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Scanning Probe Microscopy for polymer film characterization in food packaging

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Abstract. Scanning probe microscopy (SPM) is a branch of microscopy allowing characterization of surfaces at the micro-scale by means of a physical probe (with a size of a few microns) raster scanning the sample. SPMs monitor the interaction between such probe and the surface and, depending on the specific physical principles causing the interaction, they allow generation of a quantitative map of topographic properties: geometrical, optical, electrical, magnetic, etc. This is of the greatest interest, in particular whenever functional surfaces have to be characterized in a quantitative manner. The present paper discusses the different applications of Scanning Probe Microscopy techniques for a thorough characterization of polymer surfaces, of specific interest in particular for the case of food packaging applications.

1. Introduction

Scanning probe microscopy (SPM) refers to a family of techniques which allow imaging of surfaces with nanometric resolution thanks to the implementation of a sharp tip scanned across a sample interface [1]. The specific interaction occurring between such tip and the scanned sample define the microscope variant, which eventually provides the characterization of a given surface property [2]. Typically surface 3D topography is provided by Atomic Force Microscopy (AFM) which measures relies on Van der Waals or other attractive and repulsive forces [3] (Figure 1A). Tip-sample vertical interaction force can be thus converted into a relative vertical elevation, while lateral forces are useful for reconstruction of local friction in the so called Lateral Force Microscopy (LFM) [4] (Figure 1A).

Elastic properties of materials are achieved by Atomic Force Acoustic Microscopy (AFAM): in this case, the sample under investigation is vibrated at ultrasonic frequency, while the cantilever is contacting and scanning the sample surface through the tip [5]. Vibrations perceived by the probe allow dynamic mapping of elastic modulus, shear modulus or Poisson ratio properties (Figure 1C).

Optical information at the nanoscale can be also monitored, through Near-field Scanning Optical Microscopy (NSOM) [6] (Figure 1D). Such technique enables non-diffraction limited imaging and spectroscopy of surfaces thanks to implementation of a small aperture between the light source and the sample surface and the generation of an evanescent field emanated from the aperture in the near-field



region, at a few tens of nanometers from the aperture. Specific functionalization of the probing tip and of the scanning system allow collection also of other information, such as magnetic or electric properties even at relatively high experimental temperatures [1, 7, 8].

