POISSON RATIO OF CARBON FIBERS AT THE MICROSCOPIC AND THE NANOSCOPIC SCALE

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Introduction

Carbon fibers combine high tensile strength and high tensile modulus with low weight. Moreover, this high tensile strength is maintained up to extremely high temperatures. Thus, carbon fibers are an ideal material for lightweight structures, e.g. in aerospace application. Though they were firstly produced in the late 19th century by Edison for the use in incandescent lamps, the first commercial carbon fibers were not produced until the early 1960s [1]. A number of different processing techniques as well as different precursor routes were developed, the most important among them are polyacrylonitrile (PAN-fibers), mesophase-pitch-precursor (MPP-fibers) and rayon.
The structure of carbon fibers was investigated by many different methods, e.g. SEM [2,3], TEM and HTREM [2,4] as well as scattering methods [5-7]. It was proposed [5,8] that PAN-based carbon fibers are built up of basic structural units (BSUs), which consist of ribbon shaped layers of sp^2-type graphene sheets. These BSUs are forming undulating microfibrils over a range of some hundreds of nanometers. Another model proposed crumpled and folded sheets of entangled layer planes, which are interlinked at their boundaries [9]. The situation is still more complicated for MPP-fibers due to the variety of processing parameters [10,11] and the number of observed textures, e.g. radial, radial-folded or onion-like.
Recently, microfocus X-ray optics were developed, which enabled the investigation of single carbon fibers by using high brilliance synchrotron radiation sources [12,13]. This method has the advantage that the development of the structure of carbon fibers can be investigated in-situ during loading [14]. Furthermore, the experimental accuracy is significantly increased, because in fiber-bundle tests a tilt of fibers within a bundle cannot be separated from the tilt of the layers within a fiber [12]. In the presented work, this method is used to investigate the Poisson ratio of the BSUs (with a size of some nanometers) and it is compared to the Poisson ratio of the whole carbon fiber (with a size of some microns).

Experimental

The scattering experiments were carried out at the microfocus beamline (ID13) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. A monochromatic

X-ray beam with a wavelength of 0.0975 nm collimated to a diameter of 10 microns is used to determine the Poisson ratio of the BSUs in-situ during loading. Fig.1a shows a sketch of the setup. For the determination of the Poisson ratio of the whole fiber, a nearly identical setup is used (Fig.1b), differing only in the wavelength of the beam, which is now provided by a laser with a wavelength of 633 nm.

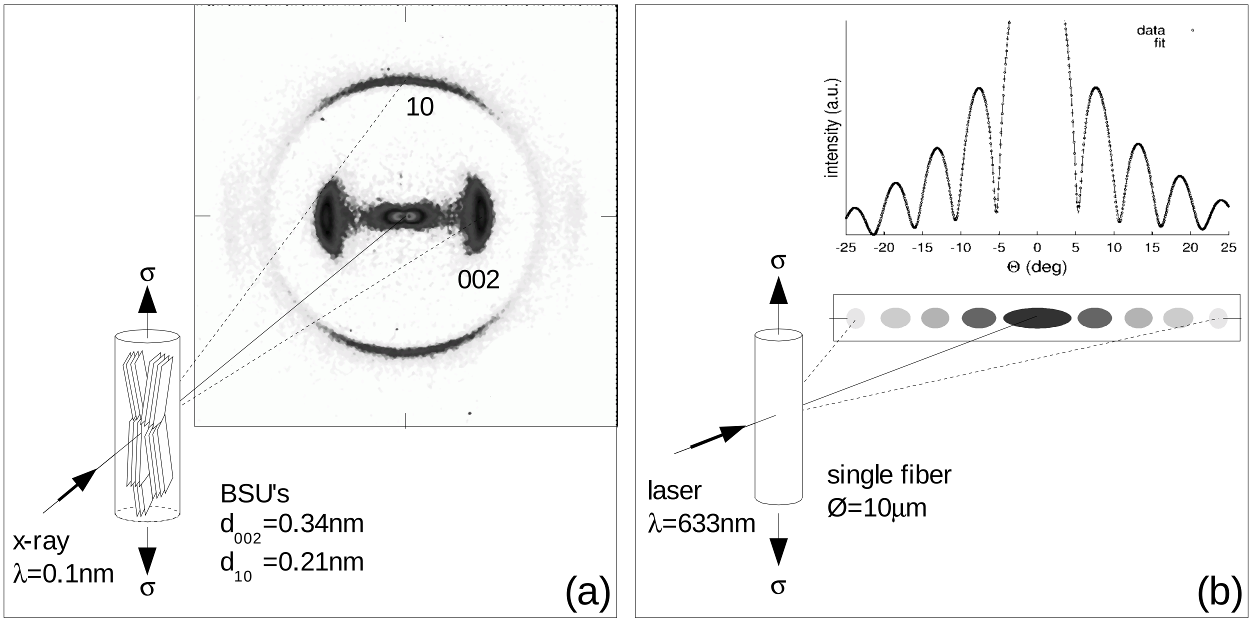

Figure 1 Sketch of the experimental setups and the obtained scattering images: (a) using synchrotron radiation, (b) using laser light

