MICROSCOPIC INVESTIGATION OF THE MICRO-STRUCTURE OF FIBRILS OF TECHNICAL POLYACRYLONITRILE FIBERS SEPARATED BY ULTRASONIC ETCHING

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ABSTRACT

In our study we present a microstructural investigation of fibrils from technical polyacrylonitrile fibers, obtained by fibril separation treatment in an ultrasonic bath. After coating the separated fibrils with platinum, the samples are analyzed by field emission scanning electron microscopy to verify the successful separation and to evaluate the fibril diameters. We find two different morphologies of the separated fibrils coexisting in the same fiber, characterized by two different average diameters. Atomic force microscopy and transmission electron microscopy measurements of the PAN fibrils confirm the existence of the two types of fibrils and provide structural details. Fibrils with lower diameter show a smooth surface and a homogeneous bulk structure. In contrast, fibrils with larger diameter show a pronounced nanoscale lamellar structure, with the lamellae oriented perpendicular to the fibril axis.

1 INTRODUCTION

Polyacrylonitrile (PAN) is the most important precursor material for carbon fiber production. The quality of these carbon fibers is tightly linked to the properties of the PAN precursor fibers and it takes comprehensive knowledge of the precursor fiber chemistry and micro-structure to improve the properties of carbon fibers [1]. From a structural point of view, the fibrillar substructure of the PAN fibers and the micro-structure of these fibrils are of high interest [2, 3]. Microscopic investigation of the surface of PAN based fibers offers information about the diameter and the orientation of the fibrils along the fiber axis, as well as the size and morphology of fibril substructures [4-7]. Analysis of cross sections of fibers gives evidence about their volume structure [8-10]. Additional information can be obtained by fibril separation using an etching process, which allows more detailed investigation of the micro-structure of the fibrils [11, 12].

Fibril separation by ultrasonic treatment has become a widely accepted preparation method for different types of fibers [13-18]. However, to the best of our knowledge, only two groups have applied this method to PAN fibers [11, 12]. They show that PAN fibers separate into their fibril substructures during extended ultrasonic treatment. Ref. [12] revealed that the fibrils flake off the PAN fibers during this process. Both groups obtain fibrils showing a periodic micro-structure along the fibril axis resulting in a rough surface. By varying the preparation parameters, Ref.[12] found a second type of fibrils with a smooth surface.

In our work we use PAN fibers taken from a technical production process and separate their fibrils according to the procedure proposed by Refs. [11, 12]. The resulting fibril morphologies are characterized by field emission scanning electron microscopy (FESEM). To shed light on the structure of PAN fibrils on nanoscale, we apply high resolution atomic force microscopy (AFM) in tapping mode and transmission electron microscopy (TEM). Additionally, a direct comparison with PAN in powder form was performed.
For preparation of the samples, the PAN fibers were cut into pieces with a length of 2-3 mm and were processed for 6 h in 95% dimethylsulphoxide (DMSO) solution in an ultrasonic bath (USB) at 75 °C. After the ultrasonic treatment, the solution was filtered using a TEM lacey carbon grid. Investigations were performed on completely and partially separated fibrils. The same ultrasonic bath procedure was used for the PAN powder which was filtered using a TEM holey carbon grid. In order to stop the solution process, the samples were washed with deionized water and dried in air for subsequent analyses.

The samples for FESEM measurements were coated with a thin platinum (Pt) layer. The results of the fibril separation were analyzed by a FESEM model LEO Gemini 982 FEG from Zeiss AG with an acceleration voltage of 1kV. For detailed analysis of the nanostructure of the separated fibrils, AFM measurements of uncoated fibrils were carried out using a Bruker Dimension ICON atomic force microscope in tapping mode with EBD-SSS NCHR AFM probes from Nanotools with a tip diameter of 2-3nm. For TEM investigations of uncoated fibrils, a JEOL JEM-2100F was used at an accelerating voltage of 200 keV.

