

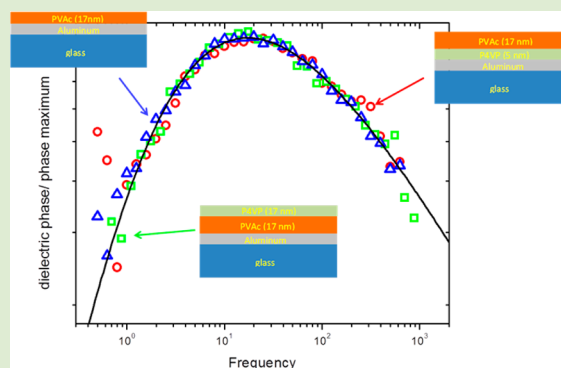
# Effect of Interface Interaction on the Segmental Dynamics of Poly(vinyl acetate) Investigated by Local Dielectric Spectroscopy

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**ABSTRACT:** The segmental dynamics of poly(vinyl acetate) (PVAc) thin films were measured in the presence of an aluminum interface and in contact with an incompatible polymer, poly(4-vinylpyridine). The local dielectric relaxation was found to be faster in thin films than in the bulk; however, no differences were observed for the various interfaces, including a PVAc/air interface. These results show that capping of thin films, even with a rigid material, does not necessarily affect the dynamics, the speeding up herein for capped PVAc was equivalent to that for the air interface. The insensitivity of the dynamics to the nature of the interface affords a means to engineer thin films while maintaining desired mechanical properties. Our findings for PVAc also may explain the discordant results that have been reported in general for the effect of air versus rigid interfaces on the local segmental relaxation of thin films.



Due to their complex configurations and irregular chemical structure, most polymers crystallize slowly or not at all, making them excellent glass forming materials. On approaching the glass transition, rubbery polymers exhibit marked changes in physical properties, including orders of magnitude increases in mechanical modulus, that transpire without any concomitant change of their microscopic structure. Indeed, the rubbery and glassy states cannot be distinguished from scattering or electron microscope measurements. The definitive property change in polymers undergoing vitrification is the progressive slowing of the segmental dynamics, reflected in increases of the associated relaxation time,  $\tau_\omega$  from small fractions of a second to times exceeding the duration of experiments. This enormous range of time scales makes it necessary to measure the dynamics over a correspondingly broad range of frequencies, which has led to dielectric spectroscopy becoming the main technique used to characterize segmental relaxation in polymers.<sup>1</sup> A recent development in dielectric spectroscopy is the use of an Atomic Force Microscope (AFM) to measure dielectric relaxation; this technique, variously referred to as local dielectric spectroscopy (LDS)<sup>2</sup> or voltage modulated atomic force microscopy,<sup>3</sup> provides a broad dynamic range with nm spatial resolution.<sup>4–11</sup>

In LDS, a thin film is deposited over a conducting substrate, and an alternating voltage,  $V(t) = V_0 \sin(\omega t)$ , is applied between the tip and the substrate. The consequent electrical force,  $F_z$ , exerted on the tip is proportional to the derivative of the sample/tip capacitance  $C$

$$F_{z(t)} = \frac{1}{2} \frac{dC}{dz} V(t)^2 \quad (1)$$

where  $z$  is the distance between the tip and substrate. The best sensitivity in LDS experiments is obtained by measuring the

shift of the resonant frequency of the tip/cantilever,  $\Delta f$  (frequency modulation mode); this shift is proportional to the gradient of the force

$$\Delta f = -\frac{f_0}{2k} \frac{dF_z}{dz} \quad (2)$$

where  $k$  is the spring constant of the cantilever and  $f_0$  is the unperturbed resonance frequency. Since additional effects related to the surface potential influence the DC and first harmonic term of  $\Delta f$ , it is preferable to measure the second harmonic,  $\Delta f_{2\omega}$ , which is directly proportional to the gradient of the electrical force. Since the dielectric permittivity is a complex quantity  $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ , the sample/tip capacitance is also complex  $C^*(\omega) = C'(\omega) - iC''(\omega)$ ; thus

$$\Delta f_{2\omega}(t) = \Delta f_{2\omega}^0 \sin(2\omega t + \delta_V) \quad (3)$$

with the phase angle given by

$$\delta_V = \arctan\left(\frac{\partial^2 C'' / \partial^2 z}{\partial^2 C' / \partial^2 z}\right) \quad (4)$$

and

$$\Delta f_{2\omega}^0 = -\frac{f_0 V_0^2}{4k} \left| \frac{\partial^2 C^*}{\partial^2 z} \right| \quad (5)$$