The scattering images and the corresponding load-displacement curves were recorded. A typical 2D-scattering pattern of the measurement at the nanometer scale is depicted in Fig.1a. The intensity maximum of the 002-reflection, evaluated in the equatorial direction and converted into real space dimensions, gives the interlayer distance d_{002} of only those BSUs, which are aligned along the fiber axis and thus the loading direction. The intralayer distance d_{10} within the graphene planes is obtained from the maximum of the 10-band in meridional direction. The Poisson ratio of the BSUs is then calculated from the ratio interlayer strain ε_{002} to intralayer strain ε_{10} in dependence on the load σ:

$$\upsilon_{BSU} = -\frac{\varepsilon_{002}}{\varepsilon_{10}} = -\frac{d_{002}(\sigma) - d_{002}(0)}{d_{002}(0)} \Bigg/ \frac{d_{10}(\sigma) - d_{10}(0)}{d_{10}(0)} \qquad (1)$$

For the measurements of the Poisson ratio of the whole fiber, the obtained 1D-scattering image (Fig.1b) has to be evaluated according to the theory of light scattering taking polarization and refractive index into account [13]. Denoting the diameter in dependence on the stress σ with D and the gauge length of the tested fiber with L, the Poisson ratio is calculated from Eq. (2):

$$\upsilon_{fiber} = -\frac{\varepsilon_{trans}}{\varepsilon_{long}} = -\frac{D(\sigma) - D(0)}{D(0)} \Bigg/ \frac{L(\sigma) - L(0)}{L(0)} \qquad (2)$$

Results and Discussion

Fig. 2a shows the interlayer strain in dependence on the intralayer strain for two types of fibers, one is PAN-based and the other MPP-based. Surprisingly, the interlayer distance increases for the PAN-based fiber with increasing stress, whereas the MPP-based fiber shows the conventional behavior, i.e. a decrease of the interlayer distance when being stretched. In other words, on a nanometer scale, the BSUs of PAN-based fibers are one of the rare materials [15] exhibiting a negative Poisson ratio. This negative Poisson ratio at the nanoscopic scale is not reflected at the microscopic scale: The Poisson ratio is positive for the whole fiber with a thickness of 7 microns (see Fig.2b).

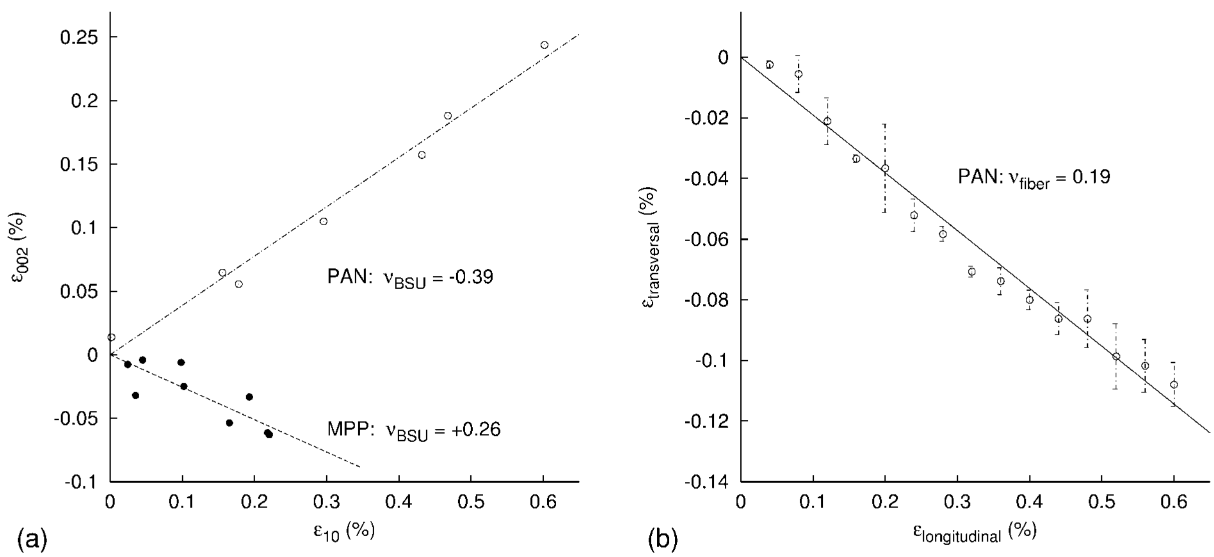

Figure 2 Poisson-ratio of (a) the nanocrystallites (BSUs), (b) of the whole carbon fiber

