

AXIAL AND RADIAL SHRINKAGE OF POLYACRYLONITRILE-BASED STABILIZED FIBERS DURING LOW-TEMPERATURE CARBONIZATION TO CARBON FIBERS

Patrick Gutmann¹, Judith Moosburger-Will², Samet Kurt¹ and Siegfried Horn^{1,2}

¹ Experimental Physics II, Institute of Physics, University of Augsburg, 86135 Augsburg, Germany
patrick.gutmann@physik.uni-augsburg.de

² Institute of Materials Resource Management, University of Augsburg, 86135 Augsburg, Germany

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ABSTRACT

The development of fiber length and diameter during thermal carbonization treatment of stabilized polyacrylonitrile fibers was investigated by means of a newly developed experimental setup. It allows carbonization treatment in the temperature range up to 1000°C with defined mechanical tensions applied to the fibers. Simultaneously, the axial fiber elongation is measured. Three characteristic temperature regions are revealed: In the first temperature region between 250°C and 450°C the fibers start shrinking. This is more pronounced for higher than for lower tensions. Crosslinking between the ladder-type polymers of the stabilized structure is supposed. The second region reaches from 450°C to 750°C and is characterized by an accelerated axial fiber shrinkage, which is supposed to result from condensation reactions of high molecular weight compounds and happens independently of the applied mechanical tension. The third region between 750°C and 1000°C is defined by a decreasing shrinkage rate. The total length change of the fibers at the final temperature of 1000°C ranges between -17% for low and -12% for high tension. The radial shrinkage is clearly higher and amounts to about -36%. The results add to the understanding of the impact of mechanical tension on shrinkage of polyacrylonitrile-based fibers during carbonization treatment.

1 INTRODUCTION

Carbon fibers have a key role in the field of fiber reinforced materials due to their outstanding mechanical properties. Numerous investigations on production, characterization and application of carbon fibers have been published, amongst others important review papers [1–5].

However, the precise chemical processes occurring during fabrication of carbon fibers are still a matter of current investigation [2,6]. During manufacturing, the polyacrylonitrile (PAN) precursor fibers are first stabilized up to temperatures of 200-300°C under oxidative atmosphere to generate a thermally stable structure suitable for further high temperature heat treatment [2,7,8]. Subsequently, the fibers are carbonized under inert atmosphere at temperatures up to 1600°C, which results in the typical turbostratic graphite structure with a carbon concentration of more than 98wt% [2]. During this carbonization process, atoms like hydrogen, oxygen and nitrogen are eliminated in a temperature region up to 1300°C [3]. In the temperature region above 1300°C the turbostratic carbon structure is further ordered and oriented which improves the mechanical properties and forms the final carbon fiber [2].

This publication is to contribute to the understanding of carbonization of PAN-based fibers in the lower temperature range from 250°C to 1000°C. It is known that most of the volatile products are emitted in this region [9]. They consist mainly of HCN, NH₃, CO₂, CO, H₂, N₂ and H₂O as well as hydrocarbons and nitriles [3,10]. According to literature two important processes take place:

Starting from a stabilized structure, that is considered to contain ladder polymers, first the cyclized chains start crosslinking. This happens through intermolecular dehydrogenation and deoxygenation at temperatures lower than 600°C [3,11,12]. Crosslinked regions of the structure are also referred to as basic structural units (BSUs) [13,14].

In the temperature region above 600°C denitrogenation is supposed. The strong N₂ emission, which is

maximal around 900°C, points to condensation reactions of existing structures leading to lateral growth of heterocyclic ring systems to form larger sheet like structures [3,15].

The described chemical changes cause a severe mass-loss especially in the temperature region between 300°C and 500°C [6,11] which comes along with radial and axial shrinkage of the fibers [11,16]. The amount of shrinkage depends on the type and history of the precursor and stabilized fibers and can be affected by the application of tension during carbonization. Shrinkage generally shows a characteristic behavior as function of temperature. It is reported that below 500°C shrinkage is strongly affected by mechanical load, while above that temperature mechanical load can reduce but not suppress shrinkage [11]. Also, it is reported that mechanical tension during carbonization can improve the mechanical properties of the resulting fibers [17].

