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An overview of new oxidation methods for polyacrylonitrile-based carbon fibers

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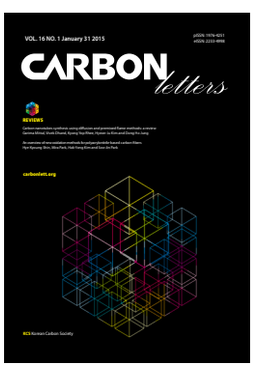

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Abstract

The process of oxidizing polyacrylonitrile (PAN)-based carbon fibers converts them into an infusible and non-flammable state prior to carbonization. This represents one of the most important stages in determining the mechanical properties of the final carbon fibers, but the most commonly used methods, such as thermal treatment (200°C to 300°C), tend to waste a great deal of process time, money, and energy. There is therefore a need to develop more advanced oxidation methods for PAN precursor fibers. In this review, we assess the viability of electron beam, gamma-ray, ultra-violet, and plasma treatments with a view to advancing these areas of research and their industrial application.

Key words: carbon fibers, polyacrylonitrile, electron beam, gamma-ray, ultra-violet, plasma

1. Introduction

Carbon fibers are thin filament materials that contain over 92 wt% carbon [1-3], which gives them high strength, stiffness, temperature resistance, thermal conductivity, and good chemical resistance in addition to light weight and low density when compared to most metals and ceramics [4-6]. As a result, carbon reinforced materials have been widely used in a variety of aerospace, automotive and marine applications, as well as various machine parts, wind turbine blades, high-grade sporting goods, etc. [7-9]. Carbon fibers can be classified based on how the fibers are derived, from polyacrylonitrile (PAN), pitch, rayon, or gaseous precursors [10-15]. PAN has tended to be the most widely used precursor for high-performance carbon fibers [16-22]. Most useful carbon materials have also been modified by several surface treatments, such as anodic oxidation [23], plasma [24,25], oxyfluorination [26], ozonization [27], or fluorination [28], Ar ion beam [29-31], several metal coatings [32-34], chemical treatments [35,36]. These treatments enable or enhance function and performance in real industrial applications, including adsorption [37], toxic removal [38,39], catalysis [40-42], adhesion or composites [43,44], electrochemistry [45-47], and so on.

The precursor PAN fiber is an atactic and linear polymer with C≡N bonding, as shown in Fig. 1. This C≡N bond means that the PAN precursor has a glass transition temperature (Tg) of around 120°C, and therefore typically decomposes before melting, meaning that it is essential that it first be stabilized prior to carbonization. Typically, this is accomplished by oxidation of PAN by thermal treatment in air at 200°C to 300°C (Fig. 2), which changes it into infusible and non-flammable fibers with a predominance of cyclic or ladder structures (Fig. 3) that prevent melting during subsequent carbonization [48-56].

Oxidation is therefore one of the most important processes in determining the mechanical properties of the carbon fiber; in this regard, most past reviews have focused on the thermal oxidation of PAN. For example, Rahaman *et al*. [57] briefly reviewed heat treatments for the conversion of PAN precursor fibers into carbon fibers, while Liu and Kumar [58] provided a more detailed report pertaining to recent developments in carbon fiber technology and demon-

strated the relationship between the processing conditions and the chemical/physical structure and tensile properties. However, thermal stabilization not only requires long periods of time (2-3 h), but also has high cost and energy consumption [59]. This has led to the development of advanced methods for oxidizing PAN precursor fibers based on various forms of radiation, which induce a change in the polymer structure, but these still need further improvement to make them more convenient and eco-friendly.

In this review, we summarize the progress that has been made in the various radiation oxidation processes for PAN precursor fibers, and provide some details as to the preparation and characterization of PAN fibers prepared by these methods.

