Quantitative Mapping of NanoDielectrics with Electrostatic Force Microscopy

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BIOGRAPHY
Dr Richard Arinero received his PhD in condensed matter physics from the University of Montpellier 2, France in 2003. He has worked in the Institut d’Electronique du Sud of Montpellier since 2006. He is notably a co-inventor of the ‘Higher harmonics atomic force microscope’ which opened the way to electrical measurements in vacuum. Currently, he is involved in the development of dielectric spectroscopy techniques by AFM. He also directs his scientific activities towards the study of radiation effects on embedded devices, at the nanometer scale, with AFM-based methods.

ABSTRACT
We present a simple method to quantitatively image the dielectric permittivity of soft materials at nanoscale using electrostatic force microscopy (EFM) by means of the double pass method. The EFM experiments are based on the measurement of the frequency shifts of the oscillating tip biased at two different voltages. A numerical treatment based on the equivalent charge method allows extracting the values of the dielectric permittivity at each image point. This method can be applied with no restrictions of film thickness and tip radius. This method has been applied to image the morphology and the nanodielectric properties of a model polymer blend of polystyrene and polyvinyl acetate.

KEYWORDS
atomic force microscopy, electrostatic force microscopy, nanostructures, polymers, dielectric, local properties, nanoscale, polymer, glass transition, imaging

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INTRODUCTION
Nanostructured polymers, nanoparticle composites and biological membranes are typical complex systems for which local properties, local structure, and composition determine their properties and their functionality on the microscale and macroscale. Understanding the behavior of these complex systems is based on parallel studies of the local structure or composition and of the local properties.

For electronic materials, an appropriate technique to realise such studies is scanning tunnelling microscopy. For soft matter, atomic force microscopy (AFM) [1] can be used but requires the development of new experiments and procedures to measure quantitatively the properties at the local scale.

In the last five years, the quantitative analysis of the dielectric permittivity at the nanoscale has become a great challenge [5-14]. Electrostatic force microscopy (EFM) is an AFM technique that senses electrostatic forces with a conductive probe. It is generally used to image localized charges on surfaces and to measure the surface potential on semiconducting materials. In this article, we show that the morphology and the dielectric properties of a model polymer blend can be measured at the nanoscale by coupling electrostatic force microscopy experiments with numerical simulations based on the equivalent charge method (ECM) [2-4].

MATERIALS AND METHODS
Materials and Sample Preparation
We have studied at the nanoscale the morphology and the dielectric properties of a model nanostructured soft material constituted by an immiscible blend of polystyrene (PS) and poly(vinyl acetate) (PVAc) (PS: $M_n = 66,900$ g mol$^{-1}$ and $M_w = 71,000$ g mol$^{-1}$; PVAc: $M_n = 33,200$ g mol$^{-1}$ and $M_w = 93,100$ g mol$^{-1}$).

The sample film was prepared from a solution of the polymers 1% w/w in toluene with 75% PS w/w and 25% w/w PVAc. The volume fraction of PVAc was 16.4%. The solution was subsequently spin coated [19] on a conductive gold substrate at 3000 rpm.

The film exhibits a nodular morphology of PVAc in a continuum phase of PS (Figure 2b).

M (t , r ) = \int \frac{kC(z)}{z} dz

Figure 1: Numerical simulations based on ECM of the curves $a_{\text{tip}}(t, z)$, where $t$ is the sample thickness and $z$ is the relative dielectric permittivity, for a tip radius $r = 19$ nm and a tip-sample distance $z_s = 8$ nm. $N: a_{\text{tip}}(t, z)$ and $N: a_{\text{tip}}(t, z)$ are typical points obtained from AFM topography and EFM images (Figure 3), respectively, on the PS matrix and the PVAc nodules of the studied polymer blend thin film. $a_{\text{tip}}$ can be deduced by interpolating these points with simulated curves. Reproduced with permission from C. Riedel et al. Physical Review E 81(1)015801, 2010. © Copyright 2010 American Physical Society.
where $k_0$ is the stiffness of the cantilever.

As expected from previous relations, the curves $\Delta f(V_{DC})$ have the parabolic form:

$$-a_{0f}(z) = \frac{1}{2} \frac{k}{k_{C}} \frac{1}{R_{z}}$$

where $a_{0f}(z)$ is related to the tip-sample capacitance by the expression:

$$a_{0f}(z) = \left( \frac{1}{4} \epsilon_0 \right) C_{z} \left( \frac{1}{\epsilon} \frac{1}{\epsilon_{r}} \right)$$

**First Experimental Step: Single Point Analysis**

EFM experiments were realized following the double pass method [15-17]: during a first scan the sample topography is acquired in the amplitude-controlled tapping mode. Then, a second scan is realized by a constant tip potential $V_{DC}$, and $a_{0f}(z)$ is extracted from the curves $\Delta f(V_{DC})$. At this stage, we used numerical simulations to calculate the $e_{r}$ value of the sample in the frame of EFM [3, 4]. For a tip-sample geometry, a discrete distribution of free and image charges is modeled such that they create a constant $V_{0}$ in the air and $V_{r}$ in the dielectric, satisfying the appropriate boundary conditions at the tip surface, air/sample interface, and sample/substrate interface. Only the paraboloidal tip extremity ($\mathrm{-1 \mu m}$) is considered in the calculations.