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The details of the measurement implementation can be found elsewhere,<sup>8</sup> as well as a description of the modeling of  $C(z)$ .<sup>11</sup>

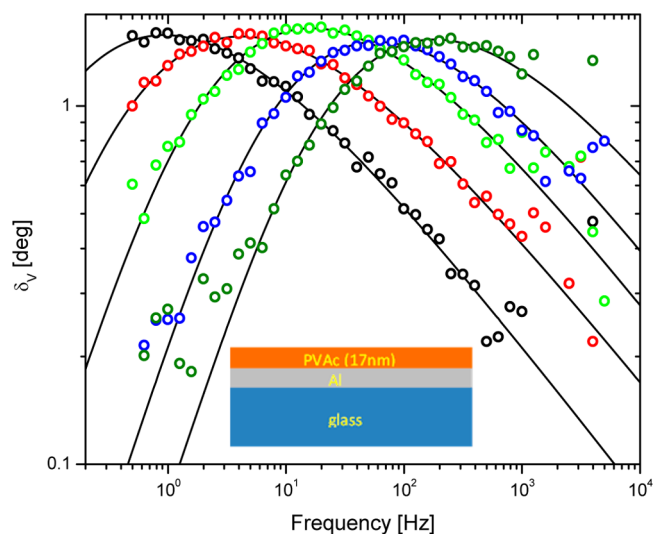
The dynamics of nm thick films has been a very active area of research in recent years.<sup>12,13</sup> The effect of nanoconfinement, however, is not entirely clear, in part because of the complicating role of the interface.<sup>14–20</sup> At least in some reports, polymer mobility is enhanced relative to the bulk at a free (i.e., air) interface, but slower if the interface is with a metallic substrate.<sup>21,22</sup> However, there are exceptions to the latter behavior,<sup>23,24</sup> and even less clear is the effect on the interfacial dynamics when two polymers are layered. In this work we use LDS to investigate the effect on the dynamics of poly(vinyl acetate) (PVAc) at the interface with poly(4-vinylpyridine) (P4VP).

PVAc ( $M_w = 121.7$  kg/mol) and P4VP ( $M_w = 50$  kg/mol) were obtained from Scientific Polymer Products and used as received. The bulk glass transition temperatures from DSC were  $T_g = 306$  K and  $T_g = 417.7$  K for PVAc and P4VP, respectively. To obtain films by spin coating, solutions of PVAc in toluene (99.9%, Fluka) and P4VP in ethanol (200 proof, Warner Graham) were prepared. The substrates were glass slides made conductive by deposition of a 20–25 nm aluminum layer. Alternating thin layers of PVAc and P4VP were then obtained by spin coating, with the insolubility of the two polymer solutions preventing alteration of the first layer by deposition of the second. The film thickness for different coating conditions (concentration, rotational speed) was measured subsequently by interferometry. To avoid plasticization of the PVAc by adsorbed water, prior to any measurements, the deposited bilayers were dried for more than 1 day under vacuum at about 60 °C. This drying temperature is below the  $T_g$  of P4VP, in order to avoid degradation of the PVAc layer. The possibility of residual solvent that might plasticize the P4VP is considered unlikely, since the results below indicate correspondence to the behavior when no P4VP layer is present.

