FABRICATION OF CARBON FIBRES FROM WET-SPUN COMMERCIAL POLYACRYLONITRILE FIBRES

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The possibility of fabricating carbon fibre from commercial PAN fibres for textile applications was demonstrated. It is necessary to make some changes in the temperature—time conditions for total completion of the thermal stabilization process. Better strength of the carbon fibres, equal to 1401 MPa, was attained in conducting thermal stabilization cycle B.

Of the different precursors of carbon fibres (CF), polyacrylonitrile (PAN) fibres are most widely used [1, 6]. PAN fibres contain up to 85 wt. % acrylonitrile (AN) units. The other 15% consists of neutral and/or ionic comonomers, which are added to improve the properties of the fibres. Neutral comonomers of the methyl acrylate (MA), vinyl acetate (VA), or methyl methacrylate (MMA) type are used to increase the solubility of PAN copolymers in the solvents used in spinning, alter the morphology of the fibre, and improve diffusion of dyes in it. Ionic comonomers, including sulfonate types of sodium methallyl sulfonate, sodium 2-methyl-2-acrylamidopropane sulfonate (SMAPS), sodium polystyrene sulfonate, sodium polysulfophenylmethallyl ether, and carboxyl-containing comonomers, itaconic acid, for example, can also be used to obtain better dyeability and increase the hydrophilicity of PAN fibres. The composition of the PAN fibre used to obtain the precursor fibre, usually contains 5-10% neutral and 0.5% acid comonomers [8-10]. The copolymer has a carbochain structure (Fig. 1). The molecular structure of this fibre is characterized by a set of chain molecules of different length [3, 11].

Production of carbon fibres based on PAN fibres consists of two basic stages — thermal stabilization and carbonization. In the thermal stabilization stage, the PAN fibres are heated to approximately 180-300°C in oxygen-containing medium, and additional orientation takes place in the structure of the polymer. The simultaneously formed intermolecular crosslinks between chains prevent pyrolysis at higher temperatures. The relatively complex chemistry of the stabilization process basically consists of cyclization of nitrile groups (C≡N) and formation of cross (intermolecular) links of chain molecules, accompanied by dehydrogenation and oxidative reactions. During this process, the linear polymer acquires a ladder structure (Fig. 1), which has higher thermal stability and prevents melting during the subsequent carbonization process [6, 11, 12].

Heat treatment of PAN fibres, where noncarbon elements in the form of different gases are eliminated: H₂O, NH₃, CO, HCN, CO₂, and N₂, takes place in the carbonization stage. Carbonization is conducted at a temperature within the limits of 1000-1500°C in inert medium. During this process, the diameter of the fibres decreases and they lose approximately 50% of their weight. The graphitization stage, where the fibre undergoes heat treatment at a higher temperature, is sometimes conducted after carbonization and increases the mechanical properties of CF [6, 13].

Carbon fibres are very expensive due to the high cost of the initial raw material — PAN fibres, used in production of carbon fibres, which differ from the commercial fibres used in the textile industry with respect to the chemical composition, type, and content of the comonomers, as well as the physicomechanical characteristics. The textile PAN fibres used for production of fabrics, blankets, and carpets have a higher cross-section area (corresponding to the linear density) and lower tensile strength than special PAN fibres. The quality of CF from this type of PAN fibres is relatively low [5], and it is impossible to change some indexes of PAN textile fibres without an important increase in the price.

Studies have recently been conducted to investigate the possibility of using PAN textile fibres with a low price which would make the CF less expensive. The positive results of these studies should be noted [14, 15]. By using different kinds of
chemical and mechanical treatments on PAN fibres before and after stabilization, CF with acceptable mechanical properties were obtained. We will examine the possibility of fabricating carbon fibres from Iranian PAN textile fibres by changing the thermal stabilization parameters.

The PAN fibres we used were manufactured by wet spinning. Their chemical composition was as follows (in wt. %): 93 AN, 6 MA, 1 SMAPS; the cross section was bean-shaped. Thermal stabilization of PAN fibre was conducted in air medium in different temperature-time conditions (at a temperature under 350°C). In the carbonization stage, the oxidized fibres were placed in a horizontal muffle furnace heated in high-purity nitrogen (99.9999%) to 1200°C and held for 10 min.

The following methods were used to study the properties of the initial PAN fibres and the fibres after thermal stabilization and carbonization:

- tensile strength testing was conducted on filaments using an Instron 5565 tester equipped with loading cells with a deformation rate of 2 mm/min; the length of the samples of each type of fibre was 25 mm; the average result of 25 tests was calculated;
- the density of the fibres was determined with density gradient columns prepared from ZnCl₂ and H₂O; the average value of three tests was found;
- a Nikon YS100 optical microscope was used to determine the area of the cross section of the initial and oxidized PAN fibres and CF; since the cross section of the initial fibres was bean-shaped, they were pressed into epoxy resin; the area of the cross section was calculated with image analysis software with images taken with the optical microscope;
- the electron-microscopic study of PAN fibres and CF was conducted with a CAMSCAN model MV2300 SEM microscope.

As noted above, the PAN textile fibres used in our study contained neutral MA comonomer and SMAPS ionic comonomer. The special PAN fibres also contained carboxylic acids, vinyl bromide, acrylic, methacrylic, and itaconic acids as comonomers. The comonomers act as catalysts of thermal stabilization, so that special types of comonomers are selected to decrease the temperature, increase the rate, and decrease the duration of thermal stabilization [10, 13, 16]. The special PAN fibres usually used for production of carbon fibre have a round cross section up to 15 μm in diameter, a cross-section area of up to 180 μm², and a low linear density of less than 0.17 tex. Commercial PAN textile fibre has a bean-shaped cross section, section area of 530 μm², linear density of 0.56 tex, tensile strength of 226 MPa, and relative elongation at break of 43.9%. The electron-microscopic image of the PAN fibres investigated is shown in Fig. 2.

The large cross-section area and high linear density of PAN fibres cause incomplete thermal stabilization in ordinary conditions. Only the surface and middle layers acquire thermal stability. The duration and temperature of the cycles were varied to attain complete thermal stabilization. The PAN fibres were treated with different variants (cycles) of thermal stabilization by determining the density and tensile strength in stretching oxidized PAN fibres after each procedure. Table 1 gives the temperature-time characteristics of the cycles, and the results of determining the density and strength of oxidized PAN fibres are reported in Table 2.