The tip radius $R$ is the main geometrical parameter and is determined using the protocol previously reported [18]. Once the position and the value of the charges and image charges are known, it is possible to calculate the tip-sample force, the force gradient $\frac{F}{F_{DC}}$, and finally the coefficient $a_{0f}(z)$ as a function of $R$, the thickness $t$ of the film, and the dielectric constant $\epsilon$ (Figure 1).

Using this calculation, the measured values of $a_{0f}(z)$ can be mapped onto actual local permittivity values. The advantage of ECM is that it allows working without any restriction on the thickness of the sample and the radius of the tip. In addition, the high sensitivity of EFM to detect electrostatic force gradients lets us to work with sharp tips with radius as low as 20 nm, giving an excellent lateral resolution.

**Second Experimental Step: Image Processing**

EFM experiments were performed at 70°C with a Veeco Enviroscope AFM equipped with a Lakeshore temperature controller. We have used a standard Pt-Ir coated tip (Nanosensors EFM). The cantilever free resonance frequency $f_{0}$ was $70.13 \, \mathrm{kHz}$ and the stiffness $k_0$ was calculated by the thermal tune method to be $4.5 \, \mathrm{N} \cdot \mathrm{m}^{-1}$ [24]. The tip radius was $19 \pm 2 \, \mathrm{nm}$. We checked that after several series of measurements the tip radius did not increase significantly, as expected for EFM polymer characterization.

Frequency shifts were measured by means of the succession of two double pass scans at a fixed value of the tip-sample distance, $z_0 = 18 \pm 2 \, \mathrm{nm}$, and applying two different voltages of +5 and -5 V (Figure 2). When the surface is characterized by a zero potential, only a single double pass scan is necessary to implement our method. However, we recommend doing two double pass scans in order to verify the good accuracy of the measurements and to check the symmetry of the parabola with respect to the $0 \, \mathrm{V}$ axis.

In the present study, the frequency shift at a zero voltage is found to be nearly null in the scanned area. In order to ensure that the two frequency shifts correspond to the same sample point, the topography of the two images at different biases should be as similar as possible (Figure 2b). However, working at 70°C a non-negligible drift is observed. Translational effects have been numerically corrected by the introduction of a correlation function. Using these two measurements and assuming a zero frequency shift for a zero voltage applied, we can calculate the coefficient $a_{0f}(z)$ at each point of the topographic image. Figures 3a and 3b present the topography and the corresponding map of the coefficient $a_{0f}(z)$, respectively. In the general case, in order to take into account the non-zero contact potential $V_{CP}$, a third image has to be recorded at another applied voltage, for example at 0 V. A map of the parabolic coefficient $a_{0f}$ could be obtained from frequency shift images using the equation:

$$\Delta f = a_{0f} \left( V_{DC} - V_{CP} \right)$$

**RESULTS AND DISCUSSION**

From EFM results and ECM numerical simulation $(a_{0f}(t, e_{r})$ curves), we calculated $e_{r}$ in each point of the image (the sample thickness $t$ was determined by AFM), measuring the height difference between the polymer surface and the gold substrate after the films were cut using a sharp steel knife.

An example, points M (PS) and N (PVAc) in Figures 1 and 3 are characterized by $t(M) = 27 \pm 2 \, \mathrm{nm}$, $a_{0f}(M) = 5.2 \pm 0.3 \, \mathrm{Hz}/\mathrm{V}^2$ and $t(N) = 50 \pm 2 \, \mathrm{nm}$, $a_{0f}(N) = 7.8 \pm 0.7 \, \mathrm{Hz}/\mathrm{V}^2$, respectively. After successive interpolations between different $a_{0f}(t, e_{r})$ curves, we found $e_{r} = 2.3 \pm 0.3$ for PS and $e_{r} = 7.5 \pm 1$ for PVAc, values in agreement with the literature [20-23].

Figure 4a shows a quantitative map of the dielectric constant of the PVAc/PS film at the nanoscale. The small asymmetry observed on the islands of PVAc on the $x$ axis is most likely attributed to the scanning process only retrace signal was recorded. We estimate an upper limit of the spatial resolution $\Delta t$ around 30 nm, which corresponds to half the distance necessary to achieve the transition between the dielectric level of the island of PVAc and the matrix of PS (Figure 4b). This value is in good agreement with the theoretical one calculated on the basis of the tip-sample electrostatic interaction [25, 26]. $\Delta t = R_{z}/2 = -20 \, \mathrm{nm}$.

This result shows that PS and PVAc are immiscible at a scale equal or lower than 30 nm. From the morphology image, we found a surface fraction of PVAc close to 14%, a value coherent with the polymer composition of the film. The direct confrontation of the topography with the dielectric map (Figures 3a and 4a) points out that small satellite nodules around 20 nm are detected in the dielectric map and not in the topography, thus showing the high sensitivity of this method.

**CONCLUSIONS**

In summary, we have developed a reliable and accurate EFM-based method to quantitatively measure and image the dielectric constant of nanostructured complex systems with unprecedented lateral resolution. This method is simple to implement on standard AFM setups and
EFM of Dielectrics

opens opportunities to study the dielectric properties in fields ranging from materials science to biology.

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