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Nanoscale dielectric properties of insulating thin films: From single point measurements to quantitative images

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ABSTRACT

Dielectric relaxation (DR) has shown to be a very useful technique to study dielectric materials like polymers and other glass formers, giving valuable information about the molecular dynamics of the system at different length and time scales. However, the standard DR techniques have a fundamental limitation: *they have no spatial resolution*. This is of course not a problem when homogeneous and non-structured systems are analyzed but it becomes an important limitation for studying the local properties of heterogeneous and/or nano-structured materials. To overcome this constrain we have developed a novel approach that allows quantitatively measuring the local dielectric permittivity of thin films at the nanoscale by means of Electrostatic Force Microscopy. The proposed experimental method is based on the detection of the local electric force gradient at different values of the tip–sample distance. The value of the dielectric permittivity is then calculated by fitting the experimental points using the Equivalent Charge Method. Even more interesting, we show how this approach can be extended in order to obtain quantitative dielectric images of insulating thin films with an excellent lateral resolution.

1. Introduction

During the last decades dielectric relaxation (DR) and more specifically dielectric spectroscopy (DS) have shown to be very useful techniques to follow the molecular dynamics of polar materials over a huge frequency range (10^{-5}–10^{12} Hz) under different temperature, pressure and environment conditions [1]. Several molecular processes, at very different time and length scales, can be observed by means of DR techniques and the pressure and temperature dependences of their characteristic relaxation times can be therefore investigated. Besides its exceptional time (or frequency) resolution and range, standard DR techniques can only measure the macroscopic average dielectric response. This means that no spatial resolution can be achieved by using standard DR techniques. This is an important limitation that strongly constrains the study of heterogeneous systems, di-block copolymers, nano-structured or biological materials among others.

Some attempts to measure the local dielectric response at nano-metric scale were recently published by different groups.

Israeloff et al. [2,3] have recently measured the frequency dependence of the dielectric response of poly(vinyl acetate) thin films by means of an ultra high vacuum atomic force microscope (UHV-AFM). By exciting the tip with an AC bias voltage, whereas the bottom part of the polymer film was grounded, they were able to measure the in and quadrature phase components of the cantilever oscillation. From these measurements the qualitative frequency dependence of the complex dielectric permittivity ($\varepsilon^*(\omega)=\varepsilon'-i\varepsilon''$) can be obtained. Although the qualitative results using this method are very promising, more work is still necessary to obtain quantitative values for the dielectric permittivity. On the other hand, and by means of a completely different approach, Krayev et al. [4,5] have also used electrostatic force microscopy (EFM) to study the dielectric permittivity of polymer blend thin films. In this case, the authors were able to obtain a quantitative dielectric image of their polymer blend. However, the quantification is based on a simple spherical capacitor model, which works only under certain assumptions about the thickness of the sample and the tip–sample distance. Moreover, this method measures the relative dielectric permittivity and therefore two reference polymers are required to measure a third unknown one. A third approach worth mentioning was recently developed by Gomila et al. [6,7]. Their method basically consists in measuring the capacitance between the tip and the bottom electrode of the

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sample by means of an ultra high sensitivity current amplifier. By measuring the current, the impedance can be calculated and then the capacitance as a function of the tip–sample distance. Finally, by fitting the capacitance–distance curve with an appropriate model, the dielectric permittivity can be estimated when the thickness of the sample is below 100 nm.

In this work we present a new approach to quantitatively measure the local dielectric permittivity of thin films with nanometric lateral resolution. This method can be easily implemented on commercial standard AFM without any special instrumentation and, especially important, under room conditions. Moreover, we will show how to extend this method to get quantitative images of the dielectric constant with unprecedented spatial resolution. Although we use similar EFM setup compared with some previous works, the main point of our approach is related to the modelling of the tip–sample interaction that allows quantifying the dielectric permittivity of the sample. The proposed tip–sample interaction model has very few assumptions concerning the tip geometry and therefore it is useful in a broader range of situations compared with previous reported models. In particular, we will test our method on polymer as well as polymer blends thin films at two different temperatures, below and above the glass transition temperature (T_g), where an important and characteristic change in the value of the dielectric permittivity is observed.