For understanding the impact of tension applied during carbonization it is necessary to investigate fiber parameters as function of both, temperature and tension. To this end, a newly developed experimental setup is used that allows for the carbonization of filament bundles under defined low heating rates and defined mechanical tension in the temperature range up to 1000°C. It permits the simultaneous measurement of the length of the fiber bundle, which is clamped completely within a homogenous temperature zone of the carbonization furnace. The aim of our publication is the identification of temperature regions with significant occurrence of length change of the fibers during heat treatment up to 1000°C under defined mechanical tension, to investigate the impact of tension on the axial and radial fiber shrinkage behavior.

2 EXPERIMENTAL

2.1 Fiber material

The precursor for all investigations presented here is a 6k polyacrylonitrile filament tow by Bluestar (Grimsby). Before carbonization the precursor is thermally stabilized in a separate experimental setup that allows for precise heating rates in the temperature range below 300°C and the application of defined mechanical tensions. Stabilization is done in a batch process, i.e. a fiber bundle is fixed within the furnace. The length of the stabilized fiber bundle is approx. 14cm. The applied tension has been chosen to that effect that carbonization of the stabilized bundle is possible over a wide parameter range. The temperature program was developed based on differential scanning calorimetry (DSC) measurements and is as follows: with a mechanical tension of 2.5MPa applied to the fiber tow a temperature of 150°C is reached at a heating rate of 5°C/min. Subsequently the fibers are heated to 250°C at 1,25°C/min. The final temperature of 250°C is held for 20min. As the investigations are focused on carbonization heat treatment, the stabilization program is the same for all presented specimens.

2.2 Carbonization of fibers

The stabilized fiber tow is mounted in a specially developed setup for carbonization under controlled mechanical tension depicted in Figure 1.

