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Nanoindentation Applied to Materials with an Inner Structure

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Abstract. Nowadays, nanoindentation is commonly applied to various materials to assess micromechanical properties. Often, exact microstructure of the material building blocks is not properly analyzed which may introduce large discrepancies in the data obtained from different tests. It is shown in the paper, that different deformation mechanisms in tension and compression take place for the tested materials which is demonstrated by large differences between the measured nanoindentation moduli and macroscopic tensile elastic moduli. The situation is illustrated on several types of biological and man-made fibers. Differences ~44-57% in elastic moduli evaluated from the two tests appear in case of biological fibers, ~68% difference was found for high strength PVA fibers and 767% (!) for carbon fibers.

Introduction

Nowadays, nanoindentation technique is commonly applied to study mechanical properties of various homogeneous as well as heterogeneous materials. The numerical procedure that is used for extracting material constants (e.g. elastic modulus, hardness) is usually based on simplified assumptions such as homogeneity and isotropy of the material in the tested volume (e.g. [1]). Quite rarely, material anisotropy is taken into account using analytical solution [2]. However, explicit derivation of elastic constants from indentation modulus is not possible in a general anisotropic case. Materials with continuous but heterogeneous isotropic phases can be successfully treated with statistical grid indentation for many materials like cementitious materials [4] geopolymers [7] or metal alloys [8].

However, none of the evaluation procedures mentioned above takes into account an inner material structure that can appear at micro-scale, i.e. the scale at which nanoindentation takes place. There might be striking differences between evaluated indentation moduli and the real elastic constants of the specimen constituents if the inner structure is not properly considered. The situation will be demonstrated on several examples of man-made and biological fibers. Although, relatively small fibers with diameters in tens of micrometers are usually treated as macroscopically homogenous, their microstructure is typically quite complicated. It will be shown later in the paper, that there is no simple recommendation how to solve the problem in general and the only solution is to disclose the true deformation mechanism that takes place under the indenter for a specific case. It will also be shown that results of elastic properties received from tension tests are not directly comparable with properties evaluated from compression indentation tests since the deformation mechanisms are different for these two cases and the same material. This is in direct contradiction to common measurements performed e.g. on metals which behave more or less similarly in tension/compression tests [8].

Methods

Several materials that are used as fibrous reinforcement in various composites at the micrometer level have been selected. As shown later, all the samples can be characterized with an inner structure that is responsible for different behavior in tension and compression. Elastic material constants were assessed in two ways. At first, fibers were indented in the nanoindenter (CSM Nanohardness tester) equipped with Berkovich tip and elastic constants evaluated using classical

assumptions of homogeneous isotropic materials. Secondly, fibers were tested in direct tension test by means of electromechanical press. Results of elastic moduli were compared and deformation mechanisms responsible for observed differences identified based on the sample microstructural composition.

Test samples

For nanoindentation, all samples were prepared in a similar way. Fibers were fixed by a low viscosity epoxy in cylindrical moulds in parallel with the cylinder axis. Sample cross sections were cut with diamond saw and polished with SiC papers to receive flat and smooth surface with low roughness. Indents were placed in the central region of fibers respecting the empirical 1/10 rule (i.e. the size of indents was prescribed to be less than 1/10 of the fiber diameter in order not to be influenced with the surrounding epoxy). Primarily, the fibers were tested in axial direction by nanoindentation, but some of them also in radial direction (i.e. in perpendicular direction to the fiber surface). Fiber cross sections were imaged in order to assess geometrical parameters like fiber cross sectional area and outer or inner diameters (in case of hollow fibers).

The first category of the tested samples was a set of biological fibers used formerly or currently as reinforcement in mortars and plasters. We selected fibers from horse, goat, and pig hair. The second category included man-made fibers, namely high tension polyvinylalcohol fibers (Kuralon II PVA fibres, Kuraray, Co.) and carbon fibers (carbon multifilament Torayca T 800 HB).

