DEVELOPMENT OF SURFACE STRUCTURE OF STABILIZED POLYACRYLONITRILE FIBERS DURING SLOW CARBONIZATION TO CARBON FIBERS

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ABSTRACT

Changes in surface structure of polyacrylonitrile fibers during thermal stabilization and carbonization were investigated. To this end, fiber specimens were heated to different final temperatures with a maximal final temperature of 1200°C. Fiber circumference decreases to approximately half of its starting value due to the well-known loss of volume and mass. Surprisingly, the fiber topography shows only minor changes within the resolution of the experiment. The contribution of different length scales to the surface roughness is not changed significantly throughout carbonization and thus appears to be widely determined by the originating PAN precursor fiber.

1. INTRODUCTION

Due to their remarkable mechanical properties carbon fibers have captured a key role as a component of fiber reinforced materials. Despite numerous investigations [1–5], there is still a lack of knowledge about the precise chemical reactions and structural rearrangements occurring during production [2, 6]. First, the polyacrylonitrile (PAN) precursor fibers are stabilized at temperatures up to 300°C under oxidative atmosphere to form a stable chemical structure suitable for the subsequent high temperature carbonization treatment [2, 7, 8]. For the carbonization process temperatures up to 1600°C are employed under an inert atmosphere. This treatment results in a turbostratic carbon structure with a typical carbon concentration of over 98wt% [2]. During carbonization heteroatoms like hydrogen, nitrogen, and oxygen are eliminated, especially in the temperature range up to 1300°C [3]. At higher temperatures the degree of structural order of the material is increased, which results in fibers with high mechanical properties [2].

In a previous publication we reported about the existence of three characteristic temperature regions during carbonization [9, 10]. These temperature regions, characterized by particular changes in fiber shrinkage, range from 250°C to 450°C (Region 1), from 450°C to 750°C (Region 2) and from 750°C to 1200°C (Region 3).

Throughout carbonization the fiber length decreases. While this shrinkage can be hindered by the application of mechanical tension in Region 1, the major part of length change occurs in Region 2, in which it is independent of applied tension. Fiber diameter decreases over the whole temperature range. The related loss of volume is correlated to a mass loss, which is maximal in Region 1 at around 380°C. In Regions 2 and 3 the mass loss continues, but at a smaller rate. Mass loss is correlated to the emission of volatile compounds.

Particular developments of crystalline properties can be associated with the different regions. In Region 1 graphite-like crystallites grow in stacking-direction of the graphene layers as well as in layer-direction. In Region 2 the crystallites grow preferred in direction of the layers and in Region 3 they grow only in stacking direction. Especially in Region 1 the orientation of the crystallites along the fiber axis increases. This increase of orientation continues in Region 2 and saturates in Region 3. Crystallinity increases for all temperature regions.

In the presented paper we investigate how the reported shrinkage and mass loss affects the surface properties of the fibers. It is known that the PAN precursor fibers consist of fibrils, dominantly oriented parallel to the fiber axis. This structure is maintained over the production chain to the carbon fibers [11]. The fibrils have typical widths of 10nm to several 100nm [12–15]. The surface of the fibrils shows nanopores with a size of several nanometers [16, 17]. Ref. [18] reports that the surface roughness changes during thermal treatment of the fibers.

A correlation of the evolution of surface topography with the development of fiber dimensions is discussed in the here presented paper for PAN-based fibers in the carbonization temperature range up to 1200°C. By employing power spectral density (PSD) curves derived from atomic force microscopy (AFM) measurements, the contribution of all length scales of surface structures to the topography is taken into account.

2. EXPERIMENTAL

2.1 Fiber material and stabilization procedure

For the here presented investigations a 6k polyacrylonitrile fiber tow by Bluestar (Grimsby) was used as precursor. Prior to carbonization the fibers were thermally stabilized in the setup described in Ref. [19] to generate a structure suitable for further high temperature treatment in a wide parameter range [9]. During stabilization a mechanical stress of 2.5MPa was applied to a tow of approximately 14cm length. The temperature program consisted of heating the fibers to a temperature of 150°C at 5°C/min and then to 250°C at 1.25°C/min. At 250°C the temperature was held for 20min. This stabilization program was the same for all presented samples.

For surface analysis the textile finish of the thermally untreated PAN precursor fibers was removed. For that purpose, the fibers were stirred in methyl ethyl ketone at room temperature and then rinsed with 2-Propanol and water.

2.2 Carbonization of fibers

The stabilized fiber tow was mounted in a specially developed setup for carbonization under controlled mechanical load described elsewhere [9, 10]. 6k tows of approx. 75mm length were clamped inside the hot section of the furnace operated under inert nitrogen atmosphere (flow rate of 250sccm). A tensile testing machine controls the load on the fiber bundle during carbonization, while simultaneously measuring the shrinkage. All samples described in this publication were carbonized under constant load corresponding to an initial stress of 1MPa. The heating rate was kept at 10°C/min for all specimens. The maximal carbonization temperature was 1200°C. The heat treatment was aborted at particular final temperatures to acquire partly carbonized fibers for ex-situ diagnostics.