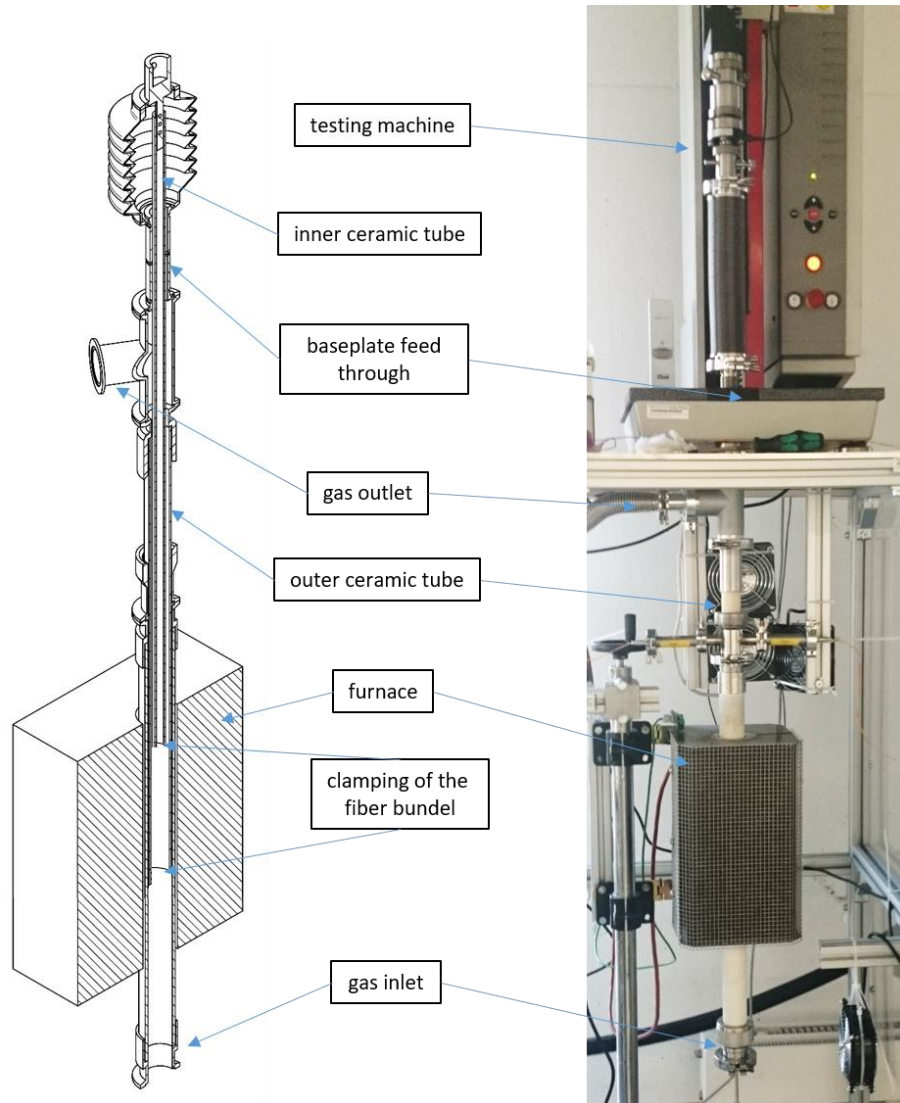


Figure 1: Setup for carbonization of fibers under defined mechanical tension.

All specimens have the same fiber length of approx. 75mm and are located entirely within the hot section of the furnace, as they are clamped there. A mechanical testing machine is integrated in the setup and connected to the fiber bundle by concentric ceramic tubes. Thus, the length change of the fiber bundle is monitored throughout heat treatment. The setup keeps the force on the fiber tow constant throughout heat treatment. Therefore, it must be considered that the mechanical tensions (force per unit area) are the initial tensions on the tow before heat treatment. The initial fiber diameter is measured by analysis of the fiber cross-section, while its development cannot be tracked during heat treatment. The setup is vacuum proof and can be evacuated and flushed in several cycles to guarantee an inert nitrogen atmosphere. The setup is thus operated at atmosphere pressure under constant nitrogen gas flow (250sccm). After the application of the desired tension and the adjustment of gas flow the temperature program is chosen and heating is started. For the presented measurements, the heating rate was 10°C/min up to a maximal temperature of 1000°C. Having performed the heating program, the oven starts to cool down without external cooling. At room temperature, the now carbonized fiber bundle is taken from the setup and is further investigated.

2.3 Measurement of fiber cross-sections

To investigate the cross-sections of the fibers, the bundle is embedded in resin (Struers epofix) and hardened. Subsequently, a cross section of the sample perpendicular to the fiber direction is prepared by grinding and polishing. With a digital optical microscope (Keyence VHX-600) the cross sections of

the fibers are recorded. The software ImageJ allows for the location of the fibers in the digital images [18]. As the microscope is calibrated in pixels per micrometer the cross-sectional areas of the detected fibers are obtained. The mean values of diameter and area of the investigated fibers, which are characterized by round cross sections, are determined.

3 RESULTS AND INTERPRETATION

3.1 Axial shrinkage during carbonization treatment

The carbonization of stabilized PAN fiber bundles in the temperature range up to 1000°C is performed at different initial mechanical tensions while the length change is measured simultaneously. Figure 2 shows the resulting elongation curves and the corresponding elongation rates for initial tensions between 0.5MPa and 4MPa. 3MPa is the highest applicable tension which allows carbonization of the fiber bundle up to the maximal temperature of 1000°C. The higher tensions lead to a premature fracture of the fiber tow, as visible for the 4MPa fiber bundle at a temperature of 610°C. The percental length change is related to the unstressed fiber bundle. Furthermore, the fiber elongation at 250°C is set to zero to settle the different elongations induced by the application of mechanical tension and to correct setting behavior of the bundle that might occur.

