However, the remarkable change in the (100) diffraction peak makes it easily possible to evaluate the degree of stabilization of the PAN fibers.

In order to verify the feasibility of the stabilization approach, we measured the tensile strength of the stabilized PAN fibers. As shown in Fig. 3, tensile strength decreases with increasing the radiation dose. This decrease in strength is due to the loss in inter-chain cohesive energy as a result of cyclization reactions. If cyclization reactions of PAN fibers occur, the tensile strength of the stabilized PAN fibers decrease with

increasing a degree of stabilization due to free shrinkage. Therefore, it was concluded that tensile strength of stabilized fibers decrease with increasing the radiation doses.

4. Conclusions

This study establishes the feasibility of producing carbon fibers from e-beam-induced stabilized PAN fibers. In DSC analysis, stabilized fibers by e-beam irradiation showed a doublet exothermic peak whereas PAN precursor fiber exhibited a very sharp exothermic peak. This doublet peaks shifted at much lower temperature, and showed broader exothermic peak with an increase of radiation dose. In XRD measurement, the intensity at 16~17°2Θ of PAN fibers exhibit the strongest diffraction peak whose intensities decreased gradually during stabilization. However, Tensile strengths of stabilized fibers decreased with an increase of radiation doses.

ACKNOWLEDGEMENT

This research was supported by Nuclear R&D program through the Korea Science and Engineering Foundation funded by the Ministry of Education, Science and Technology, Korea.

REFERENCES

[1] T. Roberts, The Carbon Fiber Industry: Global Strategic Market Evaluation 2006-2010; Materials Technology Publications: Watford, UK, 2006.
[2] J. Schurz, Discoloration effects in acrylonitrile polymers, J. Polym. Sci., Vol. 28, p. 438, 1958.
[3] P. J. Goodhew, A. J. Clarke, J. E. Bailey, A review of the fabrication and properties of carbon fibers, Mater. Sci. Eng., Vol. 17, p. 3, 1975.
[4] A. J. Clarke, J. E. Bailey, Oxidation of acrylic fibers for carbon fibre formation, Nature, Vol.243, p. 146, 1973.
[5] A. Gupta, New aspects in the oxidative stabilization of PAN-based carbon fibers, Carbon, Vol. 34, p. 1427, 1996.
[6] Y. A. Aggour, M. S. Aziz, Degradation of polyacrylonitrile by low energy ion beam and UV radiation, Polym. Test, Vol. 19, p. 261, 2000.
[7] L. G. Cardoso dos Santos, Y. Kawano, Degradation of polyacrylonitrile by X-ray radiation, Polym. Degrad. Stab., Vol. 44(1), p. 27, 1994.
[8] D. J. T. Hill, A. P. Lang, J. H. O'Donnell, P, J, Pomery, The effect of gamma radiation on polyacrylonitrile, Polym. Degrad. Stab., Vol. 38(3), p.193, 1992.

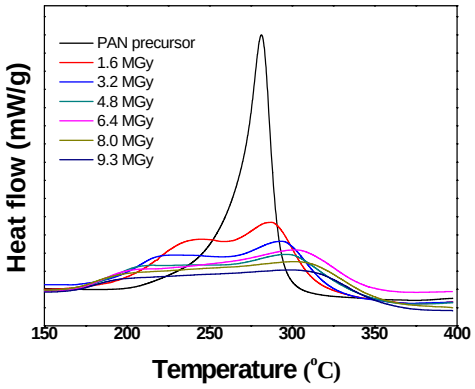

Fig. 1. DSC curves of the PAN precursor fiber and the PAN fibers stabilized by e-beam irradiation at various dose.

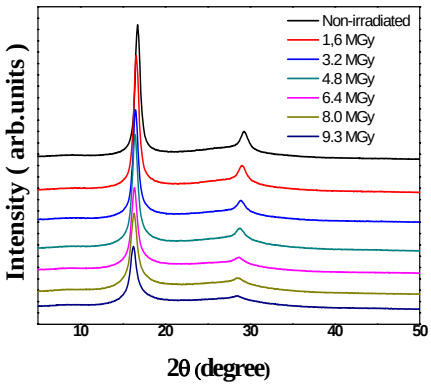

Fig. 2. XRD patterns of the PAN precursor fiber and the PAN fibers stabilized by e-beam irradiation at various dose.

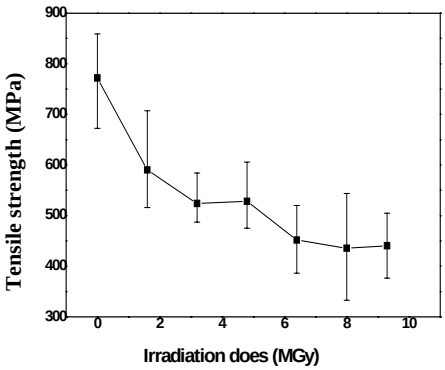

Fig. 3. Tensile strength of PAN fibers stabilized at various irradiation dose.