2. Radiation Induced Stabilization of PAN Fibers

2.1. Oxidation by electron beam irradiation

Electron beam irradiation (EBI) is ionizing radiation process performed by a linear accelerator, and has been used industrially ever since it was first applied to the crosslinking of polyethylene wire insulation in the late 1950s. In more recent years, the number of electron accelerators has grown to exceed 1500, as they are now widely used for a range of scientific and industrial applications [60]. Generally speaking, electron beam (EB) accelerators can be divided into three broad categories, based on their energy output [61]. Low-energy EB accelerators (120-300 keV) are most commonly used for adhesives, coatings for paper, multilayer packaging, and the surface grafting of membranes [62]. Mid-energy EB accelerators (300 keV to 5 MeV) are utilized for the polymerization of monomers, the grafting of monomers onto polymers, the cross-linking of polymers, the degradation of polymers and fiber modification [63-76]. Finally, high-energy (5-10 MeV) EB accelerators are used for the sterilization of medical devices, pharmaceutical and biological products, bio-ethanol products, and the treating of industrial effluent [60,65,77-101]. Through careful selection and control over the EBI conditions used for modifying polymer materials, physical, chemical, and biological properties can be improved without the use of a solvent. Furthermore, since only normal temperatures and pressures are required, it provides a simple and eco-friendly means of producing carbon fibers. Fig. 4 is a schematic illustration of EBI stabilization and the carbonization of PAN fibers.

Shin *et al*. [102] investigated the possibility of using an EB accelerator at an acceleration of 1.14 MeV and beam current of 8

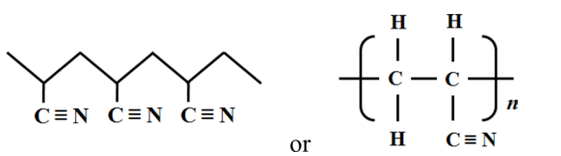

Fig. 1. Molecular structure of polyacrylonitrile precursor.

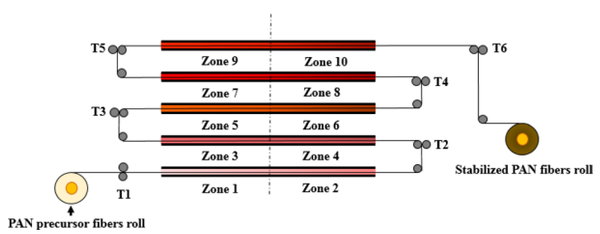

Fig. 2. Schematics of thermal oxidation process line; (Zone 1-Zone 10): temperature zoned, (T1-T6): stretching rollers. PAN: polyacrylonitrile.

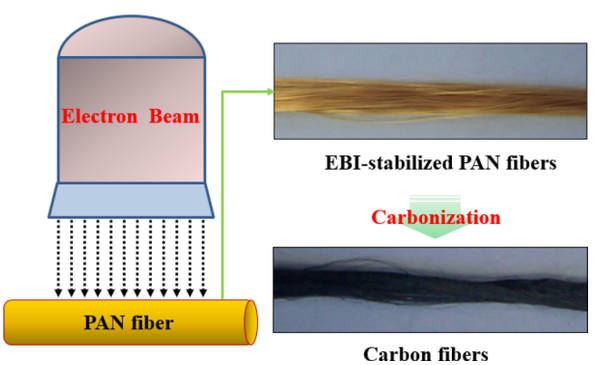

Fig. 4. Schematic illustration of electron beam generation by a linear accelerator and photos of electron beam irradiation (EBI)-stabilized polyacrylonitrile (PAN) fibers and carbon fibers.

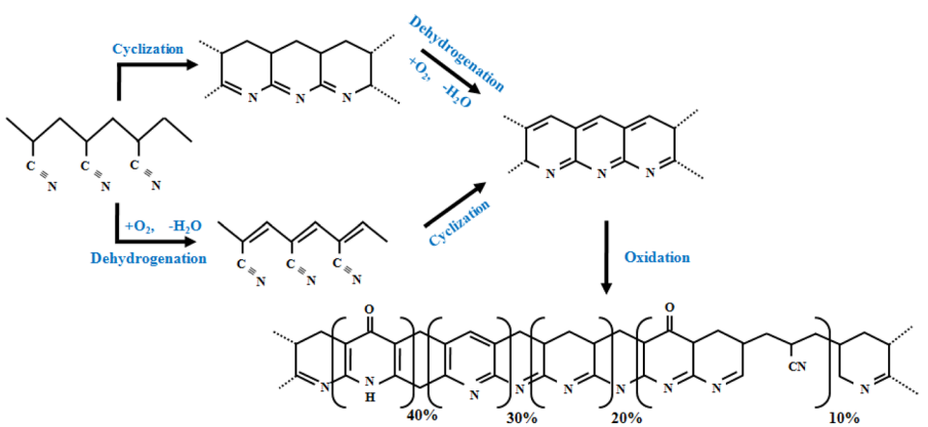

Fig. 3. Schematic depicting the thermal chemistry during the oxidation of polyacrylonitrile fiber.

