Graphitized Carbon Fibers Based on Lyocell Precursors

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Abstract. For the first time, graphitized fibers from Lyocell cellulose precursors spun from solutions prepared via the solid-phase dissolution method in N-methylmorpholine-N-oxide were obtained. Carbonization was performed up to processing temperature of 2400 °C. Comparative studies of cellulose precursors and carbon fibers, carried out by means of scanning and transmission electron microscopy, X-ray and thermal analysis, allowed us to establish the structural-morphological features and thermophysical properties of carbon fibers. It is shown that graphitized fibers consist of randomly arranged regular lamellae of graphite-like layers. Using transmission electron microscopy, the interplanar distance between the layers (d002) was estimated to be ~ 0.341 nm. Graphitization of the fibers leads to content of carbon ~99.75% and oxygen ~0.25% and to reach the tensile strength up to 1.5 GPa.

1. Introduction

Carbon fibers (CF) are widely used as an arming filler in composite materials. As a rule, such composite materials have unique engineering and functional properties that are provided by the high thermal stability of the CF while maintaining the strength values and the Young's modulus to high operating temperatures. Depending on the application area, the heat treatment of cellulose precursors to temperatures of 1500 °C or 2400 °C is performed [1]. According to the accepted classification of the international committee BISFA (International Bureau of Standardization of Man-Made Fibres (Brussels, Belgium)), the fibers formed from cellulose solutions in NMMO received the general name Lyocell [2]. Until this time, the main suppliers of raw materials for processing into CF remain producers of viscose fibers. As to carbonization of Lyocell fibers, the rare publication appeared last time only [3].

In one of the first papers [4], it was shown that the structure of Lyocell provides the better mechanical properties of the carbon fibers compared to viscose precursors. Thus, the strength of CF reaches 1 GPa, and the modulus of elasticity is about 100 GPa. The diffratograms of the CF fibers presented in this paper demonstrate a very low intensity of the main peaks, that does not correlate with the high strength values. The morphology of the fibers is described as defect-free, and the surface of the samples is smooth.

In subsequent works, the authors focused on the effect of catalysts in processing of Lyocell precursors into CF [3, 5-7]. It was shown that such catalysts as diammonium phosphate or Si-containing compounds can significantly increase the carbon yield during the heat treatment of precursors.
The pioneering research in obtaining graphitized carbon fibers from Lyocell precursors is described in [8-10]. The use of various heat treatment modes, as well as catalysts, including silicon-containing, allowed the authors to obtain CF with a graphite-like structure and mechanical strength of more than 1 GPa. The dopes for fiber spinning were prepared in this case by traditional methods, i.e. via preliminary obtaining the pulp of the cellulose with aqueous NMMO containing approximately 50% of water (non-solvent). Subsequent removing of water by evaporation in step by step manner up to 13% leads to solution preparation. In our case, so-called solid-phase dissolution method was used, according to that the cellulose and the solvent powders was treated by mechano-chemical activation resulting in formation of “the solid solutions”. Their heating to the temperature higher than melting point leads to obtaining liquid dopes.

This is the original approach to preparing dopes and namely this method was used in this paper for spinning the precursor fibers and their subsequent carbonization and graphitization. That is why, the main aim of this research consists in studying the deep heat treatment processes of Lyocell fibers spun from solutions prepared according to original technique [11] and investigation of their structure, morphology and mechanical properties.

2. Experimental

2.1. Materials

Sulfate cellulose with DP = 600, moisture content ~ 8%, mass content of the alpha cellulose ~ 95% was provided by Baikal Pulp and Paper Mill (Russia). This cellulose was ground to a powder with an average size of 200 μm. Direct solvent of cellulose N-methylmorpholine-N-oxide (NMMO) with T_m ~ 120 °C (H_2O <10%) was supplied by Demochem (China).

2.2. Fibers spinning

After mechanical mixing of powdered cellulose with a solvent and an antioxidant, the system was subjected to solid-phase activation in extruder following the procedure described in [11]. The activated mixture (solid solution) was entered the extruder-feeder equipped with three heating zones. The temperature of the first zone is ~ 45 °C, the last zone ~120 °C. At transporting along the extruder a solid solution transferred to viscoelastic state. The liquid solution was metered to the spinneret set using a spinning pump. The fibers were spun through a die with 17 channels (a hole diameter of 250 μm) at 120 °C. The length of the air gap between the spinneret and the “mirror” of the coagulation bath was 100 mm. A coagulation bath was filled with water of room temperature. The gel-fibers were wounded at the drum with a rate from 35 to 50 m/min. After coagulation, the thread passed through a series of water washing baths of various temperature. This allowed completely removing the residual solvent: nitrogen content is zero. Drying the thread was carried out with the passage through three drums heated to 80-100 °C with a gradual increase in temperature.

The bobbin with spun fibers is shown in Figure 1.
2.3. Carbon fiber production

Preparing the carbon fibers was performed in two stages. At the first stage, the precursors underwent carbonization in the temperature range of cellulose pyrolysis (from room temperature to 1200 °C). Then the fibers were graphitized at temperatures up to 2400 °C [12]. Ammonium chloride and ammonium sulfate were used as catalysts (flame retardants).