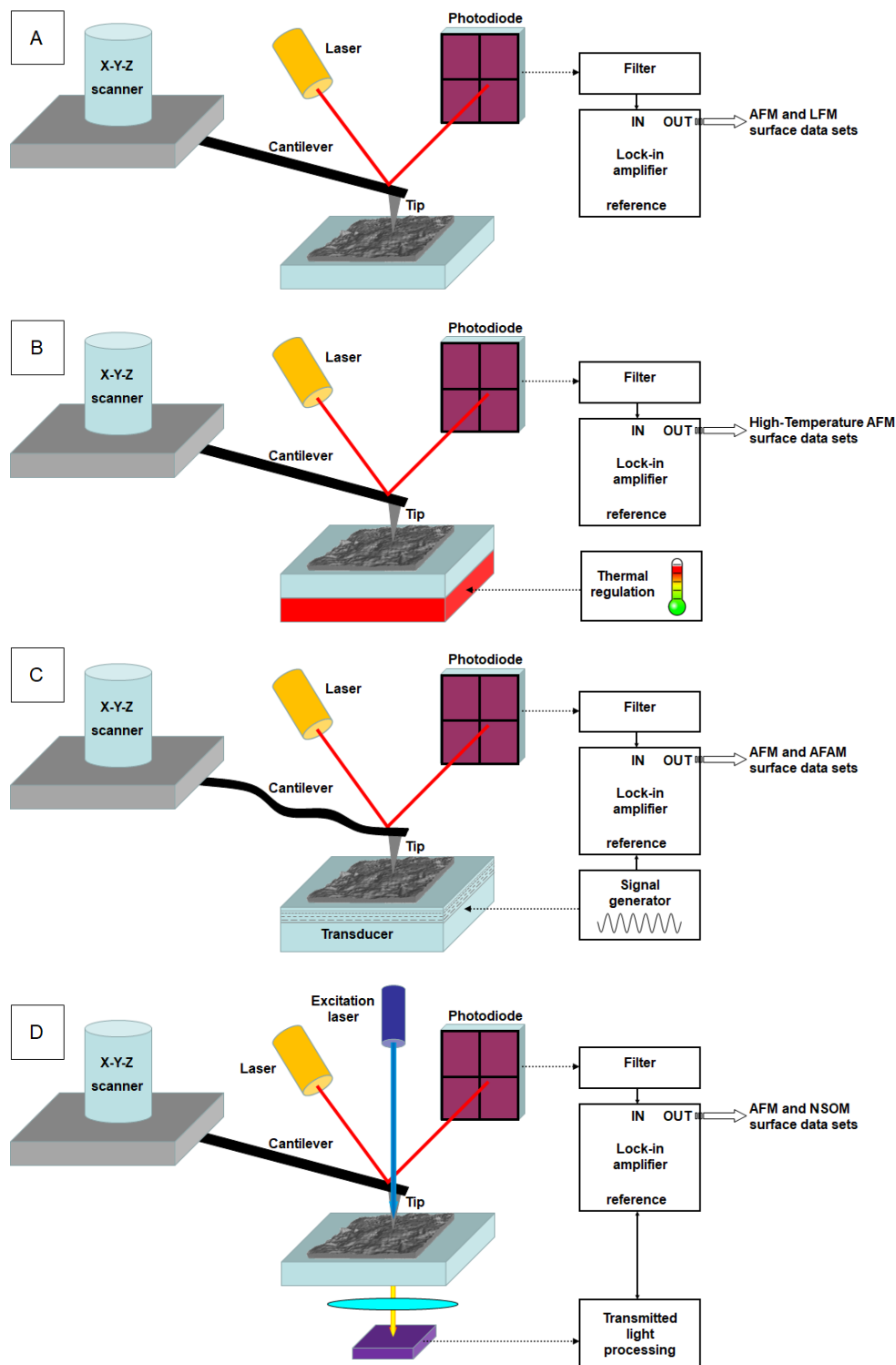


Figure 1. Schematic representation of the four discussed SPM techniques: A) Atomic Force Microscopy and Lateral Force Microscopy; B) High-temperature Atomic Force Microscopy; C) Atomic Force Acoustic microscopy and D) Near-field Scanning Optical Microscopy.

The present paper specifically deals with the applications of Atomic Force Microscopy (AFM), High Temperature Atomic Force Microscopy (HT-AFM), Atomic Force Acoustic Microscopy (AFAM), Lateral Force Microscopy (LFM) and Near-field Scanning Optical Microscopy (NSOM) to polymer film characterization, highlighting the applicative potential for food packaging analyses.

2. Techniques description

2.1. Measuring instruments

SPM is an interesting family of technique allowing characterization both of food packaging materials [10] and of processes occurring on packaging interfaces [11].

Atomic Force Microscopy (AFM) is certainly the most widespread SPM technique, implemented to allow 3D reconstruction at the microscale and to geometrical characterization of micro-features. With regard to food packaging, AFM allows characterization of surface topographies of active packaging which can help preservation of food, such as low roughness, higher permeability or self cleaning structures. Also AFM can help monitoring phenomena occurring at the interface as for instance the evolution of cells surfaces when specific treatments are implemented. This is even more interesting when temperature is modulated, allowing AFM to monitor the packaging film evolution at relatively high temperatures.

Atomic Force Acoustic Microscopy (AFAM) is a dynamic AFM-based technique for fast nanomechanical non-destructive measurements, exploiting the spatial resolution typical of SPMs. AFAM has been widely used not only to analyze the surface elasticity modifications of biological samples, but also for recognizing buried structures in packaging films such as bubbles or nanoparticles which might alter the functional characteristics of the film itself.

Lateral Force Microscopy (LFM) is associated with torsional movements of the probe, which can be associated to frictional properties at the interface. As for AFM, LFM can highlight local dishomogeneities or portions of the surface with higher or lower friction properties which will be related to different levels of interaction between packaging and food.

Aperture Near-field Scanning Optical Microscopy (NSOM) is an interesting technique for high resolution optical imaging of nanostructured surfaces, allowing overcoming the diffraction limit. It can be successfully applied to monitor the distribution of fluorescent nanoparticles, as well as accumulation or propagation of light energy associated with plasmons.