Experimental details and results

Geometrical characteristics of the tested fibers received from image analysis of their cross sections (Fig. 1) on several tens of fibers are summarized in Table 1.

Nanoindentation of biological fibers was prescribed as load controlled to maximum force 1 mN with linear loading 12 mN/min, holding period 15 s and unloading at 12 mN/min. PVA fibers were loaded at 6 mN/min to maximum force 0.5 mN. Peak force was kept constant for 15 s and unloaded at 6 mN/min. Oliver and Pharr method [1] was used with assumed Poisson's ratio 0.45 for all the fibers. Similarly, carbon fibers were loaded to maximum force 10 mN at loading/unloading rate 60 mN/min with holding period 5 s. Poisson's ration for carbon fibers was set to 0.4.

Maximum indentation depths varied according to the tested sample. The final depths did not exceed 1/10 of the fiber diameter (Table 1). Elastic moduli received from nanoindentation are summarized also in Table 1 together with elastic moduli measured in macroscopic tensile tests of individual fibers. Macroscopic elastic moduli are related to the true cross sectional area of fibers, i.e. excluding inner hollow (medullar) part, to receive true elastic moduli of a solid. It can be seen that there are large differences in the values. Tensile moduli are about 44-57% lower than those from nanoindentation in case of biological fibers. Tensile moduli of PVA fibers are by 68% higher than indentation moduli. Surprisingly, tensile moduli of carbon fibers are about 7.6 times (!) higher than those received from nanoindentation. Such striking differences can not be caused by usual effects such as surface roughness (which typically influences scattering of the data) or wrong assumption of Poisson's ratio. The only explanation of the differences is that the tensile deformation mechanism is different from the mechanism that appears in case of nanoindentation (mostly compression). To solve this problem, one must look at the inner fiber structure and find appropriate mechanisms of the fiber basic building blocks.

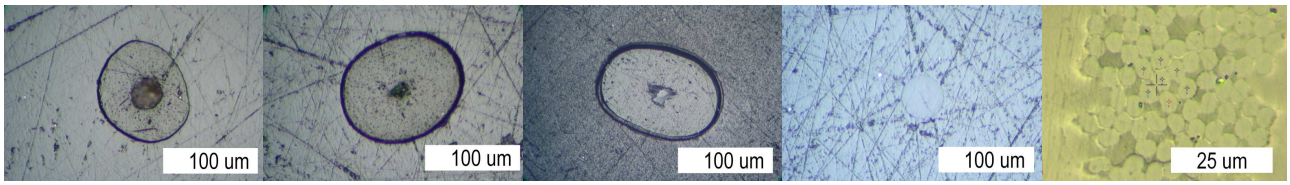

Fig. 1 Fiber cross sections (left to right: goat, horse, pig, PVA, carbon fiber)

Table 1 Geometrical and mechanical characteristics of fibers in longitudinal direction

Fiber	Equivalent outer diameter [μm]	Indentation depth [nm]	Nanoindentation E_{nano} [GPa]	Tensile test E_t [GPa]	$(E_{nano}-E_t)/E_{nano}$
Goat	112.2±5.8	423±20	4.86±0.5	2.71±0.5	0.442
Horse	140.4±25.4	448±14	4.69±0.2	2.67±1.1	0.431
Pig	206.0±40.6	422±12	5.12±0.6	2.22±0.9	0.566
PVA	40±0	291±14	8.30±0.9	13.94±2.0	-0.680
Carbon	4.6±0.2	406±17	33.92±1.7	294* (*Torayca)	-7.667

