Study of Relaxation and Transport Processes by Means of AFM Based Dielectric Spectroscopy

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Abstract. Since its birth a few years ago, dielectric spectroscopy studies based on atomic force microscopy (AFM) have gained a growing interest. Not only the frequency and temperature ranges have become broader since then but also the kind of processes that can be studied by means of this approach. In this work we analyze the most adequate experimental setup for the study of several dielectric processes with a spatial resolution of a few nanometers by using force mode AFM based dielectric spectroscopy. Proof of concept experiments were performed on PS/PVAc blends and PMMA homopolymer films, for temperatures ranging from 300 to 400 K. Charge transport processes were also studied by this approach. The obtained results were analyzed in terms of cantilever stray contribution, film thickness and relaxation strength. We found that the method sensitivity is strongly coupled with the film thickness and the relaxation strength, and that it is possible to control it by using an adequate experimental setup.

Keywords: Dielectric spectroscopy, AFM, Polymer blends
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INTRODUCTION

During the last decades, broadband dielectric spectroscopy (BDS) has shown to be a very useful technique in the study of the molecular dynamics of insulating materials. Within BDS experimental window, molecular and collective dipolar fluctuations, charge transport and polarization effects take place, in turn determining the dielectric response of the material under study[1]. However, the lack of spatial resolution in standard BDS seriously restricts its use to investigate heterogeneous or nano-structured systems. The growing interest in nano-structured materials highlighted the need of measurements providing local material properties with nanometer resolution; in this sense, atomic force microscopy (AFM) provides outstanding spatial resolution and has been recently used as the basis to develop local dielectric spectroscopy[2]. Within this approach, the electrical tip-sample interaction resulting by applying an AC voltage to a conductive AFM probe is used to reveal information about the dielectric relaxation processes within the material at local scale[3-7]. The study of the local relaxation dynamics is of utmost relevance from both scientific[8] and technological[9,10] points of view. By using this AFM based approach, different relaxation processes in polymers, like the segmental or secondary dipolar relaxations (β,γ) can be studied. In addition, charge transport and polarization processes, providing information about the diffusion of charged species in the materials, can also be analyzed. Thus, this technique appears as a very useful tool in the design and development of nanostructured materials.

In this work, we focus our study in the characterization of three different relaxation processes: the segmental relaxation of poly(vinyl acetate) (PVAc) in an immiscible blend with polystyrene (PS); the secondary relaxation of poly(methyl methacrylate) (PMMA) and the diffusion of charged species in SiO_x. In particular, we analyze the effect of the relaxation strength of the different processes on the local dielectric spectra along with the stray cantilever contribution and the film thickness in order to determine the optimum experimental setup for each case.

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EXPERIMENTAL SETUP

Polymer films of PVAc (M_w=83000 g/mol)/PS (M_w=73950 g/mol) (25/75 wt %) were prepared by spin-coating polymer-toluene solutions onto a gold sputtered glass, which in turn was mounted on metallic disks of 12 mm diameter. Thicknesses of about 150 and 250 nm were obtained by using 2 and 4 wt % solutions. PMMA samples of about 1000 nm (16 wt % PMMA/Toluene solution) were prepared by using the same procedure.

Sample topography and mechanical phase images were simultaneously obtained in moderate tapping mode with an Atomic Force Microscope MultiMode 8 (Bruker). The measurements were performed by using Antimony (Sb) doped Si cantilevers, coated with Pt/Ir (SCM-PIT Bruker) or by using gold coated NN-HAR-FM60 AFM probes (Nauganeedles). The sample temperature was controlled by using a Thermal Applications Controller (TAC, Bruker). A silicone cap was used as sealing to improve the thermal stabilization of the system. The atmosphere inside the silicon cap was controlled by using a dry nitrogen flow. An external Lock-in amplifier (Stanford Research SR830) was used for the electric measurements. Local dielectric relaxation spectra were recorded by using a homemade LabVIEW routine. A reference experiment was performed over a gold substrate without any polymer on it (θref). The dielectric spectra were obtained by evaluating the phase shift, i.e. $\Delta\theta = \theta ref - \theta$, as a function of electrical excitation frequency[9,11].