mA to oxidize PAN fibers, testing the effects of 500, 1000, 2000, 3000, and 5000 kGy doses of absorbed radiation. In that work, both the PAN precursor fibers and EBI-oxidized fibers were analyzed by Fourier-transform infrared spectroscopy (FT-IR), gel fraction, density, differential scanning calorimetry (DSC), X-ray diffraction (XRD) and mechanical measurements. The structural change in PAN fibers resulting from oxidation by EBI was evidenced by a decrease in the intensity of the peaks at 1451 cm^{-1} and 2244 cm^{-1}, which were attributed to the stretching vibration of C-H and C≡N. The gel fraction and density test results revealed an increase in the degree of cyclization with increasing EBI dose, with a resulting increase in amorphization, causing a reduction in the tensile strength of the fibers. In the typical DSC curves, however, the EBI-oxidized PAN fibers showed a decrease in the activation energy required for exothermic reaction with increasing EBI dose.

Shin *et al*. [103] also looked into producing carbon fiber from PAN fibers through a combination of short thermal treatment and EBI, wherein PAN fibers, irradiated by 1000 kGy of EB energy, were thermally oxidized at 200°C or 250°C for 20 or 40 min, respectively. The results of FT-IR analysis showed that the C≡N peak at 2244 cm^{-1}almost disappeared after 40 min at 250°C, while the intensity of the C=N peak at 1628 $cm^{-1}$was indicative of an increase in cyclization. Through DSC analysis, thermal treatment at either 200°C or 250°C was found to cause a sharp decrease in the majority of exothermic peaks. The stabilization index of PAN fibers treated at 250°C for 40 min was 99.21%. Finally, the tensile strength of the resulting carbon fiber was around 2.3 GPa, with the cross-sectional image of a single fiber clearly demonstrating the brittle nature of its morphology. This therefore demonstrates that a combination of EBI and thermal treatment can reduce the time normally required for oxidation (2-3 h) by over an hour, yet still produce carbon fibers with a high tensile strength.

Kim *et al*. [104] applied an EB accelerating voltage of 1.14 MeV and a beam current of 1 mA to stabilize PAN nanofiber (NF) mats using dosages ranging from 500 to 5000 kGy. The stabilized mats were subsequently used to form carbon NF mats, which exhibited a similar morphology to the pristine PAN NF mats and contained no significant defects.

Choi *et al*. [105] used the EBI-H_2O_2 method to oxidize PAN NFs, in which 1% H_2O_2 solution-sprayed PAN NFs were irradiated by an EB. In the FT-IR spectrum obtained, EBI-H_2O_2 stabilization was shown to induce the transformation of C≡N to C=N in PAN NFs with significantly less defects than if EBI treatment alone were used. This was particularly evident in the DSC analysis, which revealed that 50 kGy EBI-H_2O_2 treatment reduced the activation energy of exothermic reactions in PAN NFs to a level comparable to that obtained with 500 kGy EBI treatment. Thus, in the EBI-H_2O_2 treatment, electrons are capable of oxidizing PAN NFs at a lower radiation dose than EBI alone.

2.2. Oxidation by gamma-ray irradiation

Gamma-ray radiation, emitted in all directions from radionuclides such as ^{137}Cs or ^{60}Co (Fig. 5) or high energy EBI, which is ionizing radiation generated by electricity and magnetism accelerating electrons to a high energy level, are both known to similarly influence materials [106-108]. However, the gamma

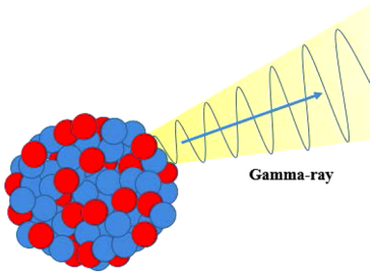

Fig. 5. Schematics of gamma-ray emission from atomic nucleus.

irradiation process is different than that for EBI. Gamma radiation can completely penetrate materials and can be applied to various kinds of materials, but has some drawbacks. The dose is a few orders of magnitude lower and therefore requires a longer residence time compared to EBI.