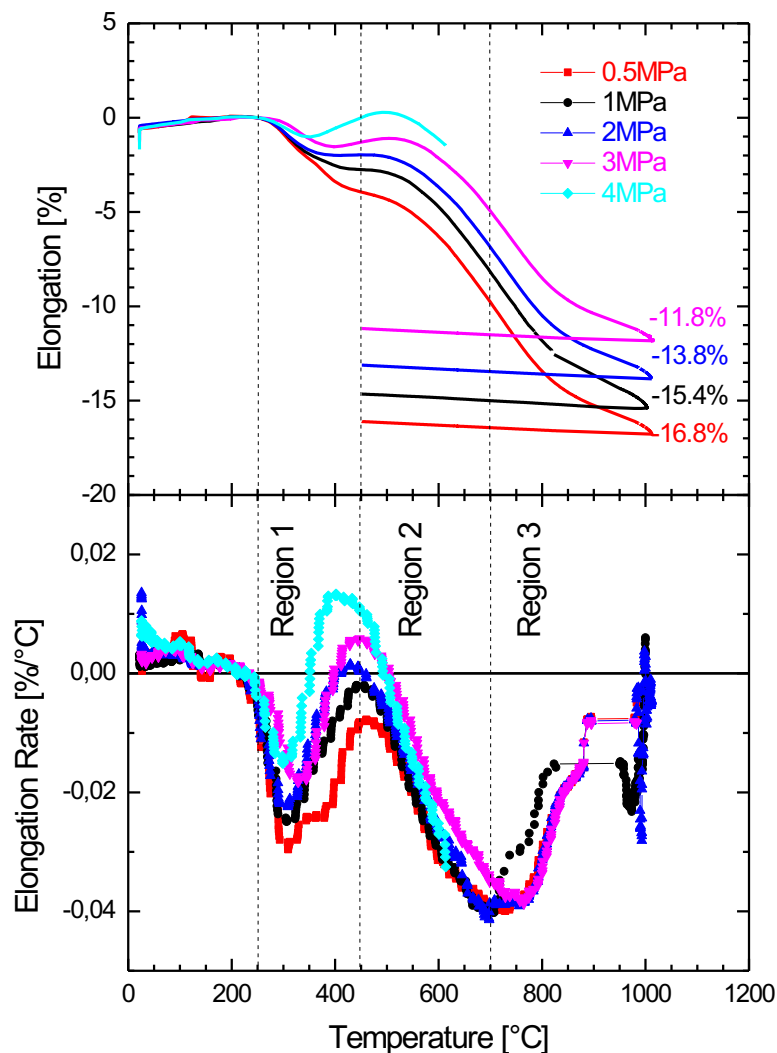


Figure 2: Elongation behavior of stabilized PAN-fibers during carbonization at different tensions.

In the temperature region of the stabilization, i.e. up to 250°C, no significant length changes are detected. Above 250°C the measurements show a characteristic temperature dependence of the elongation and can be divided into three temperature regions ranging from 250°C to 450°C, from 450°C to 750°C and from 750°C to the maximal temperature of 1000°C, which are described in the following.

Region 1: 250 – 450°C

At a temperature of 250°C axial shrinkage of the fiber bundle starts. The axial shrinkage rate is maximal at approx. 300°C and declines up to approx. 400-450°C. Application of higher tension leads to lower shrinkage rates and an earlier decrease of the shrinkage rate. For tensions above 2MPa the fibers can even be stretched at the end of this temperature region.

Region 2: 450 – 750°C

The next region starts with either axial elongation or shrinkage of the fiber bundle, depending on the applied tension. Then for all applied tensions a section of shrinkage follows, which is characterized by an increasing rate until approx. 750°C. The maximal axial shrinkage rate of -0,04/°C at a temperature of 750°C is independent of the applied tension.