2.4. Characterization

The structure of the fibers was tested at room temperature by X-ray diffraction method (Rigaku Rotaflex RU-200 device equipped with a rotating copper anode, linear focus 0.5 10 mm, source operating mode 50 kV - 100 mA, characteristic Cu Kα radiation wavelength \( \lambda = 1.542 \ \text{Å} \), secondary graphite was used monochromator, horizontal D-Max / B goniometer and scintillation detector). X-ray imaging was recorded in “transmission” and “reflection” geometries according to the Bragg-Brentano scheme in the continuous \( \theta-2\theta \) scan mode in the angular range of 5-40°, at a speed of 2° / min and at a scanning step of 0.04°. The yarn consisting of 100-150 monofilaments was used as the object, which were fixed on a flat square aluminum frame.

The morphology of the surface and cross section of fibers was investigated by low-voltage scanning electron microscopy (SEM) using an FEI Scios microscope (USA) with an accelerating voltage less than 1 kV in the secondary electron mode and an JSM U-3 (JEOL, Japan). To obtain SEM micrographs of cellulose precursors, they were preliminarily placed in an epoxy resin and after curing, the sample was cut by microtome cutter. To visualize cross sections of brittle carbon fibers they were grinded by mechanical action.

The mechanical properties of the fibers were measured on an Instron 1122 tensile machine (UK) on the working length of 10 mm at a tensile rate of 10 mm/min.

The thermal behavior of samples was examined on a TGA / DSC combined thermal analysis instrument, Mettler Toledo (Switzerland). The measurements were carried out in the temperature range from 30 to 1000 °C at a heating rate of 10 K / min. The flow rate of the argon was 10 cm³/min. Alumina crucibles of 70 μl were used.
3. Results and Discussions
The mechanical characteristics of the precursors were measured on monofilaments. The tensile strength for a single fiber is \(~ 650\) MPa, the modulus of elasticity \(~ 12\) GPa, and the elongation at break \(~ 7\%\).

The equatorial diffractograms of cellulose fibers obtained in the "transmission" mode at room temperature are shown in Figure 2.

![Figure 2](image)

**Figure 2.** Equatorial (1) and meridional (2) diffractograms (a) and TGA curve (b) (atmosphere: argon 10 cm3 / min., linear heating at 10 K / min) of cellulose precursors.

It can be seen that the precursors have the traditional structure of cellulose II [13]. The thermal behavior of such fibers is characterized by three regions with different rates of mass loss on the TGA curve. These stages correspond to the loss of adsorbed water, the reactions of dehydration and depolymerization, and above 400 °C there is a loss of remaining oxygen. The carbon yield at 1000 °C is about 12.7%. To increase the carbon yield and mechanical properties of the CF, it is recommended to use pyrolysis catalysts and flame retardants [5-7, 14]. In this research, ammonium chloride and ammonium phosphate were used. The appearance and micrographs of graphitized fibers with different magnification are shown in Figure 3.

![Image](image)
The diameter of the CF varies from 8 to 10 μm. The surface of carbon fibers is textured. At high magnifications, craters with an average diameter of 20-50 nm are observed. The shape of the cross section is a circle. Pronounced defects are absent.

The equatorial diffractogram and TEM micrographs of the fibers after heating to 2400 °C are shown in Figure 4.

**Figure 3.** Photo (a) and micrographs of the surface (b, c) and cross section (d) of the CF obtained by heating to 2400 °C.

**Figure 4.** Equatorial diffractogram (“reflection” mode) (a) and TEM micrograph of the CF (b).

The maxima of the main reflections 002 and 100 of CF are observed in the region of 2θ ~ 26 and 43°. The width of the reflections suggests the presence of some amorphous carbon phase in accordance with analysis of diffractogram published in [15]. Estimation of the interplanar distance between the layers (d_{002}) according to the Wulf–Bragg’s law gave a result of ~ 0.341 nm, that corresponds to the data of transmission electron microscopy.

EDS spectroscopy results allow the determination of carbon and oxygen content in the fiber (Figure 5).
Figure 5. The distribution of the C and O, obtained for the fibers after thermolysis up to 2400 °C.

From the superimposed charts of carbon and oxygen, it can be seen that the amount of oxygen is not more than 0.25% of the sample. The carbon content in the fiber is more than 99%.

Heat treatment of precursors leads to a drastic change in the mechanical properties of CF: elongation at break decreases to 1%, while the values of the elastic modulus increases several times and the strength reaches 1.0-1.5 GPa.

4. Conclusion
The graphitized fibers from precursors spun from solutions of cellulose in N-methylmorpholine-N-oxide, prepared in solid-phase manner, were obtained. The morphology of CF consists of ordered lamellae with a spacing of ~ 0.341 nm between the layers, that corresponds to graphite. High processing temperature renders it possible to produce CF with small amount of oxygen. The carbon content in the fiber reaches 99.75%. The mechanical properties of new CF allow their further processing, as into woven materials, as an arming phase for reinforcing composites.

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