Dielectric Signature of a Dead Layer in Ultrathin Films of a Nonpolar Polymer

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Extremely thin films of poly(styrene) ($h \leq 6$ nm), in the geometry of “model” nanocomposites, show a continuous increase of the capacitance with temperature. This phenomenon is discussed in terms of a gradual defreezing of the interfacial zone between the so-called dead layer and the bulk. Such a mechanism shows a strong analogy to the dielectric response of the rigid amorphous fraction in semicrystalline materials. The defreezing process, foregoing the dynamic glass transition, is responsible for the temperature dependence of the deviations from bulk behavior.

Polymer layers at the very interface with an attractive substrate are usually modeled as regions with almost null expansion coefficients and an absence of molecular mobility;¹ due to these extreme characteristics, those regions are usually denoted as dead layers. Being a direct manifestation of changes in the system properties in the proximity of an interface, dead layers are a general issue of the reduction or enhancement of the material's performance on the nanoscale² rather than a specific feature of ultrathin polymer films.

Though the existence of these layers is still a subject of controversy, indirect proof of their presence in polymer/metal interfaces comes from the analysis of the thickness dependence of the expansions coefficients^{1,3} of ultrathin films both in the supercooled and in the glassy state. Similarly, an increase in the glass transition temperature, T_g , upon reduction of the sample thickness is usually imputed to the presence of an attractive substrate⁴ and thus to a dead layer. In fact, interfaces are treated as boundary conditions, introducing a gradient of mobility⁵ within the film thickness, extinguishing over a temperature-⁶ process,⁷ and material-dependent⁸ length scale δ . Being almost impossible to characterize these layers in terms of morphological changes or spectroscopic analyses, mostly simulations were carried out to improve the understanding of the structural perturbations generated at the interfaces and their propagation into the core of the sample. The origin of the slowing down in the dynamics of a glass former in the presence of a rough wall⁹ was, among others, attributed to the longer time intervals necessary for the simulated units to escape the cage formed by the surrounding units. Similarly, in an energy landscape approach, the potential energy minima connected to the different relaxation modes are supposed to be deeper for the molecules in the proximity of an attractive interface and smoothly recover the bulk behavior, implying a gradient of the physical properties interrelated with the involved relaxation modes.

Experimentally, by selectively recording the dynamic response of labeled layers, the propagation of the changes due to interfacial interactions on the diffusion coefficients,¹⁰ the glass transition temperatures,^{5,11} and the physical aging¹² of ultrathin polymer films was verified. However, with the state-of-the-art approaches, it is not possible to map such a mobility profile

and reveal the fine structure of the deviations from bulk behavior for layers thinner than 10 nm.

In this Article, we introduce an approach aiming to characterize the transition zone at the boundary between the regions at the interface with the bulk-like layer by analyzing the dielectric response of extremely thin polymer films, thinner than 6 nm. These localized motions are attributed to defreezing of the molecular mobility and free-volume upon increasing the temperature and are expected to be precursors of the α modes related to the dynamic glass transition of the interfacial layer. The proposed relaxation mechanism is consistent with the complex scenario characterizing the dynamics of ultrathin polymer films.

Recently, we have shown that, in the presence of a substrate interaction, the glass transition temperature as extrapolated from the temperature dependence of the structural relaxation time does not correspond to the effective glass transition temperature averaged over the whole film thickness.^{13,14} In order to avoid similar ambiguities, we analyzed the response of a nonpolar polymer via capacitive dilatometry,^{3,15,16} a technique that is sensitive to changes in the density of the material, via the temperature dependence of the capacity of the sample itself.

