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Three-dimensional imaging of polymer materials by Scanning Probe Tomography

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ABSTRACT

Scanning Probe Tomography (SPT) is a new method for nanoscale volume imaging of sample morphology and property distribution based on Scanning Probe Microscopy (SPM). In this review we describe and discuss recent results obtained with different SPT techniques on polymer samples. The design of the existing SPM based instruments used for tomography in principle allows for volume reconstruction of any kind of mechanical, functional or chemical property distribution, which can be measured by SPM. We describe some recent volume reconstruction results from several types of polymer materials and critically discuss limitations and future prospects of SPM tomography.

Contents

1. Introduction

In materials science the request for local information at the nanometer scale makes high-resolution microscopy techniques essential tools for morphology characterisation. In this respect, Transmission and Scanning Electron

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Microscopy (TEM, SEM) and Scanning Probe Microscopy (SPM), in particular Atomic Force Microscopy (AFM), are the most important techniques extensively utilised for characterisation of soft matter.

Standard high-resolution microscopy provides mainly information on the lateral organisation by acquisition of two-dimensional (2D) projection images through the thin-film specimen volume (TEM) or, on the other hand, probes mainly the topography at the sample surface (SEM and SPM). In modern polymer research, however, information on the local nanoscale volume organisation of complex material systems becomes more and more important; in fact better understanding of essential parameters determining interface organisation in the bulk of materials systems, phase separation and network formation in polymer blends and composites, to name but a few, and its influence on the macroscopic materials properties makes access to nanoscale volume information imperative.

Three-dimensional (3D) imaging of the organisation of complex material systems is one of the most actively developing areas of modern microscopy, and tomography is the main approach [1,2]. Tomography, in its old Greek meaning, refers to a technique to draw (reconstruct) a section of an object, referring to inner sections as opposed to surfaces. Since then tomography has become associated with mapping of inner sections across an object and therefore refers to a 3D reconstruction method. Nowadays, tomography essentially means to reconstruct the 3D structure of objects from a series of two-dimensional projections or sections. 3D imaging of structure was successfully performed with different techniques like X-ray and TEM tomography, confocal microscopy tomography, and combination of mechanical sectioning by focused ion beam (FIB) or microtome with optical or electron microscopy [1–8].

Recently, advances in instrument and software development made electron tomography (ET), also referred to as transmission electron microtomography and 3D TEM, a versatile tool for nanoscale volume reconstruction of biological and polymer materials. A series of 2D TEM projection images is acquired at different angles during tilting the specimen with respect to the electron beam. After off-line alignment and reconstruction a 3D image of the specimen is obtained that can be analysed voxel by voxel (volume pixel) [1–3]. An alternative approach for volume reconstruction is so-called slice-and-view, in which the 3D morphology is obtained by repeating cutting away some material from the sample by applying FIB and subsequent imaging of the fresh surface by SEM [4]. Afterwards the stack of images is aligned and the volume organisation is reconstructed. However, polymer materials as well as biological samples are very electron beam sensitive with low critical electron dose before their initial organisation might be altered [9–11].

An alternative approach for volume reconstruction is so-called slice-and-view, in which the 3D morphology is obtained by repeating cutting away some material from the sample by applying FIB and subsequent imaging of the fresh surface by SEM. Afterwards the stack of images is aligned and the volume organisation is reconstructed. However, this approach has similar limitations as discussed for TEM and the high energy ion beam certainly alters the sample organisation at the cut surface. In addition, SEM has lower lateral resolution and the z-resolution of the reconstructed volume is determined by the thickness of the removed sections, which commonly is in the order of tens of nanometers. In contrast to electron microscopy, SPM can be considered as a non-destructive surface characterisation technique for soft matter analysis [12,13], which can be operated at ambient or liquid conditions and potentially overcomes several of the above mentioned limitations of EM. For 3D analysis, however, SPM as a surface technique has to be combined with a surface material removing tool to gain access to volume information. In this review we describe methods and technical solutions, as well as reconstruction procedures and data interpretation, which allow for 3d imaging of sample structure and properties measured by SPM methods. Moreover, we are aiming on critically exposing advantages, limitations and challenges of different approaches.

2. Methods of Scanning Probe Tomography

First of all, existing methods of SPM tomography can be destructive and non-destructive. Destructive methods of SPM tomography are based on sequential removing thin layer of material from sample surface and following measurement of surface by some of the SPM method. The general principle of 3D tomography by stacking conventional 2D SPM images is shown in Fig. 1a. Destructive SPT methods can be classified by method of material removal. Until now there are three main methods of removal of thin slices from sample surface: 1. Wet or plasma etching, 2. Ultramicrotome slicing, 3. Scratching by stiff cantilever.

In a first attempt to obtain volume data by SPM repeating plasma etching of a sample's surface, followed by SPM imaging of the fresh surfaces and subsequent volume reconstruction of the obtained data was applied [14]. The result of 3D reconstruction of the microdomain structure of the triblock copolymer poly-(styrene-*block*-butadiene-*block*-styrene) (SBS) is shown in Fig. 1b. The sample surface was imaged with ~10 nm lateral resolutions by using amplitude modulation mode (AM-AFM, also known as tapping mode) and phase imaging each time after surface was etched by plasma. For volume imaging, on average ~7.5 nm thick layers of the block copolymer were successively removed 13 times by plasma etching. The combination of topography information and phase imaging for all 14 images separated by the etching step of 7.5 nm resulted in reconstructed volume $200 \times 160 \times 45\ nm^3$. The 3d phase contrast image in Fig. 1b can be interpreted as organisation of PS cylinders within the SBS film. The disadvantage of this experiment is that the etching process was performed ex situ by transferring the sample to the etching chamber forth and back between subsequent SPM image acquisitions, which may lead to difficulties precisely recognising and aligning the sample area of interest at the nanoscale.

The same research group has advanced their instrument design so that in situ automated wet chemical etching [15]