Tan and Wan [109] used gamma-ray irradiation to investigate structural changes in irradiated PAN precursor fibers. PAN fibers were wound onto a frame of about 20 cm in a glass container and exposed to gamma radiation for 25 or 50 h with an irradiation dose rate of 2.0 kGy/h. Structural changes of the irradiated PAN fibers were characterized by FT-IR, DSC, thermogravimetric analysis (TGA), and XRD. In the FT-IR spectra, gamma-ray irradiated PAN fibers exhibited reduced peak intensity of C≡N groups but increased peak intensities of C=O, C=N and C=C groups. These results suggest that gamma-ray irradiation induces chemical conversions of the linear structure of PAN precursor fibers into ladder structures of stabilized PAN fibers, similar to thermal stabilization. In the DSC analysis, the PAN precursor fibers showed a sharp exothermic peak at 280.9°C while the gamma-ray irradiated PAN fibers showed a broad and reduced peak intensity due to reduction of activation energy by conversion of their chemical structure. In addition, the irradiated PAN fibers showed smaller weight loss in TGA.

As these results show, gamma-ray irradiation exhibits the potential to improve the stabilization of PAN precursor fibers as compared with thermal methods. To increase the yield of carbon fibers, Liu *et al*. [110] preoxidized gamma-ray irradiated PAN fibers and researched the variation in density of the gamma-ray irradiated PAN fibers with and without preoxidation. Density in the stabilized fibers increased due to cyclization and oxygen uptake during stabilization. Density measurement was particularly important in evaluating the influence of radiation processes on the preoxidized PAN fibers. Finally, they found that the gamma-ray irradiated PAN fibers with various types of peroxidation increased in density with an increase in the peroxidation time and temperature.

In addition, Liu *et al*. [111] studied the radiation oxidation of PAN fibers in ways unlike previous researchers. Generally, PAN fibers have mainly been irradiated without oxygen to avoid oxidation degradation. However, the introduction of oxygen in PAN fibers can facilitate thermal oxidation curing, for producing carbon fibers. In the results of the gel fraction, they observed that oxidation reactions were limited to the surface of the PAN fibers because oxygen has difficulty in penetrating the fibers. But, the radiation-oxidized regions have been completely changed to gel by inducing the thermal composition. The above gamma-ray ir-

radiation technologies illustrate the method's potential advantages, and suggest gamma-ray irradiation is one of the advanced oxidation methods that can be applied for oxidation of PAN fibers, except for the very long residence time during oxidation.

2.3. Ultra-violet oxidation

Electromagnetic radiation in the ultra-violet (UV) spectrum has the ability to excite electrons to higher energy orbital levels, which directly affects the nature of atomic bonds and changes the physical and mechanical properties of materials [112,113]. Several researchers have therefore investigated the effect that UV treatment has on the mechanical and chemical properties of various fibers [114,115]. Among them, Paiva *et al*. [116] explored the possibility of using UV oxidation to produce carbon fibers from melt-processible PAN-based copolymers (acrylonitrile [AN]:methyl acrylate [MA] = 88:12), wherein UV-irradiated melt-spun fibers were thermally oxidized prior to being carbonized at 1500°C. However, the carbon fibers obtained by this method exhibited a low mechanical strength of around 350 MPa due to the number and size of defects contained within them.

A later study by Morales and Ogale [117] achieved the UV-assisted stabilization of wet-spun, photoinitiator-modified PAN precursor fibers by adding 4,40-bis(diethylamino)-benzophenone (BDP) as a photoinitiator to reduce the thermal oxidation processing time, and thereby enhance the physical properties of the resulting carbon fibers. The precursor fibers were spun from a solution consisting of PAN powder dissolved in BDP to a mass ratio of 99:1, with the resulting fibers then being irradiated using a UV curing lamp with two different UV sources (mercury or iron halide bulb). They found that those fibers irradiated by a halide bulb exhibited a higher tensile modulus than PAN fibers irradiated by a mercury bulb, which was attributed to the difference in the spectral output of each bulb type. However, in both instances, the tensile modulus was still higher than that of pure PAN fibers, thermally treated PAN fibers with 1 wt% BDP, and UV-irradiated and pure PAN fibers. In addition, the application of 5 min of UV treatment to PAN precursor fibers containing 1 wt% BDP was found to be roughly comparable to the first 83 min of thermal oxidation. These results illustrate the potential savings that UV irradiation can offer in the stabilization of PAN precursor fibers, while still retaining the mechanical properties of the final carbon fiber.