2.3 Measurement of fiber circumference

To measure the circumference of fibers the fiber tow was embedded in resin (Struers Epofix) and a cross section perpendicular to the fiber orientation was prepared by cutting, grinding and polishing. Micrographs of the fiber cross section were obtained by a digital optical microscope (Keyence VHX-600). An automatic particle-analysis of the fiber cross sections was performed by the software ImageJ [20] to obtain the mean circumference of approximately 150 individual fibers per sample.

2.4 Microscopic investigation of fiber surface

The fiber surface topography was investigated using a Zeiss DSM 982 Gemini scanning electron microscope (SEM). To avoid damaging the fibers the acceleration voltage was kept at 1kV. To ensure the electric conductance necessary for SEM-diagnostics, a thin gold-layer was sputtered on the fiber surfaces prior to examination.
AFM measurements were performed using a Bruker Dimension ICON. Standard TESPA probes from Bruker with a tip radius of 8nm were used. Scan direction was chosen perpendicular to the fiber axis. The images have a resolution of 512 x 512 pixel and map an area of 5 x 5 µm².
For each specimen nine AFM images were acquired. For each image the power spectral density was calculated, which is the Fourier transformation of the surface topography. This gives a measure for the contribution of structures of different length scales to the surface topography. According to Parseval's theorem the root mean squared roughness equals the frequency integral of the PSD curve [21, 22]. By varying the integration boundaries, a frequency filter is introduced and a roughness curve as function of structure size is obtained. In a last step, the obtained roughness curves were averaged over the nine images.

3. RESULTS

3.1 Changes of fiber circumference during carbonization

Figure 1 shows the development of fiber circumference due to the shrinkage of the PAN precursor fiber during stabilization and carbonization to final temperatures of 400°C, 750°C, and 1200°C.

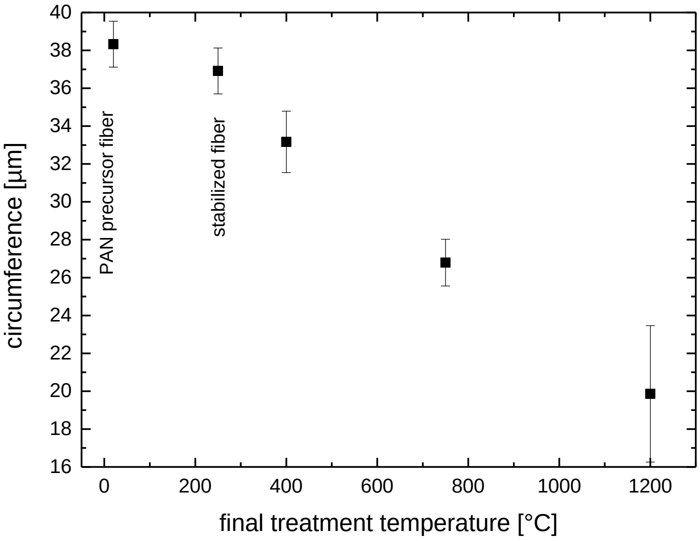

Figure 1: Evolution of circumference of PAN-based fibers during stabilization and carbonization.

During stabilization the circumference of the fiber is reduced from approximately 38.3µm for the PAN fiber to 36.9µm for the stabilized fiber. During the subsequent carbonization treatment, circumference decreases further. At the maximal heat treatment temperature of 1200°C a minimal value of 19.9µm is found. The skin surface area of the fiber thus decreases by a factor of approximately 1.9 throughout heat treatment.

3.2 Surface characterization by scanning electron microscopy

It is expected that such a drastic decrease in surface area is correlated to corresponding changes in surface topography. To investigate such possible changes a microscopic investigation of the surface topography was performed. A first impression of surface topography is provided by scanning electron microscopy. The surfaces of the PAN fiber and of fibers heat treated to different final temperatures (400°C, 750°C, 1200°C) are shown in Figure 2.

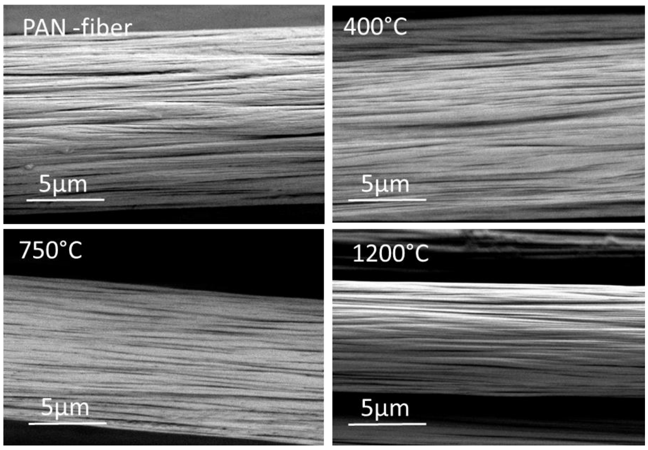

Figure 2: SEM micrographs of PAN precursor fiber and fibers heat treated to different final temperatures.