2. Theory

The basic idea of our method is to measure by means of an AFM the electric force gradient (∇F) between the tip and the sample when a DC voltage is applied between them. ∇F can be then related to the capacitance of the cantilever-tip–sample system and therefore the dielectric permittivity of the sample can be obtained by using an appropriated model. In our case we have modelled the tip–sample interaction by means of the so-called equivalent charge method (ECM). Additionally, we will show how this method can be extended from a single position ∇F

measurement to the whole sample using the double pass method. We will briefly describe here these three points.

2.1. Force gradient measurement

The electric force gradient between the tip and the sample, when a DC voltage (V_{DC}) is applied, is related to the cantilever-tip–sample capacitance $C(z)$ by $\nabla F = ((1/2)\partial^2 C(z)/\partial^2 z)V_{DC}^2$ z being the tip–sample distance. ∇F can be determined using a standard commercial AFM either by measuring the resonance frequency shift (Δf_o) keeping the phase shift constant or by measuring the phase shift ($\Delta \Phi$) keeping the resonance frequency constant. Both Δf_o and $\Delta \Phi$ can be easily related [8] with ∇F by $\Delta f_o/f_o = -(1/2)\nabla F/k_c$ and $\Delta \Phi = -Q/k_c \nabla F$, respectively, k_c being the stiffness of the cantilever and Q the quality factor. By combining either of these equations with the previous one for ∇F it is clear that Δf_o (or $\Delta \Phi$) as a function of the applied V_{DC} voltage should have a parabolic profile of the form $-a_{\Delta f_o}(z)V_{DC}^2(or-a_{\Delta\Phi}(z)V_{DC}^2)$. Therefore, by measuring Δf_o (or $\Delta \Phi$) as a function of the applied voltage V_{DC} at different tip–sample distances (z), $a_{\Delta f_o}(z)(=(f_o/4k_c)(\partial^2 C(z)/\partial^2 z))$ or $a_{\Delta\Phi}(z)(=(Q/2k_c)(\partial^2 C(z)/\partial^2 z))$ can be determined. The last step consists in finding the most appropriated model to obtain $C(z,\varepsilon)$, where ε is the dielectric permittivity of the sample. As already mentioned in the Introduction, some analytical expressions have been recently proposed in the literature. However, due to serious limitations for applying these expressions we have chosen to use a numerical method to account for the tip–sample interaction and therefore to relate the capacity with the dielectric permittivity of the sample.

2.2. Equivalent charge method (ECM)

The ECM allows simulating the tip–sample interaction when a V_{DC} voltage is applied between them. The basic idea is to find a discrete distribution of charges that creates the potential V_{DC} at the tip surface (test points) and simultaneously satisfies the appropriate boundary conditions at the air–sample and sample–electrode interphases. For a detailed description on how to find
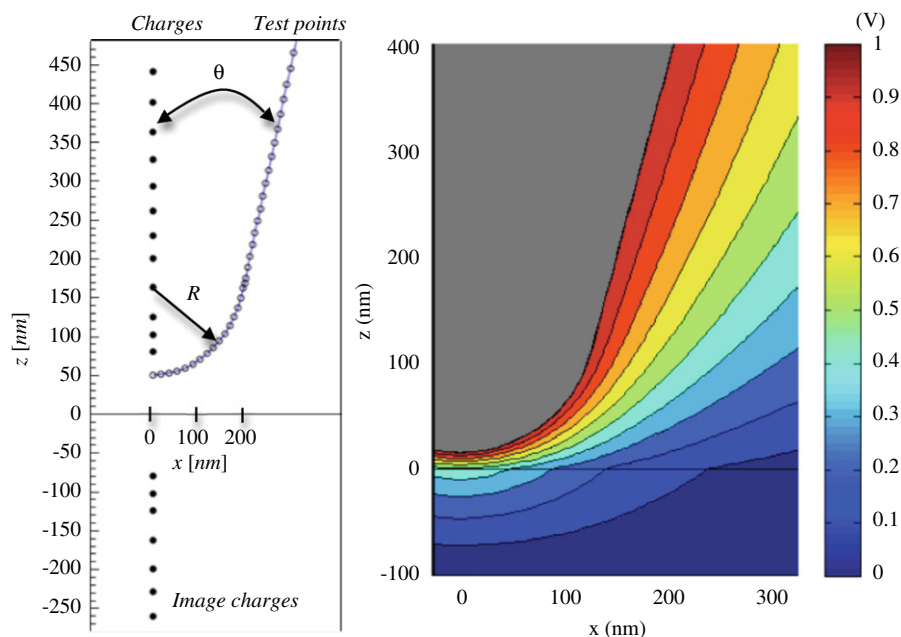