2.4. Plasma oxidation

Plasma can be described as a strongly ionized gas that contains ions, radicals, excited molecules, and free electrons. Owing to its free electrical charge, plasma is electrically conductive and its magnetic field can strongly influence a gas. By applying these principals, polymer materials treated with plasma can be drastically altered in terms of their chemical structure and surface properties. In addition, plasma treatment (Fig. 6) is a simple, effective, and versatile technique for stabilization or surface treatment in the plasma zone [15,118-121].

Lee *et al*. [121] researched the effect of plasma assisted oxidation on the tensile properties of PAN based carbon fibers at different plasma exposure times. PAN fibers were thermally oxidized at 220°C for 30 min with an added plasma treatment for 5 min more. In the FT-IR spectra, the peak intensity at 1595 cm^{-1} assigned to C=N bonds increased more than that of PAN fibers which had been thermally oxidized at 220°C for 30 min. This peak was stronger with plasma treatment. However, the peak intensity at 2243 cm^{-1} assigned to C≡N decreased with more exposure to plasma treatment. In the tensile test results of the obtained carbon fibers, carbon fibers obtained from PAN fibers oxidized by heat and plasma treatment did not exhibit outstanding improvements in tensile properties, compared to PAN fibers oxidized by conventional thermal treatment. However, the results of plasma treatment showed that it could reduce time and temperature in the oxidation process for manufacturing carbon fibers.

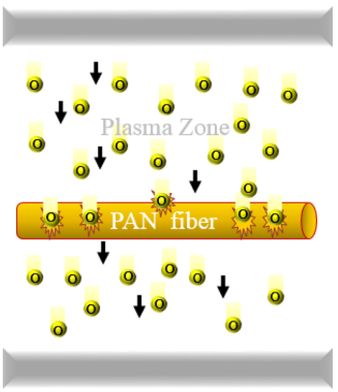

Fig. 6. Schematic diagram of plasma treatment. PAN: polyacrylonitrile.

The mechanism and efficiency of the plasma oxidation of PAN fibers, and the mechanical properties of the resulting carbon fiber, were further investigated by Lee *et al*. [122]. By comparing the degree of cyclization in plasma- and thermal-oxidized PAN fibers using FT-IR, they found that the extent of cyclization reaction is equal to the intensity of the 1595 cm^{-1} peak for C=N divided by the intensities of the 1595 cm^{-1} and 2243 cm^{-1} peaks. Their results showed that the extent of cyclization in plasma-oxidized PAN fibers is much higher than in thermally oxidized PAN, to the extent that 15 min of plasma treatment is comparable to 120 min of thermal treatment. This means that PAN fibers are more easily and more rapidly oxidized by the oxygen species induced by plasma treatment, and the resulting carbon fiber has a tensile strength (2.8 ± 0.3 GPa) that is 30% greater than carbon fiber produced from thermally oxidized PAN fibers.

3. Conclusion

This review summarizes the feasibility of the three major categories of radiation induced polymer stabilization processes: EB, γ-radiation, UV, and plasma treatment. Of the various precursors available for carbon fiber, PAN precursor fibers were selected as the subject of focus. All three forms of treatment have been proven capable of efficiently transforming the C≡N bonds of PAN into C=N bonds in a manner that is both simpler and faster than conventional thermal treatment. Furthermore, the carbon fibers produced from EB and plasma oxidized PAN fibers exhibit an enhanced tensile strength over carbon fiber obtained by thermal stabilization. It is therefore concluded that further development of these radiation-based oxidation processes can not

only significantly improve the speed of carbon fiber production, but also reduce its environmental impact.

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