2.2. Measuring tasks

Measuring tasks allowed by the SPM measuring techniques discussed in the previous paragraph have been depicted in Figure 2. The first two lines in the figure are descriptive of geometrical characterizations. In particular, all of the proposed techniques (AFM, HT-AFM, LFM, AFAM and NSOM) allow extraction of information of feature dimensions in terms of:

- areal surface roughness parameters, i.e. indices descriptive of amplitude, functional, volume, hybrid, spatial and miscellaneous parameters, as defined by ISO 25178 [9] (Figure 2A)
- surface waviness and curvatures or shape (Figure 2B)
- distance between isolated or periodical features (Figure 2C)
- height and width of isolated features (Figure 2D and 2E)
- volume of porosity and particles, including nanoparticles layers (Figure 2F and 2G)

All of the previous geometrical characterizations can be repeated at relatively high temperatures (through HT-AFM), in order to monitor and quantify surface evolution over time typically up to 100-150°C (Figure 2H).

The third line in the figure is indicative of other properties which can be measured at the interface, and in particular:

- elastic properties both of bulk materials and thin films (Figure 2I and 2J), as allowed by AFAM techniques

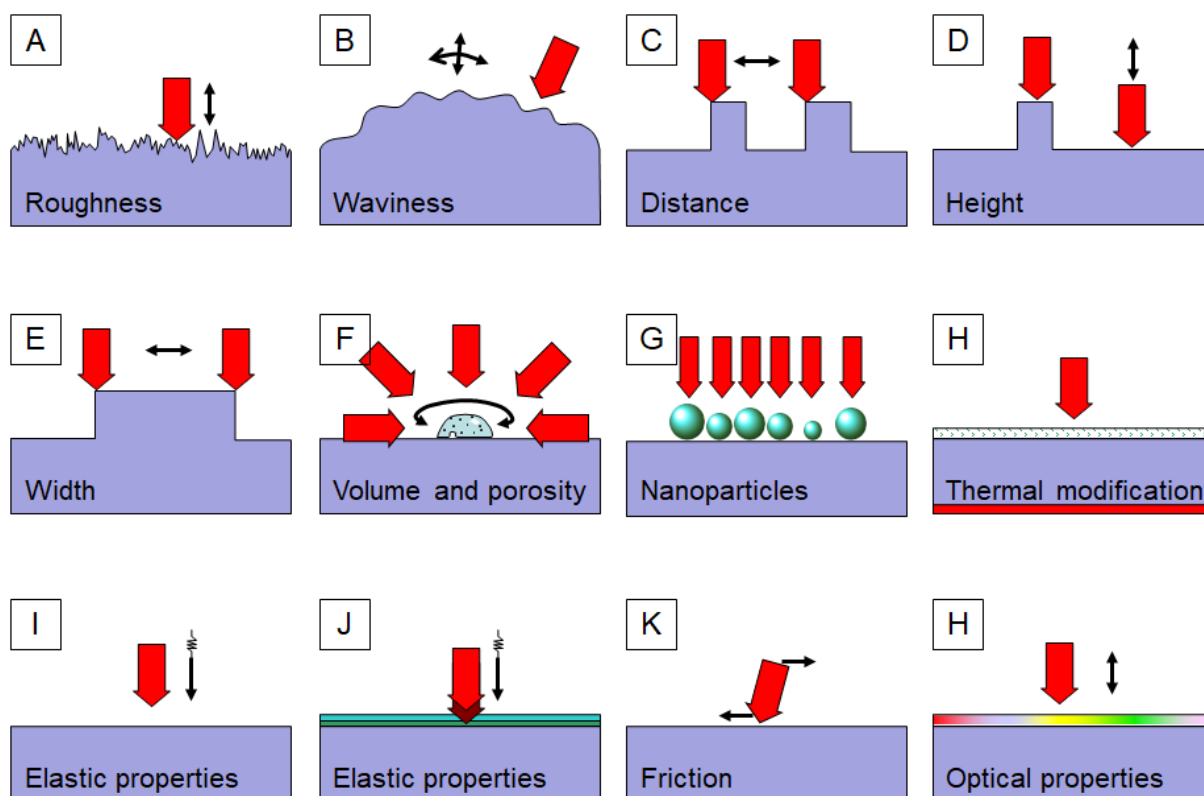


Figure 2. Main tasks to be fulfilled by SPMs techniques. The first two lines refer to extraction of geometry related parameters; the third line refers to other interface properties.