Fig. 1. Left. Charge distribution (filled circles) for a tip of radius R and cone angle θ in front of a conductive plane at $z=0$. Open circles represent the test points on the tip surface. Right. Potential created by the same charge distribution in air ($z>0$) and in the dielectric ($z<0$) by a tip with $R=130$ nm and $\theta=15°$ in front of a dielectric film of $h=100$ nm and $\varepsilon_r=4$. The tip voltage was set to 1 V whereas the lower part of the dielectric was grounded.
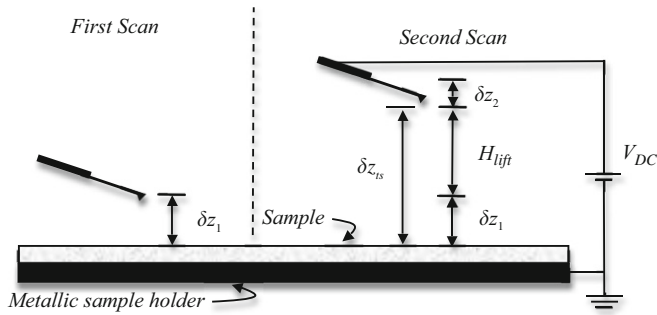
Fig. 2. Schematic illustration of the double pass method. During the first scan, with the tip at an average distance from the sample surface of δz_1, the topography is acquired. During the second scan the tip–sample distance is increased by H_{lift} whereas a V_{DC} voltage is applied to the tip. Under these conditions the frequency shift due to the force gradient is measured.

the value (q_i) and the position (z_i) on the z-axis of the N charges see [9] and references therein. Once the charge distribution is found the electric potential created by them can be easily calculated. Fig. 1 shows the distribution of the charges and the potential created by them in air and in the dielectric. The tip geometry is represented by a semi-sphere of radius R mounted on a cone with a characteristic angle θ. It is worth mentioning here that no restriction about the sample thickness (h), the tip radius (R) or the tip–sample distance (δz_{ts}) is imposed by this model, which represents a clear advantage compared with previous analytical expressions [7].

2.3. Double pass method

So far the proposed method is appropriated for single site measurements. For imaging the dielectric permittivity of a given sample we propose using the so-called double pass method [10,11] as a trivial extension of the previous protocol. Thus, for each line of the image we perform two scans; during the first scan the topography of the sample is recorded whereas during the second scan the tip is retracted at a given constant height (lift mode) following the topography of the sample at a distance δz_{ts}. Fig. 2 shows a schematic representation of the double pass method. During this second scan a bias voltage is applied to the tip and the frequency (or phase) shift induced by the force gradient is then measured. The same mathematical equations already presented in the previous sections can be used for each point of the thus acquired image. In this way a quantitative image of the dielectric permittivity can be obtained with a standard commercial AFM and the here-presented measure protocol and ECM simulation.

3. Materials and methods

3.1. Sample preparation

In order to test the here-proposed method two different neat polymers were chosen for this study: polystyrene (PS—[C8H8]$_n$– M_w=70950 g/mol) and PVAc—[C4H6O2]$_n$–M_w=83200 g/mol). These two polymers were chosen due to the high dielectric permittivity contrast above their respective T_g's and because they are immiscible and therefore form a nanostructured heterogeneous blend when mixed. According to this, a PVAc/PS (25/75 w/w) blend was also prepared to map the local variations of the dielectric permittivity at nanoscale. This heterogeneous polymer blend consists of PVAc islands of around 300 nm in a PS matrix.

The film samples were obtained by spin coating 1% (w/w) toluene solutions of the polymers (neat and blend) over a gold

sputtered glass electrically grounded to the sample holder. The samples were dried, first at room conditions for 2 h and then at 120 °C under vacuum for another 2 h. A scratch with a sharp tool was made on each sample in order to measure the polymer thickness from the profile measured by AFM.