RESULTS AND DISCUSSION

Figure 1a shows a typical topography image for a PS/PVAc blend with PVAc islands of about 1 µm on a PS matrix. Figure 1b represents the dielectric phase contrast map measured for the same sample at 350 K and 5kHz. Brighter regions represent higher phase shifts, which in turn correspond to higher dielectric losses. Therefore, these brighter regions correspond to areas where PVAc molecular mobility takes place with a time scale in the range of the reciprocal of the applied electric voltage frequency. The observed contrast between PVAc and PS areas arises from the fact that PS does not significantly contribute to the phase shift whereas PVAc is relaxing well above its glass transition temperature. Figure 1c shows the corresponding dielectric loss spectra for PVAc acquired over an island as indicated by the black circle in Figure 1a. As shown, the detected phase shift peak moves to higher frequencies as the temperature increases in well agreement with the bulk behavior reported in literature for PVAc[12]. The presence of these peaks confirms that islands are only composed of PVAc.

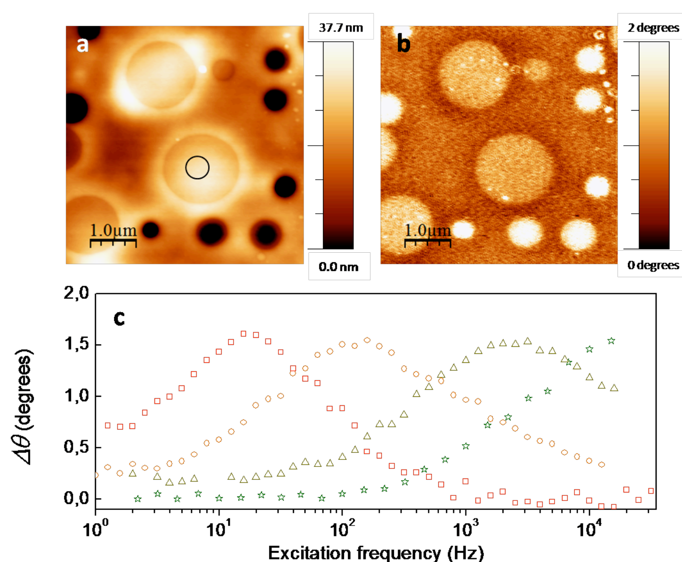

FIGURE 1. AFM based images and spectra for PVAc/PS (25/75 %). (a) AFM topography image. (b) Phase shift obtained at 5KHz and 350 K. (c) Spectra obtained over a PVAc island at 323, 328, 335 and 345 K (from left to right).

It is worth to mention here some considerations concerning to the sensitivity of this approach. The experiments were performed by detecting the oscillation amplitude of the cantilever as a function of the excitation frequency (i.e. force mode); as a result, for this thickness range there is a strong part of the signal originated from the cantilever stray capacitance. The effect of this stray capacitance is mainly related with the intensity of the detected peak, i.e.

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the sensitivity; as the stray capacitance increases the measured electrical phase shift decreases. This is not a problem for PVAc, which has a high dielectric strength ($\Delta\varepsilon \approx 7$). However, for polymers with smaller $\Delta\varepsilon$, or very small thicknesses, it is necessary to reduce/neglect this cantilever capacitance, either by using larger cones or by shielding the cantilever[11]. In addition, it is also important to notice the effect of the tip/sample distance (lift scan height, LSH) in the measurements: as the tip/sample distance increases, the air gap between the upper electrode and the polymer also increases, thus reducing the detected phase shift. Therefore, it is recommendable to decrease this air gap as much as possible, especially for very thin films. However, a very small LSH could introduce other undesired effects, like a coupling with sample topography. All these effects have to be taken into account for quantitative analysis of the spectra and have been recently analyzed by means of a probe/sample interaction model [11].

As a second step, PMMA secondary relaxation process was analyzed by following the same procedure. Due to the comparatively lower relaxation strength, the film thickness was increased to 1000 nm. Figure 2a shows the spectra obtained by using a SCM PIT probe. As expected, despite the higher thickness, the signal is still in the range of the previously presented results for PVAc. In addition, these higher thicknesses could increase the cantilever contribution to the detected losses, which in turn affects the detected relaxation time and the spatial resolution. Therefore, in order to properly measure the local relaxation the use of a different approach is mandatory. Figure 2b shows the phase shift peaks obtained with NN-HAR-FM60 probes, which present a needle at the end of the cone that increases the cantilever/sample distance by a factor 2. The observed peak intensity increases about 40% but, more important, the cantilever contribution to the detected losses now becomes negligible[11].