3 RESULTS AND DISCUSSION
3.1 Morphologies of fibrils of PAN fiber

FESEM was used to get a general overview of our samples. Investigation of a partially dissolved PAN fiber shows that fibrils flake off the PAN fiber in bundles of different thickness (see Figure 1a). These fibrillar bundles are composed of multiple fibrils arranged in flat tape-like structures. Detailed investigation of fully separated fibrils reveals two different types of fibril morphologies, labeled type I and type II, and one spherical cluster structure, labeled type III. Type I fibrils, shown in Figure 1b, show a very smooth surface and an average width of 23±7 nm. In contrast, type II fibrils (see Figure 1c) show an average diameter of 461±162 nm and are characterized by a lamellar micro-structure. These lamellae are arranged along the fibril axis with an orientation perpendicular to the fibril axis. These fibrils look like a shish kebab structure, which is typical for polymer crystallization of semi-crystalline polymers under shear flow stress and uniaxial tension [19-22]. Due to the shear conditions during the spinning process of polymer fibers, the molecular chains of the polymer are stretched, array in lines, and form fibrils which are called shish. The not fully stretched polymer chains fold into lamella-shaped crystals growing perpendicular to the direction of the shish, and are called kebab [21, 22]. Moreover, we observe spherical cluster formations (type III) in the same sample, with an average diameter of 629±94 nm (see Figure 1d). Their three-dimensional nature is in clear contrast to the fibrillar structures.
3.2 AFM investigation of micro-structured surface of PAN fibrils

To obtain more detailed information on the surface of the PAN fibrils, uncoated samples have been examined using AFM. Applying AFM to semi-crystalline polymers it has been shown that the surface has a granular structure [23]. This granular structure is caused by the alternation of crystalline and amorphous areas [24]. In AFM, the tapping mode is an established method for analysis of polymers. Due to the amplitude modulations a very high resolution in height images can be achieved, without damaging the sample. Furthermore, phase imaging results in a very high image contrast. In the following AFM investigations of the three different fibril morphologies are presented. For each fibril type two different magnifications of height and phase AFM images are shown. For fibrils of type I, AFM measurements reveal a smooth, unstructured surface in height as well as in phase imaging mode, in accordance with FESEM (Figure 2a-d). Due to this absence of substructures we assume that the smooth fibrils are formed from stretched polymer chains, similar to the shish part of the shish kebab structure. In contrast, fibrils of type II (Figure 2e-h) show lamellar micro-structures oriented perpendicular to the axis also in AFM. The lamellae are not smooth and are not orientated completely parallel to each other; each lamella is individually shaped and exhibits a nodular surface. This is in particular apparent in the higher magnification images showing a section of a lamella (Figure 2g-h). The lamellae have an average width of 99±20 nm.

The cluster morphologies of type III (see Figure 2i-l) reveal granular structures, which could be an indication of small polymer crystallites [23].
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Figure 2: AFM height and phase images from a-d) Type I: smooth fibrils, e-h) Type II: lamellae of shish kebab fibrils, and i-l) Type III: cluster micro-structures (each with 5x5µm and 1x1µm magnification). Blue rectangles mark the area of the corresponding detailed sections.

3.3 TEM investigation of PAN fibril micro-structure

TEM images support the findings of AFM and FESEM. Smooth fibrils of type I have a low TEM contrast, show smooth fringes, and reveal a homogenous volume structure, consistent with an amorphous fibril structure (Figure 3a). Fibrils of type II have a filigree appearance in TEM images and the shish kebab structure is visible (Figure 3b). These fibrils feature a straight shish in their center surrounded by lamellae orientated perpendicular to the shish axis, the kebab structures. The shish of these fibrils has an average diameter of 51±18 nm. The individual shapes of the lamellae became apparent in this figure with an average lamella thickness of 11±3 nm. All of those observations match our findings from FESEM and AFM.
Micro-structures of type III also appear in the TEM images (see Figure 3c). They reveal a core from which structures similar to the lamellae of type II extend outwards. In the TEM images, these substructures appear darker than the regions between them. The contrast can be created by density differences, thickness differences due to layered substructures or crystallinity variations. The average thickness of these lamellae is $11 \pm 3$ nm. We interpret the spherical cluster micro-structures of type III as spherulites, a common crystalline form of polymers. They consist of circularly arranged crystalline lamellar structures tightly connected by amorphous regions [24]. The lamellae are an agglomeration of numerous small crystallites. This interpretation is consistent with our AFM observations and explains the granular structures on the surface of the spherically shaped micro-structures [25].

### 3.4 Illustration of spherulitic growth with PAN powder

In the following, we want to investigate the possible influence of our preparation procedure on the morphology of our samples. Back in 1976, Gobil et al. had produced spherulites from polyacrylonitrile [26]. The group showed that PAN polymer chains form different spherulitic structures, depending on the solvent and the conditions for crystallization. Fast cooling and/or addition of crystallization seeds resulted in a relatively large number of nucleation sites and the resulting spherulites were numerous and small. Similar conditions occur during our preparation procedure. Here, at 75 °C parts of the fiber are solved but most of polymer remains unsolved and can act as crystallization seeds. Then the hot solution cools to room temperature in about one minute. The spherulitic structures in our samples therefore could be generated by crystallization of solved PAN as a result of the USB treatment in DMSO.