3.2. EFM measurements

The experiments were performed on a Veeco Enviroscope AFM equipped with a Lakeshore temperature controller. We used PtIr$_5$ coated tips (Nanosensors EFM) having a free oscillation frequency (f_o) of about 71 kHz and stiffness (k_c) of about 4 N m^{-1}. The experiments were performed at room temperature as well as at 70 °C. As aforementioned, we can use either $a_{\Delta f_o}(z)$ or $a_{\Delta\Phi}(z)$; however, for high DC voltages phase shift saturates (the previous expression is no longer valid) whereas the frequency shift still exhibits a parabolic dependence; hence we have chosen in the present work to measure $a_{\Delta f_o}(z)$.

4. Results and discussion

4.1. Single location measurements

For the neat polymers (and for gold sample) we have measured the frequency shift as a function of the V_{DC} voltage, at different lift
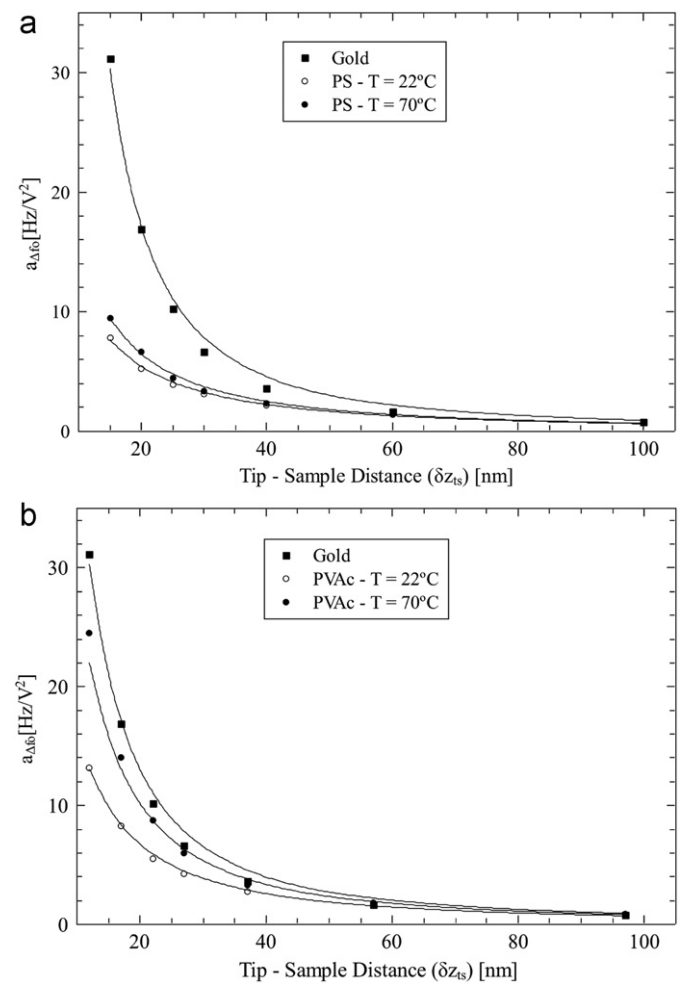

Fig. 3. Parabolic coefficient $a_{\Delta f_o}(z)$ as a function of the tip–sample distance for PS (top) and PVAc (bottom). Measurements on the gold sample are also included in both figures. Solid lines correspond to the best fit using the ECM.

heights, on a single location of the sample. Actually, we have measured on several locations of the sample to check the reproducibility of the method but each set of measurement was done on a single location. The thickness of the samples was about 50 ± 2 nm. First, we verified the expected parabolic dependence; then, by fitting these curves with a parabolic function, we obtained the coefficients $a_{\Delta f_o}(z)$ as a function of the tip–sample distance. Fig. 3 shows the so obtained experimental data points for PS and PVAc at different temperatures. Additionally, the coefficients for the gold sample are also shown in both figures. We have first to fit the data measured on gold with the ECM to find the equivalent tip radius. We found in this case $R=(32 \pm 2)$ nm. Once the tip radius and the film thickness are known, we can fit the polymer data with the ECM to quantify the dielectric permittivity (solid lines in Fig. 3). Table 1 shows the obtained values for the dielectric permittivity of the here-studied neat polymers at different temperatures. The permittivity values in Table 1 are in good agreement with the corresponding macroscopic ones [12–18] and reflect several well known