Region 3: 750 – 1000°C

Above 750°C axial shrinkage slows down, as the shrinkage rates decrease. Also in this region the shrinkage is independent of the applied tension.

At the final temperature of 1000°C for each fiber specimen a characteristic fiber length and a characteristic total shrinkage is reached. As this total shrinkage is resulting from the integration of the shrinkage over the whole temperature range, it shows a dependency of tension. It lies between -16.6% for fiber bundles loaded by the minimal tension of 0.5MPa and -11.8% for loading by the maximal tension of 3MPa. Loading the fibers by a higher mechanical tension thus reduces the axial shrinkage of the fibers during carbonization heat treatment.

3.2 Radial shrinkage during carbonization treatment

Additionally, also the change of fiber dimensions perpendicular to the fiber axis is of interest. As no continuous monitoring of the fiber diameter during heat treatment is possible, partially carbonized fiber samples were produced which underwent carbonization up to defined final temperatures of 400°C, 600°C, and 750°C. The diameter of these partially carbonized fibers, of an untreated PAN fiber and of the stabilized fiber was analyzed. Exemplary cross section images are shown in Figure 3.

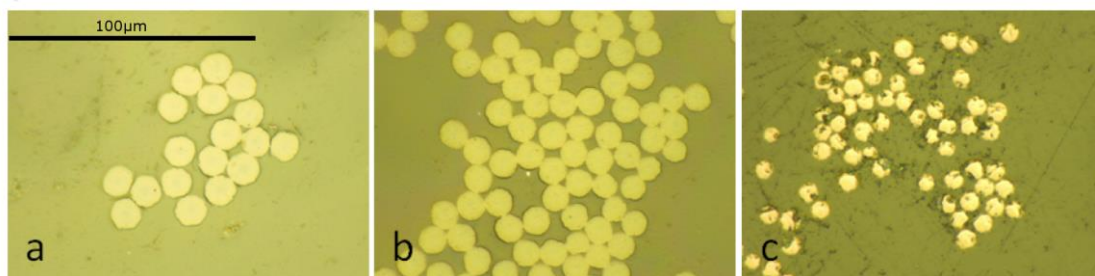


Figure 3: Cross-section of fibers during heat treatment at 3MPa: PAN-fiber (a), partially carbonized to 400°C (b), carbonized to 1000°C (c).

Figure 4 shows the dependency of fiber diameter on final carbonization temperature for different applied tensions. Also, the diameters of the corresponding PAN and stabilized PAN fibers are shown.

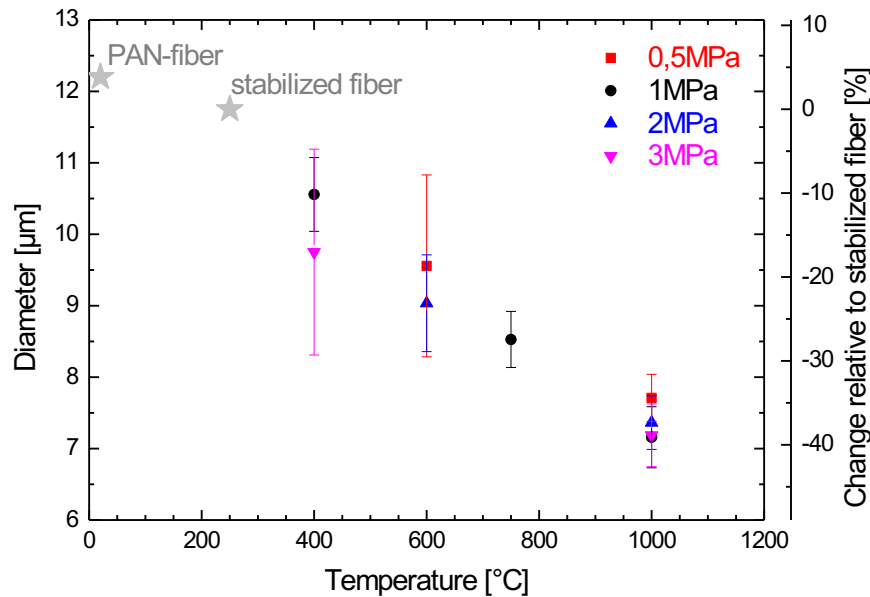


Figure 4: Diameter of fibers after partial carbonization at different tensions.