In fact, for nonpolar systems, at sufficiently high frequencies, where the structural relaxation process appears well above the glass transition region, the temperature dependence of the real part of the capacity $C'(T)$ can be related to the linear expansion coefficient of the material in the direction normal to the substrate α_n . In the case of the constant interfacial area,^{3,15} the required relation is $\alpha_n = -\zeta(\epsilon_\infty)C_0^{-1}(dC'/dT)$, ζ being a coefficient taking into account the temperature dependence of the dielectric constant, and C_0 being the geometrical capacity. Thus, similar to other techniques sensing the temperature dependence of the thickness on the nanoscale, even this approach allows determination of T_g . The glass transition temperature is, in fact, assigned to the temperature at which $C'(T)$ shows a kink,³ separating the glassy state from the melt, as the two regions show a different slope, that is, different expansion coefficients, α_G and α_M .

Ultrathin samples of monodisperse atactic poly(styrene), PS ($M_w = 160.000$, $M_w/M_n = 1.06$), a weakly polar polymer, capped between aluminum electrodes were prepared in the geometry of “model” nanocomposites.¹⁷ Dilute solutions of the polymer in toluene were spin-coated on freshly flash-evaporated layers of aluminum.¹⁸ After spin-coating and prior to evaporation

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Figure 1. Thermal evolution of the normalized capacity, recorded at 11 kHz, for ultrathin films of PS of different thickness (series A). The dashed lines are linear fits of the data, and the arrows indicate T_g . The apparent activation energy of the thinnest film, at the same frequency, is reported in the inset of the bottom panel.

of the upper electrode, a series of films (A) was annealed for 12 h at the bulk dry $T_g + 25$ K ($T_g = 373 \pm 6$ K from differential scanning calorimetry), while a second series (B) was annealed for 12 h at 373 K. Before measuring, the samples were annealed inside the measurement cell for 1 h at 423 K. Dielectric spectra of the samples were collected under a continuous nitrogen flow in isothermal steps of a cooling program, from the melt to the deep glassy state.

Figure 1 shows the changes in the temperature dependence of the capacity upon variation of the film thickness, (data from series A are shown). For rather thick films (top panel, 48 nm), the separation in the two regions with distinct slopes is immediate, while for thinner films (central panel, 7 nm), a reduction of the expansion coefficients is observed both above and below T_g (see Figure 2) along with a shift of the kink toward higher temperatures, indicating an increase in T_g . As already reported for data collected via other techniques,¹⁹ the contrast, that is, the difference between the slopes in the glass and in the melt $|\alpha_M - \alpha_G|$, decreases upon thickness reduction. This inconvenient feature limits the proper determination of T_g for very thin films and reflects the broadening of the distribution of relaxation time observed by dielectric spectroscopy.^{3,13}

The expansion coefficients in the glassy state and the melt normalized to their bulk values, α_G^∞ and α_M^∞ , respectively, are plotted in Figure 2. Upon thickness reduction, samples from series B show a divergent trend of the normalized expansion coefficients (an increase in the glassy state and a reduction in the melt), as already observed in films with a free surface.¹⁹ On the contrary, both the normalized coefficients decreased in samples from series A. Moreover, within the experimental uncertainties, the same slope was found for the thickness dependence of the data collected both above and below T_g . This

Figure 2. Normalized expansion coefficients in the melt and the glassy state for ultrathin films of PS as a function of the inverse of the sample thickness. The dashed lines are linear fits to the data. The inset shows the thickness dependence of the glass transition temperature for the same samples, and the lines are guides for the eye. Semi-open symbols indicate data from series A, and open symbols indicate data from series B.

behavior can be rationalized by assuming that the annealing conditions used for series A removed the fast components related to residual solvent or the memory of a free surface²⁰ and allowed the formation of a dead layer at both polymer/metal interfaces.

In fact, by fitting the response of such a system within a linear three-layer model (dead layer + bulk + dead layer) through the relation

$$\frac{\alpha_G(h)}{\alpha_G^\infty} = \frac{\alpha_M(h)}{\alpha_M^\infty} = \left(1 - \frac{2\delta_A}{h}\right)$$

a value of $\delta_A = 2.7 \pm 0.4$ nm was obtained. The value found for series B was $\delta_B = 2.7 \pm 0.5$ nm and is comparable to the length scale obtained by using a similar fit in ultrathin polymer films of PS prepared in the same geometry and investigated with the same technique.³ See the Supporting Information for a detailed description of the multilayers' data analysis.

