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Nano-scale modulus mapping of biological composite materials: Theory and practice

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ABSTRACT

The mechanical behavior of materials depends to a large extent on their properties at the nanoscale and, therefore, novel characterization techniques with sub-micron spatial resolution were developed in the last decades. Among them are the variety of tools for probing local elastic and viscoelastic properties of materials, the methods such as nanoindentation and AFM- and nanoindenter-based measurements using force modulation. In this review, we describe the nanoindenter-based nanoscale modulus mapping technique, which emerged as an extremely powerful tool for providing quantitative information on the storage and loss moduli distributions in complex nanocomposites. Since the tip penetrates only a few nanometers into the materials, this technique provides a superior lateral resolution in the order of 20 nm. All aspects of the method are covered, including a historical perspective, theoretical analysis, instrumentation, and examples of its application for studying multiphase structures and interfaces. The main focus of this review is the challenging field of natural bio-composites, which consist of stiff and compliant components, often with nanometric dimensions. Gradients of mechanical properties across the nm-sized features in biological materials are of upmost importance for their mechanical performance. Quantitative information on the nano-scale moduli distributions in these structures can hardly be achieved by other means.

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1. Introduction

The invention of atomic force microscope (AFM) by Binnig, Quate, and Gerber in 1986 [1] opened a new era in surface science in general, and in studying the near-surface mechanical properties of materials, in particular. From the very beginning, this instrument was intended to measure contact forces between an AFM tip and sample surface, as follows from the name of the microscope. The benefits of the instrument comprised the ability to measure ultra-small forces (down to pico-Newtons) in various samples (including non-conductive materials) without the need of keeping them in vacuum, and the capability of contact force mapping across the surface of a sample. Many efforts have been directed towards improving the sensitivity and spatial resolution of AFM by using different force modulation techniques [2]. One of the principal benefits of force modulation is the possibility to separate between elastic and inelastic signals when analyzing the time response of the cantilever tip to an external periodic force when in contact with the studied material. The common methods, such as ultrasonic force microscopy [3,4], and atomic force acoustic measurements [5,6], use ultrasonic transducers for this purpose. However, extraction of elastic moduli and viscoelastic constants from such measurements still remains problematic due to several reasons: the difficulty to accurately describe the tip-surface contact area, which is needed to convert the measured force to the applied stress [2,7–9]; the need for an appropriate contact mechanics model, which is required to analytically describe the physics of the tip-sample interaction and sensitivity limitations introduced by the stiffness of the cantilever, especially when measuring a composite structure made of materials with extremely different characteristics [10–12].

Another approach to measure mechanical properties on the nanoscale is nanoindentation, utilizing diamond indenters with very sharp tips, a few hundred nm in size. As in classical hardness tests, nanoindentation was primarily invented for measuring local hardness of materials in small volumes [13,14] based on the area of the indentation trace (indent) measured by AFM or electron microscopy. Nowadays, this has been replaced by the measurement of the indenter's penetration depth into a material as a function of the applied load, which can be converted to the same information using the tip geometry but without the need of an additional microscopic investigation of the sample after the indentation. As was shown by Oliver & Pharr in 1992 [15], in addition to local hardness, these measurements also enable obtaining the contact stiffness and, consequently, some information on the local Young modulus. The latter parameters are extracted from the slope of the initial part of the load-displacement curve upon unloading, i.e. when the elastic displacement is recovered. At the same time, we note that typical diameter of the indent can reach few microns, which probes a near-surface region that is often much larger than the characteristic features of interest. Nanoindentation is not intended for raster mapping of mechanical properties, but provides their magnitudes in discrete sampling points. In addition, in some cases, reversible plastic deformation, creep, and viscoelasticity can make the extraction of elastic moduli very problematic.

In order to overcome these difficulties and to develop an adequate method for measuring elastic and viscoelastic moduli across the surface of the sample with high spatial resolution, the nanoscale modulus mapping was introduced, which instrumentally combines a nanoindenter with a force modulation system [16–18]. In this method, the sample is rastered using a piezoscanner and a tiny static force, F_{DC}, is applied to the nanoindenter tip at every node of the raster. Due to the smallness of the static force, the tip penetrates only a few nanometers beneath the surface of the sample. Subsequently, two main advantages are achieved: first, practically pure "elastic" contact between the tip and the surface is realized with negligible amount of plastic deformation in terms of dislocation glide, twinning, etc., which introduces irreversible local changes of sample's shape upon nanoindentation; secondly, the contact area remains very small, less than 20 nm in size, thus providing an