A possible interpretation of this behavior might be the existence of cross-links, maybe particular close to the boundaries of the BSUs. Because in PAN-based fibers the graphene planes develop from polymer chains after stabilization, cyclication and graphitization, the resulting structure is less ordered than the one of MPP-fibers. This can be deduced for example from the larger stacking size of this type of fibers, which are produced from prestructured mesophase-pitch precursor. Thus, a higher number of out-of-plane bonds can be expected in PAN-fibers, i.e crosslinks between the layers. These crosslinks may be the reason for the significant increase of the shear modulus of PAN-based fibers in comparison to MPP-fibers [14]. The out-of-plane bonds could also lead to the observed negative Poisson-ratio, because they are acting as rigid columns between the layers and therefore inhibit the decrease of the layer distance, on the other hand enforcing the expansion of the interlayer graphene sheets. Of course, this is only possible, because the layers of the BSUs of PAN-based fibers are less restricted by other BSUs than that of MPP-based fibers – the porosity for this type of fibers is about 30 percent whereas it is less than 10 percent for MPP-based fibers.

Conclusions

- The behavior of the lateral contraction at the nanoscopic scale of the BSUs of PAN-based and MPP-based fibers is directly opposed – MPP-based exhibit the normal positive Poisson-ratio whereas the ratio is negative for PAN-based fibers.
- This surprising characteristic does not affect the properties on the microscopic scale insofar as the Poisson-ratio of the whole fiber is positive for PAN- and MPP-based fibers.

Acknowledgements

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References

[1] Young RJ, Day RJ, Zakikhani M. The Structure and Deformation Behaviour of Poly(p-phenylene benzobisoxazole) Fibres. J. Mater. Sci. 1990;25(1A):127-136.
[2] Endo M. Structure of Mesophase Pitch-Based Carbon Fibres. J. Mater. Sci. 1988;23(2):598-605.
[3] Barnes AB, Dauch FM, Gallego NC, Fain CC, Thies MC. As-Spun Orientation as an Indication of Graphitized Properties of Mesophase-Based Carbon Fiber. Carbon 1998;36(7-8):855-860.
[4] Oberlin A. Carbonization and Graphitization. Carbon 1984;27(6):521-541.
[5] Perret R, Ruland W. The Microstructure of PAN-Base Carbon Fibres. J. Appl. Cryst. 1970;3(6):525-532.
[6] Takaku A, Shioya M. X-ray Measurements and the Structure of Polyacrylonitrile- and Pitch-Based Carbon Fibres. J. Mater. Sci. 1990;25(11):4873-4879.
[7] Gallego NC, Edie DD. Structure-Property Relationships for High Thermal Conductivity Carbon Fibers. Composites Part A 2001;32A(8):1031-1038.
[8] Fischer L, Ruland W. The Influence of Graphitization on the Mechanical Properties of Carbon Fibers. Colloid and Polymer Science 1980;258:917-922.
[9] Guigon M, Oberlin A, Desarmot G. Microtexture and Structure of Some High Tensile Strength, PAN-Base Carbon Fibres. Fibre Sci. and Techn. 1984;20:55-72.
[10] Ruland W. Carbon Fibers. Advanced Materials 1990;2(11):528-536.
[11] Edie DD. The effect of Processing on the Structure and Properties of Carbon Fibers. Carbon 1998;36(4):345-362.
[12] Paris O, Loidl D, Peterlik H, Müller M, H. Lichtenegger, Riekel C, Fratzl P. The Internal Structure of Single Carbon Fibers Determined by Simultaneous Small- and Wide-Angle Scattering. J. Appl. Cryst. 2000;33:695-699.
[13] Paris O, Loidl D, Peterlik H. Texture of PAN- and Pitch-Based Carbon Fibers. Carbon 2002;40:551-555.
[14] Loidl D, Peterlik H, Müller M, Riekel C, Paris O. Elastic Moduli of Nanocrystallites in Carbon Fibers measured by in-situ X-ray Microbeam Diffraction.
[15] Lakes R. Foam Structures with a Negative Poisson's ratio. Science 1987;235(4792):1038-1040.