Fiber microstructures and deformation mechanisms

Biological fibers. It can be assumed that all tested biological fibers are similar in the composition and inner structure. Their microstructure is quite complex, but in general, each fiber is composed of three layers - cuticle, cortex and medulla. Cuticle is an outer protective layer which is composed of flat cells that overlap each other from root to the fiber tip (cuticle thickness ~1 μm). Cortex takes up a major portion of cross-sectional area of the fiber. It is composed of cortical cells (~1-5 μm in diameter, ~100 μm long) and intercellular binding material. Elongated cortical cells are aligned in the fiber direction. These cells are composed of macrofibrils (~0.1-0.4 μm in diameter) and a nuclear remnant. Macrofibrils are further divided to intermediate filaments called microfibrils (composed of α-keratin helical proteins having ~7 nm in diameter) embedded in an elastomeric matrix (composed of keratin-associated proteins). The medulla is the central part of a hair that contributes negligibly to the mechanical properties of the fiber.

When a hair is subjected to tension, microfibrils are stretched together with the surrounding matrix. However, after reaching a critical stress at the microfibril (2% extension), small open regions in which α-keratin transforms to mechanically weaker β-keratin appear. More details concerning microstructural changes and related tension mechanism can be found in detailed review by Hearle [9]. The mechanism of α–β transition in microfibrils is responsible for lower macroscopic elastic modulus measured in uniaxial tension. We can directly hypothesize that no transition appears in microfibrils in case of compressive load. This can explain the higher modulus measured in nanoindentation.

PVA fibers. Kuralon II are synthetic fibers made from polyvinyl alcohol (PVA) solution produced by extrusion and spinning of polymeric melt. The resultant fiber is characterized with high strength, low elongation and high modulus of elasticity. It finds applications e.g. as reinforcement in cementitious or plastic composites. Due to spinning process the polymeric chains in the material volume are highly oriented along the fiber direction which causes material anisotropy. From the microstructural point of view, we can image the fiber as a set of parallel fibrils of polymeric chains having high modulus in longitudinal direction compared to transverse direction. In case of compression loading, the transverse modulus contributes to the indentation modulus measured in the longitudinal direction (8.3 GPa) which is manifested by 68% decrease of indentation modulus compared to macroscopic uniaxial tension modulus (13.94 GPa, see Table 1). In this case, fiber anisotropy is possibly the major reason for obtained differences. An effect of polymer chain debonding caused by sharp indenter could also contribute to this phenomenon.

Carbon fibers. Similar situation can be found in case of carbon fibers. Carbon fibers consist of stacks of graphitic layer planes which are strongly linked in the direction of the fiber axis and weakly in the perpendicular direction. Tensile longitudinal modulus of the fiber reaches 294 GPa (taken from the producer information) whereas transverse modulus is typically an order of magnitude lower. Since the transverse modulus was not supplied by the producer, we tested a single fiber by nanoindentation in perpendicular direction to the fiber. Indentation modulus reached 12.8±0.43 GPa in this case. The effect of fiber anisotropy is obvious since indentation modulus measured in the longitudinal direction of a single fiber was ~34 GPa (Table 1). This value is still very far from the macroscopic uniaxial tensile modulus (294 GPa).

Therefore, the deformation mechanisms must be very different in case of tension/compression. There are no stability problems of the graphitic layers when they are subjected to tension which cases high modulus. In contrast, they can experience debonding and buckling problems in case of compression. Due to the wedge effect caused by a sharp indenter, graphitic layers are separated from each other and compressive load in longitudinal direction involves tensile stresses in transverse direction. Such mechanism that may be enhanced by the presence of pores between the layers was proposed e.g. by Diss et al. [10]. Described deformation mechanisms are responsible for drastic differences between uniaxial tension modulus and indentation modulus.

Summary

It was shown in the paper that direct comparison of the results received from nanoindentation and uniaxial tension tests is not possible for materials with an inner structure. The situation was demonstrated on several examples of biological and man-made fibers for which nanoindentation and tensile elastic moduli have been monitored. Differences in tens (biological fibers) or even hundreds of percents (carbon fibers) have been obtained. The deformation mechanisms responsible for different material behavior in tension and compression have been described in the paper. An emphasis was put on the behavior of basic building blocks for the distinct materials.

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