3. Measurement tests

3.1. Tested instruments and polymer films

In order to quantify the performances of different SPM techniques, and their potential in polymer film characterization, six different scanners were involved in the investigation: two Nt-Mdt Ntegra Prima with different configurations (implemented for AFM, HT-AFM, LFM and AFAM), a DME Dualscope DS 95-200 (implemented for AFM, and LFM), a Witec Alpha300 S (for NSOM), an APE Research A100 (for AFM and LFM) and a Veeco Dimension 3100 (for AFM and LFM). Technical specification and drawings have been already reported in a previous work [12].

The different SPM techniques were studied and analysed with different polymer samples which can be representative of different food packaging polymers. In particular the study included the following materials:

- polypropylene with glass fibres (30% FG),
- polymethylmethacrylate and styrene-butadiene-styrene blend (50% PMMA and 50% SBS)
- polycarbonate and acrylonitrile butadiene styrene blend (70% PC and 30% ABS)
- polypropylene and styrene-butadiene-styrene blend (70% PP and 30% SBS)

3.2. Main results

The main results from several experiment on the application of different SPM techniques to different polymer blends are summarized in Table 1.

It can be noticed how Atomic Force Microscopy as a stand alone technique can provide the highest resolution in terms not only of lateral but also of vertical characterization, with minimum measurable features that can be far below 1 nm. The main limitation is ascribable to the fact that only topographical information can be collected, thus related exclusively to geometry and roughness information. In case of relatively high temperature analyses, the same measurements are carried out on heated samples: despite implementation of insulation systems, sample stability and thermal drift can be an issue, causing

an overall reduction of achievable resolution. In this scanning mode, scan time is kept low in order to minimize the influence of thermal related distortions: the effect of high temperatures and high scan rates often result in increased tip wear or contamination phenomena.

Lateral Force Microscopy provide information on local friction properties which might be useful for food-packaging adhesion. Such scan mode relies on lateral bends of the probe: scan operations have the same high performances of AFM measurements, however probe torsions can be affected by many disturbances sources, which reduce the overall signal to noise rate, increasing the difficulty in the interpretation of collected signal.

Exploitation of quantitative Atomic Force Acoustic Microscopy measurements is strictly depending on a number of influencing factors, mainly related to the probe and its interaction with the surface, as for instance tip radius, cantilever stiffness and scan or integration time. Additionally, the tip can undergo severe wear phenomena, mainly due to the strict interaction between the probe and the surface. As in the case of LFM, interpretation of resonance frequency variations and extrapolation of surface elasticity information is typically not easy, and depending on the specifically applied calibration procedures.

Aperture Nearfield Scanning Optical Microscopy relies on large aperture tips, which reduce the minimum achievable resolution and cause large convolution distortions. Also focusing of a laser source inside a probe cavity can rapidly increase the temperature in the very apex of the tip, thus reducing both sample and probe stability.

Table 1. Main SPM performances

Technique	Lateral resolution	Scan time per image (512×512 points)	Main distortions or limiting factors
AFM	<1 nm	<10 min	Only topography information
HT-AFM	<10 nm	<10 min +heating time	Thermal drift, Sample stability, Tip contaminations
LFM	<1 nm	<10 min	Noise, Data interpretation
AFAM	<20 nm	<40 min	Slow scan rate, Tip wear, Data interpretation
NSOM	<50 nm	<30 min +optical alignment	Tip convolution, Thermal drift, Sample and probe stability

4. Conclusions

The present research provides a fast review on most interesting Scanning Probe Microscopy techniques for polymer characterizations. If by one side AFM is the most widespread scanning technique, on the other side different SPM technologies could provide further relevant information, which is useful for the characterization and definition of phenomena at the interface.

Some considerations are proposed on SPMs, based on different measurements carried out with different polymer samples. The comparison in terms of resolution and scanning time and main limiting factors highlight interesting performances which could be implemented in order to profitably characterize polymer surfaces in the food sector.

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