In analogy with these findings, the trends observed in the thickness dependence of T_g are consistent with the general observations in ultrathin polymer films. In the presence of a nonzero liquid-like component (or general enhancement of mobility at the free surface), the glass transition shows a reduction, as in series B, while an increase of T_g is observed in the presence of interfacial interactions, as for series A.²¹

Restricting the analysis to samples showing an increase in T_g , we gain insight into the modeling of these layers of ideally null mobility by analyzing the dielectric response of much thinner films (bottom panel of Figure 1). An apparent negative expansion coefficient was observed for films thinner than 6 nm.²² This finding does not require a real shrinkage of the total film thickness. Instead, the observed trend reflects a temperature-dependent gradual defreezing of the material at the interface between the bulk and the completely immobilized layer. The layer at the boundary can be thus related to the reduced mobility layer (RML), already discussed for other systems^{13,23,24} as a transition zone ensuring continuity in the mobility profile from the substrate to the bulk fraction. Such a RML has a strong analogy with the rigid amorphous fraction (RAF),^{25–27} the region at the interface between the immobilized crystalline chains and the mobile amorphous phase, showing intermediate properties between the two. The correlation between these two different transition zones allows the rationalization of the thermal

response of the capacity observed in the 4 nm layer. The RAF is known to be temperature dependent and to decrease upon an increase of the temperature. A reduction of the RAF corresponds to an increase of the amorphous volume fraction that, being dielectrically active, results in a higher dielectric signal, that is, higher capacity. Similarly, for the thinnest films, the increase in the capacity at higher temperatures corresponds to a gradual conversion of the material from the reduced mobility layer to a bulk-like region. Additional proof for this mechanism comes from the analysis of the fine structure of the relaxation parameters given in terms of the apparent activation energy of the process. The apparent activation energy was evaluated^{28,29} at the frequencies and the temperatures of the spectra recorded from the real part of the capacity via the relation

$$E_{\text{act}}(\omega, T) = R \frac{\partial C' / \partial (1/T)}{\partial C' / \partial (\ln \omega)}$$

where R is the universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. The results, displayed in the inset of the bottom panel of Figure 1, indicate a continuous increase of E_{act} upon heating. This confirms the idea of a broad defreezing transition, similar to the mechanism of absorption–desorption²³ suggested for the reduced mobility layer of poly(2-vinyl pyridine), P2VP. Before being able to relax on the time and length scale of the structural relaxation, the chains at the interface must defreeze. This implies that the proposed mechanism is a precursor of the dynamic glass transition of the reduced mobility layer.

Finally, a correlation can be established between the apparent thickness of the layers with a different mobility (like the dead layer and the transition zone) and the temperature dependence of the deviation from bulk behavior, as determined for different experimental conditions.³⁰ By indicating with $T_T(\tau_T)$ a general characteristic temperature related to a procedure to assign T_g on the time scale τ_T , that is, the kink, the maximum of a peak, or the midpoint of a step in the temperature dependence of a given physical property, we write $\Delta T_T(T) \propto (\delta/h)(T)$, in analogy to that recently proposed³¹ for T_g , $\Delta T_g \propto \delta/h$, considering the changes in the difference of density of the two layer negligible. The assumption that the ratio between the “nonbulk” and the bulk components decreases upon heating due to the defreezing mechanism implies that the deviations from bulk behavior are temperature dependent and vanish at high temperatures. This last finding is a possible explanation for the severe discrepancies between various experiments aiming to characterize the dynamics of ultrathin polymer films at different time scales and thus different temperatures.^{14,30}

In conclusions, we have proven the existence of molecular relaxations at the boundary between the bulk and the so-called dead layer. These motions are related to a gradual defreezing of the chains absorbed in the layers at the very interface with an attractive substrate. The defreezing acts as precursor of the dynamic glass transition of the reduced mobility layer and is the direct link between interfacial interaction and molecular relaxations.

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Supporting Information Available: Detailed description of the multilayer data analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

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