The diameter of the PAN precursor fiber is 12.2 μm . After stabilization, it measures 11.8 μm . As the stabilized fiber represents the starting point of our carbonization experiments, its diameter is used as reference value. With the start of carbonization, the diameter shows a rapid descend. At 400 $^{\circ}\text{C}$ it measures 10.6 μm (-9.8%) and 9.7 μm (-17.4%) for 1MPa and 3MPa, respectively. This temperature corresponds to the above defined Region 1. The decrease seems to show a dependence on the applied tension, in analogy to the decrease of fiber length. Nevertheless, the percental decrease in diameter (-10 to -17%) is much higher than the percental decrease in length (-1.5 to -3.4%) in that region. With increasing temperature, i.e. in Region 2 and 3, the diameter decreases continuously. The diameters corresponding to the different tensions converge more and more. At a final temperature of 1000 $^{\circ}\text{C}$ fiber diameter measures between 7.2 μm (-38.7%) and 7.7 μm (-34.5%) for all applied tensions. Compared to the measured length changes this is a considerably higher decrease in diameter. Especially in Region 2 and 3 the highest length changes and shrinkage rates are observed. At 1000 $^{\circ}\text{C}$ the length changes measure between -11.8% and -16.6%, whereas the diameter changes amount to -34.5% to -38.7%. This is a clear sign for the anisotropy eminent within the fibers. Also it becomes evident that tension has a more prominent impact on the evolution of fiber length than on fiber diameter.

3.3 Interpretation

According to Manocha [11], shrinkage in Region 1 is mainly due to the evolution of high molecular weight compounds and crosslinking between parallel ladder polymers via condensation reaction. This crosslinking probably fixes the structure and makes it mechanically more stable [3]. Therefore, in this region length change is still dependent on the mechanical load. The severe lessening of diameter underlines the loss of material due to gas emission and comes along with mass loss in this region [11]. The more prominent loss of diameter compared to shrinkage in length points to the high initial alignment of polymer chains in direction of the fiber axis which cause radial shrinkage by crosslinking of ladder chains [1,3].

Region 2 marks the beginning of a phase of denitrogenation which is continued in Region 3 [3,11,15,16]. Sheets of turbostratic carbon are developed and are growing due to crosslinking of the intermediate high molecular weight compounds. Shrinkage is probably caused by the relative shift of the sheets when linking [3]. According to our measurements in Region 2 and 3 diameter and length act more similarly than they did in Region 1, but still fiber diameter shrinks somewhat faster than fiber length. This points to the anisotropy of the fibers in which the sheets are arranged along the fiber axis [19].

4 CONCLUSIONS

In a newly developed experimental setup 6k PAN-fiber bundles were carbonized under different mechanical tensions. Simultaneously the length change of the fiber bundles was measured. To complete the investigations, the diameter of the fibers at various temperatures were determined by stopping the carbonization at those temperatures and analyzing the cross section of the resulting fibers. It was found that three characteristic regions of length change exist, namely from 250°C to 450°C, from 450°C to 750°C and from 750°C to 1000°C. Tension only has significant impact on length and diameter in the first region where - according to widely accepted models - polymer chains condense to high molecular compounds. At higher temperatures, where the existing structures are supposed to crosslink, tension has minor impact on shrinkage which here happens at a high rate.