features of the dielectric behaviour of these two polymers. On the one hand, we observe that at room temperature the permittivity values for the two polymers are rather similar as expected since they are both below their respective T_gs. In the glassy state the segmental molecular motions are frozen and therefore the molecular dipoles (irrespective of whether they are weak or strong) cannot contribute to the permittivity. On the other hand, at 70 °C, PVAc is above its T_g and therefore the molecular motions allow the molecular dipoles aligning with the electric field. The relatively big value for the dielectric permittivity of PVAc at 70 °C reflects the strong relaxation strength of this polymer. For PS, whose T_g is around 105 °C, we observe a small (or even negligible) change in the value of the dielectric permittivity from 22 to 70 °C as is also found for most polymers below its T_g.

4.2. Quantitative dielectric permittivity images measurement

The previously described protocol for single location measurements can be easily extended to map the dielectric permittivity of a given area on the sample surface. In principle, we have to repeat the same protocol on each point of the sample, i.e. to measure Δf_o (or $\Delta \Phi$) at different V_{DC} voltages to determine the $a_{\Delta f_o}(z)$ as a function of the tip–sample distance and then to fit the thus obtained curve with the ECM to obtain the dielectric permittivity on each point. Instead of this difficult and time consuming method we can simplify the dielectric image measurements by

Table 1
Local dielectric permittivity for PS and PVAc at two different temperatures.

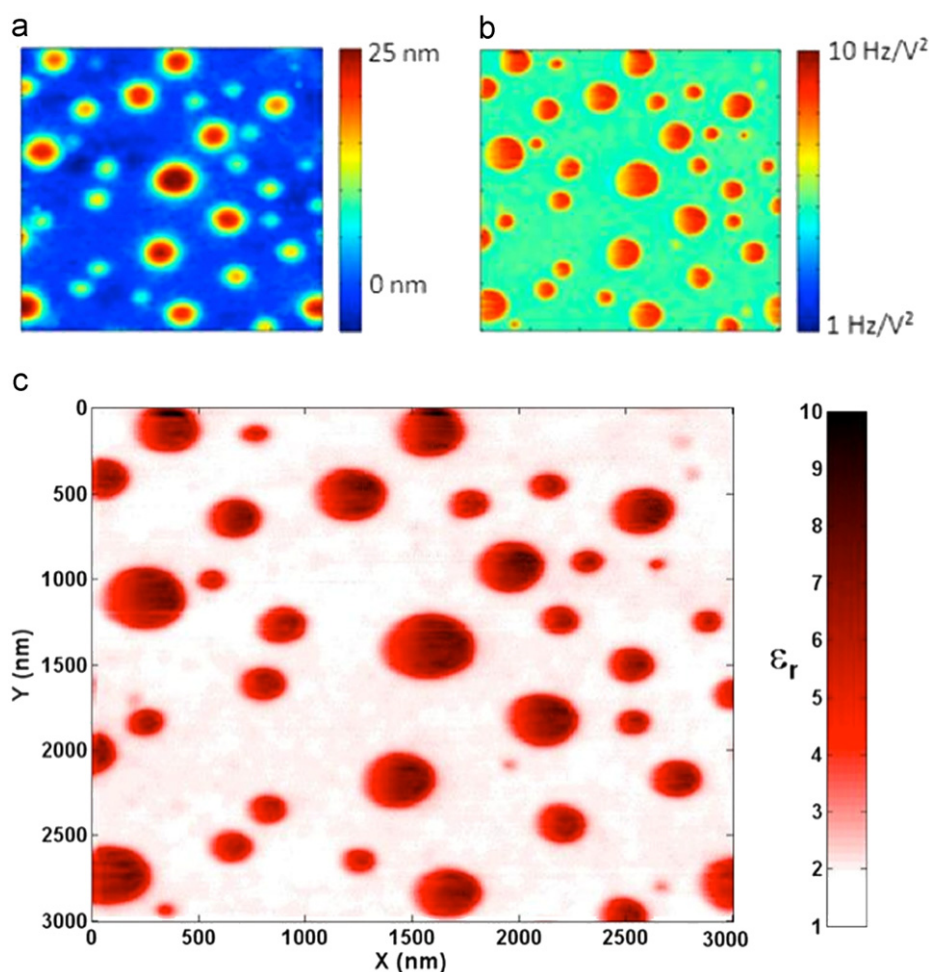| Polymer	ε (T=22 °C)	ε (T=70 °C)
Polystyrene	2.2 ± 0.2	2.6 ± 0.3
Poly(vinyl acetate)	2.9 ± 0.3	8.2 ± 1.0