In order to investigate this assumption, we analyze PAN powder which was dissolved by the same USB treatment. The solution was prepared on a holey carbon grid and the resulting structures are compared to those of untreated PAN powder. The untreated PAN powder is characterized by small ball-like structures with a smooth surface and an average diameter of $138 \pm 52$ nm, as shown in Figure 4a and Figure 5a. The treated PAN powder forms two structures. Firstly, ball-shaped structures with an average diameter of $166 \pm 44$ nm are found. In contrast to untreated powder, here the FESEM images clearly show that their surface is characterized by granular micro-structures. Secondly, detailed TEM investigation of this sample reveals that spherulites have grown, too. Due to their lamellar structure and average size of $456 \pm 118$ nm, they can be clearly distinguished from the ball-shaped structures. It should be noted that these spherulites are similar in size to the spherulites observed in samples of USB-treated PAN fibers shown in Figure 3c.
This experiment shows that PAN solved in DMSO crystallizes into small spherulites under the given preparation conditions. This indicates that the spherulitic structures of type III observed in our samples could be artefacts of the preparation method. However, this does not exclude the possibility that spherulitic structures of type III could also be created during the wet spinning process of PAN. In the latter case, they possibly are formed in those areas of the fiber subjected to minimal shear flow.

3.5 Relationship between polymer crystallization and micro-structure

The type and average size of the different features observed in our investigation are summarized in Figure 6. As clearly indicated by the diagram, the three types do not only differ in their shape, but also in their sizes. The smooth fibrils of type I have the smallest diameter of 23±7 nm. The shish structures observed in fibrils of type II reveal a similar diameter of 51±18 nm. The lamellae exhibit a thickness of only 11±5 nm and arrange along the fibril axis. The resulting fibrils with shish kebab structure show a total average diameter of 629±94 nm. The broad distribution of sizes of the identified shish kebab structures is reflected in a relatively large standard deviation. The width of the kebab structures, i.e. the diameter of the fibrils of type II, are similar in magnitude to the diameter of the spherulites (type III). Similarly, lamellae occurring at type II and type III structures, have the same thickness of 11±3 nm. These observations suggest that the lamellae of the fibrils and the spherulites are similar in nature.
Figure 6: Different features and micro-structures of PAN Fiber after USB treatment and their size distribution.

Figure 7 shows a schematic model of the relation between the three different features, type I, II and III, obtained by USB treatment of PAN fibers in DMSO. It visualizes the observed features and the corresponding orientations of the polymer chains of polyacrylonitrile. Smooth fibrils of type I can be explained by stretched molecular chains of the PAN polymer which align along a common axis. The same kind of smooth fibrils probably form the backbone of the lamellar fibrils of type II, i.e. the shish of the shish kebab structure. The corresponding kebab can be described by lamellar crystallites oriented perpendicular to the fibril axis. These lamellae consist of small polymer crystallites, which are formed of regions of regularly folded polymer molecule chains linked by amorphous regions of unfolded molecule chains. Since the small polymer crystallites are not perfectly oriented with respect to each other a nodular surface structure is found in AFM measurements. The preferred direction of growth resulting in the lamellar form can be explained by the growth process starting outwards from the surface of the shish. The so formed lamellae can build major structural units like the shish kebab. Isolated spherulites can grow during cooling from solutions without preferred orientation of the lamellae.

Figure 7: Schematic model of the three morphologies and the relationship of polymer chain folding.
CONCLUSIONS

Summarizing the results from FESEM, AFM and TEM investigations, we found two different fibril morphologies within technical PAN fibers separated by ultrasonic etching. On the one hand, homogeneous type I fibrils with a diameter of 23±7 nm and a smooth surface are observed. On the other hand, type II fibrils with lamellar micro-structure and diameters of 629±94 nm exist. TEM investigations reveal that these lamellar fibrils have a straight backbone, called shish, resulting in a typical shish kebab structure. Smooth fibrils are formed by polymer chains stretched under uniaxial stress during the spinning process. In some cases, folded polymer chains grow as lamellar crystallites perpendicular to these smooth fibrils’ axis and build shish kebab structures. Moreover, spherulitic structures of type III can be identified which have a similar structure compared to the kebab of fibrils of type II.

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REFERENCES