The presented measurements are a contribution to the understanding of the chemical and physical processes during carbonization of PAN-based fibers, as the impact of mechanical tension applied to the fibers during carbonization is investigated dedicatedly.

References

- [1] B.A. Newcomb, Processing, structure, and properties of carbon fibers, *Composites Part A: Applied Science and Manufacturing* 91 (2016) 262–282.
- [2] E. Frank, L.M. Steudle, D. Ingildeev, J.M. Spörl, M.R. Buchmeiser, Carbon Fibers: Precursor Systems, Processing, Structure, and Properties, *Angew. Chem. Int. Ed.* 53 (21) (2014) 5262–5298.
- [3] P.J. Goodhew, A.J. Clarke, J.E. Bailey, A review of the fabrication and properties of carbon fibres, *Materials Science and Engineering* 17 (1) (1975) 3–30.
- [4] X. Huang, Fabrication and Properties of Carbon Fibers, *Materials* 2 (4) (2009) 2369–2403.
- [5] S. CHAND, Review Carbon fibers for composites, *JOURNAL OF MATERIALS SCIENCE* 35 (2000) 1303–1313.
- [6] S. Lee, Structural Evolution of Polyacrylonitrile Fibers in Stabilization and Carbonization, *ACES* 02 (02) (2012) 275–282.
- [7] M. Rahaman, A.F. Ismail, A. Mustafa, A review of heat treatment on polyacrylonitrile fiber, *Polymer Degradation and Stability* 92 (8) (2007) 1421–1432.
- [8] E. Fitzer, W. Frohs, M. Heine, Optimization of stabilization and carbonization treatment of PAN fibres and structural characterization of the resulting carbon fibres, *Carbon* 24 (4) (1986) 387–395.
- [9] V. Rašković, S. Marinković, Processes in sulfur dioxide treatment of PAN fibers, *Carbon* 16 (5) (1978) 351–357.
- [10] M.K. Jain, A.S. Abhiraman, Conversion of acrylonitrile-based precursor fibres to carbon fibres, *J Mater Sci* 22 (1) (1987) 278–300.
- [11] L.M. Manocha, O.P. Bahl, G.C. Jain, Length changes in PAN fibers during their pyrolysis to carbon fibers, *Angew. Makromol. Chemie* 67 (1) (1978) 11–29.
- [12] M. Jing, C.-g. Wang, Q. Wang, Y.-j. Bai, B. Zhu, Chemical structure evolution and mechanism during pre-carbonization of PAN-based stabilized fiber in the temperature range of 350–600 °C, *Polymer Degradation and Stability* 92 (9) (2007) 1737–1742.
- [13] A. Deurbergue, A. Oberlin, Stabilization and carbonization of pan-based carbon fibers as related to mechanical properties, *Carbon* 29 (4–5) (1991) 621–628.

- [14] M. Guigon, A. Oberlin, G. Desarmot, Microtexture and structure of some high-modulus, PAN-base carbon fibres, *Fibre Science and Technology* 20 (3) (1984) 177–198.
- [15] W. Watt, Nitrogen Evolution during the Pyrolysis of Polyacrylonitrile, *Nat Phys Sci* 236 (62) (1972) 10–11.
- [16] R.B. Mathur, T.L. Dhimi, O.P. Bahl, Shrinkage behaviour of modified PAN precursors—Its influence on the properties of resulting carbon fibre, *Polymer Degradation and Stability* 14 (2) (1986) 179–187.
- [17] J.-S. Tsai, Tension effects on the properties of oxidized polyacrylonitrile and carbon fibers during continuous oxidation, *Polymer Engineering and Science* 35 (16) (1995) 1313–1316.
- [18] W.S. Rasband, ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, 1997-2016.
- [19] S.C. Bennett, D.J. Johnson, W. Johnson, Strength-structure relationships in PAN-based carbon fibres, *J Mater Sci* 18 (11) (1983) 3337–3347.