Fig. 4. Different measured and calculated images for PVAc/PS (25/75) blend at 70 °C: (a) corresponding to the topography image; (b) representing the obtained $a_{\Delta f_o}$ coefficient at V_{DC}=5 V; (c) corresponding to the quantitative dielectric permittivity image calculated by ECM using the topographic and $a_{\Delta f_o}$ coefficient information.

taking into account some particular characteristics of the here-proposed method. During the single location measurement we have observed that the measurements of $\Delta f_o(V_{DC})$ are symmetrical and centred on zero when the surface is free of charges. Based on these facts only one measurement (for instance $\Delta f_o(V_{DC}=5\,V)$ would be necessary to determine $a_{\Delta f_o}$ at a given tip–sample distance. Now, instead of measuring $a_{\Delta f_o}$ at several tip–sample distances we use the ECM to calculate $a_{\Delta f_o}(z,\varepsilon)$, at a fixed z (of the order of R), where ε is the local dielectric permittivity of the sample. This method results in a larger uncertainty compared to the one that fits the whole $a_{\Delta f_o}(z)$ curve but is fast enough to minimize the thermal drift, which would severely degrade the image quality. We are currently working on a method to measure $a_{\Delta f_o}(z)$ at two or three tip–sample distances (during the same scan line), which would give a good compromise between speed and accuracy.

Thus, by applying the double pass method, we measure the topography during the first scan and the tip–sample interaction during the second scan with the tip at a fixed distance from the sample surface and with a given V_{DC} voltage between the tip and the sample. The thickness of the sample was in this case 27 nm. Fig. 4a shows the topography image measured for the PVAc/PS (25/75) blend at 70 °C. Fig. 4b represents the tip–sample interaction, i.e. $a_{\Delta f_o}(z)$ values, in the lift mode by applying 5 V between the tip and the bottom electrode of the sample. Thus, we used the topographic information together with the calculated coefficients $a_{\Delta f_o}$ to determine, by means of the ECM, the value of the dielectric permittivity. Fig. 4c shows the thus calculated quantitative dielectric image for the here-studied polymer blend. We observe in Fig. 4c islands of PVAc, with a dielectric permittivity of about 8, embedded in a matrix of PS with an estimated ε of about 2.5. These values are in agreement with the macroscopic ones and with those previously calculated for the neat polymers by means of the single location measurements at the same temperature.

Finally, by analyzing the transition in the dielectric permittivity value at the edge of each PVAc island, we can estimate an upper limit for the lateral spatial resolution of our method. The width of this transition at several PVAc-PS interphase points was about 30 nm, which would be an estimation of the lateral resolution. Moreover, this value is in good agreement with the theoretical one calculated on the basis of the tip–sample electrostatic interaction [19,20] $\Delta x = (R\delta z_{ts})^{1/2} \cong 20\,nm$ and does not depend on film thickness. The lateral resolution depends on the tip radius and it is therefore expected to obtain even lower values with sharper tips.

5. Conclusions

We have presented a new method to quantitatively determine the local dielectric permittivity of thin films with nanoscale spatial resolution. The proposed method is simple enough to be implemented on standard commercial AFM under room conditions. The tip–sample interaction was modelled with the ECM, which is less restrictive than previously reported methods. The here-presented approach can be used for either single location measurements or complete scanned images by means of the double pass method. The presented method could open a new door for studying the local dielectric properties of nano-structured, biological and electronic materials.

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