The images reveal a pronounced fibrillar structure for all fibers. The typical range of length scales of these structures measures between 0.1µm and 0.5µm for all fiber types. The images show the decrease in fiber diameter – and thus in circumference – throughout heat treatment.

3.3 Surface characterization by atomic force microscopy

To quantify possible changes in surface topography during heat treatment AFM measurements were performed. Figure 3 shows typical AFM measurements of the PAN fiber and of fiber specimen heat treated to temperatures of 400°C, 750°C and 1200°C.

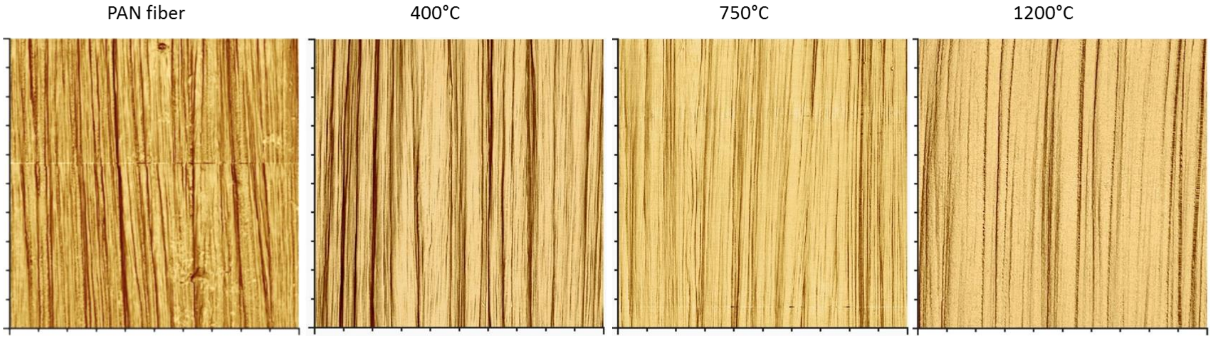

Figure 3: AFM measurements (5µm x 5µm) of PAN precursor fiber and fibers heat treated to different final temperatures.

Again, a fibrillar structure is visible and the length scale of typical structures is between 0.1µm and 0.5µm for all samples.

Figure 4 shows the roughness curves generated by PSD spectra of the PAN fiber, the stabilized PAN fiber, and the fibers heat treated to different final temperatures (400°C, 750°C, 1200°C) according to Ref. [22].

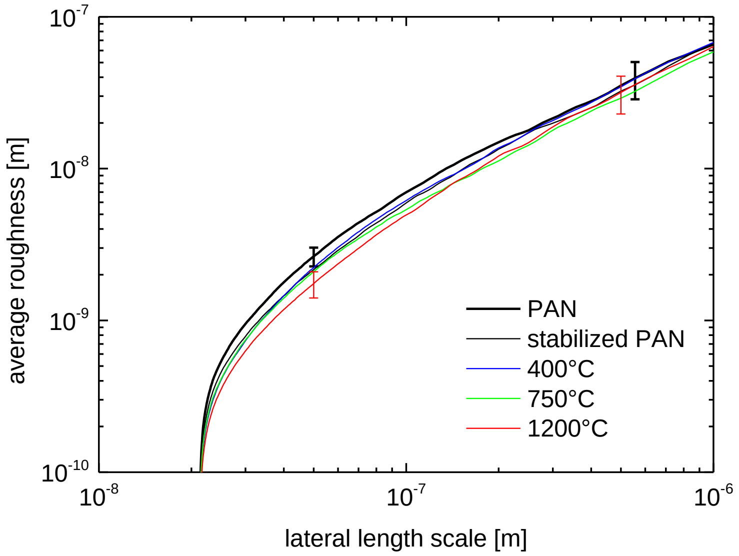

Figure 4: Roughness curves of the PAN precursor fiber, the thermally stabilized fiber and the fibers heat treated to different final temperatures.

For all fibers all length scales contribute to the roughness. Systematic decrease of roughness during heat treatment is found for the contribution of length scales between 2×10^{-8}m and approximately 2×10^{-7}m. This is attributed to a decrease of amplitudes in this range of length scales due to smoothening of the surface by the carbonization process.

It should be noted that the roughness curves start at a lateral structure size of around 2×10^{-8}m, determined by the lateral size of the AFM tip, independently of the type of fiber investigated, i.e. changes of contributions to the roughness of smaller length scales are inaccessible to the measurement.

In conclusion the contribution of different length scales to the roughness does not change significantly throughout heat treatment of the fibers, i.e. the surface structure of the precursor PAN fiber also determines the surface structure of the carbon fiber.

4. SUMMARY

PAN fibers were thermally stabilized and carbonized to different final treatment temperatures to investigate the changes of fiber surface topography. Fiber circumference decreases to approximately half the starting value, whereas the topography of the fiber surface shows only minor changes during carbonization. Thus it is concluded that the surface of the carbon fiber is determined by the surface of the originating PAN fiber.

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