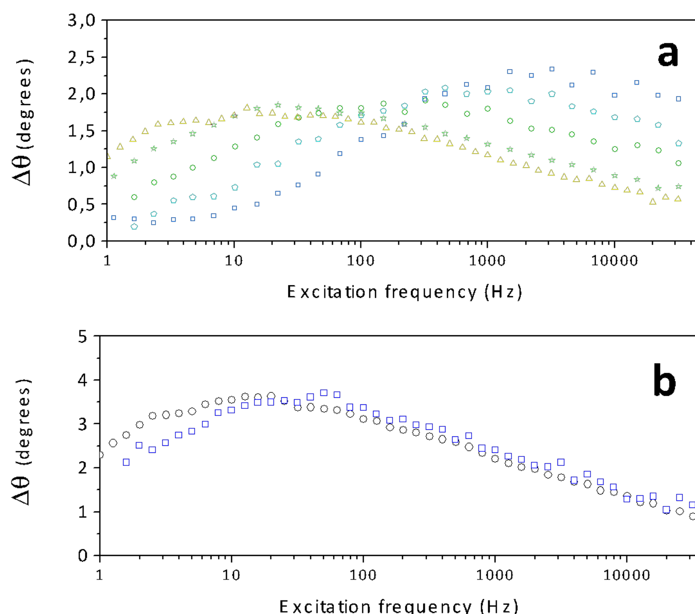

FIGURE 2. AFM based dielectric loss spectra for the β relaxation of PMMA. (a) Spectra obtained at 313, 323, 333, 343 and 353 K (from left to right) with a SCM PIT probe. (b) Spectra obtained with a NN-HAR-FM60 probe at 313 and 323 K.

Finally, we studied a dielectric process related to the motion of charges in a SiO_2 sample. In this particular case, the information obtained through AFM based dielectric spectroscopy differs from that of BDS due to the differences in geometry. As shown in Figure 3, the losses related to the diffusion of charge carriers in the material appear as peaks in the AFM spectra, whereas in BDS only a monotonous increase of both ε' and ε'' is observed due to the electrode polarization. Although the same information is present in both experiments, AFM approach allows an easier determination of the relaxation time for the diffusion processes. In addition, other polarization processes can also be analyzed by using thin films; the so called Maxwell-Wagner-Sillars processes has been recently studied in composite materials by means of this approach[9]. In particular, it is noteworthy that the amplitude of the detected signal for these processes is substantially higher than that related to dipolar relaxations, due to the fact that the relaxation strength is much higher for polarization processes.

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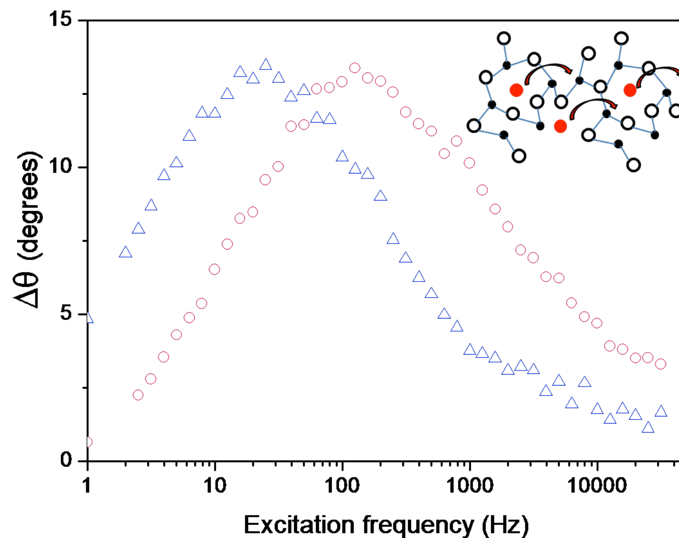

FIGURE 3. AFM based dielectric loss spectra acquired for a SiO_x sample at 343 and 383 K (from left to right). The inset shows a schematic illustration of the charge carrier diffusion through the material. (●) represent the charged species, (●) represent Si atoms and (○) represent the O atoms.

In summary, we have studied the most adequate experimental setup for detecting different relaxation and transport processes with AFM based dielectric spectroscopy. We have shown that both segmental and secondary relaxations in polymers can be studied by taking into account the relaxation strength, the contribution of the cantilever stray capacitance and the sample thickness. The possibility of detecting polarization and transport processes has been also discussed, thus opening a very interesting way for the local study of charge transport in widely used materials for solid state ionic devices (such as lithium ion batteries and fuel cells).

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