For LDS measurements, a Veeco Multimode AFM was operated in lift mode. For each scan line, during a first pass the topographic height is stored, and during a second scan the same line is traced at a lifted height  $h_{\text{lift}}$ , while the cantilever is oscillated at resonance (oscillation amplitude  $A_r$ ) with an ac voltage applied between the substrate and tip. LDS measurements were performed in the frequency modulation mode described above. The resonant frequency was tracked by a phase-locked loop controller (RHK Technology PLLPro2).  $\Delta f_{2\omega}$  and  $\delta_V$  were measured using a dual phase lock-in amplifier (Stanford Research Systems SR830DSP). The platinum-coated, doped silicon AFM cantilever (Nanosensors PP-NCLPt) had a tip radius,  $R$ , less than 30 nm; spring constant  $k = 38$  N/m, and  $f_0 = 175$  kHz. The microscope was operated under a nitrogen atmosphere with controlled temperature. Measurements were performed with  $A_r = 12$  nm and  $h_{\text{lift}} = 10$  nm. All the data presented herein were obtained at NRL with a set up similar to that used in refs 8–10.

## RESULTS

**Measurements of PVAc Thin Films on Aluminum.** The phase angle at five temperatures for a 17 nm film of PVAc on the aluminum/glass substrate is shown in Figure 1. The  $\delta_V$  peak is due to the  $\alpha$  relaxation, and similar to the dispersion in the dielectric loss, it moves to higher frequency with increasing temperature. To analyze the spectra and determine the



**Figure 1.** LDS phase spectra for a thin film of PVAc (17 nm) on an aluminum-coated glass substrate. The solid lines are the fits using the procedure described in the text. The spectra were measured at  $T = 318.1, 321.1, 324.1, 327.1,$  and  $330.1$  K (from left to right).

relaxation time, we followed the analysis previously published,<sup>8–10</sup> which gives for the capacitance<sup>25</sup>

$$C^*(z, \omega) = 2\pi\epsilon_0 R \ln \left\{ 1 + \frac{R(1 - \sin \theta)}{z + h/\epsilon^*(\omega)} \right\} \quad (6)$$

where  $h$  is the thickness of the polymer film,  $\theta$  the aperture half angle of the tip shaft (assumed to have a conical shape), and  $\epsilon_0$  the vacuum permittivity. Using this analytical form, the second derivative of  $C^*(z, \omega)$  was fit to the data, with the Kohlrausch function<sup>1,26</sup> used to describe the dielectric  $\alpha$  process

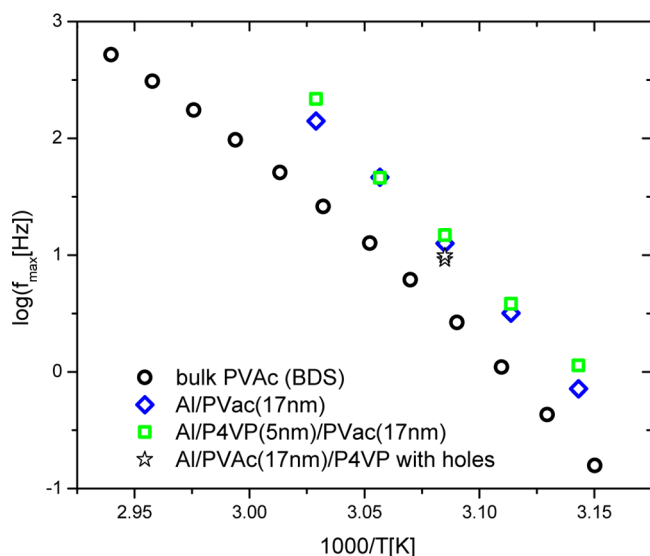
$$\epsilon^*(\omega) = \Delta\epsilon_\alpha L_{i\omega} \left[ -\frac{d\varphi_\alpha(t, \tau_\alpha)}{dt} \right] + \epsilon_\infty \quad (7)$$

with  $\varphi_\alpha(t, \tau_\alpha) = \exp[-(t/\tau_\alpha)^{\beta_{\text{KWW}}}]$

where  $L_{i\omega}$  indicates the Laplace transform,  $\beta_{\text{KWW}}$  is the stretch parameter, and  $\Delta\epsilon_\alpha$  the dielectric strength. It is important to note that although the relation between  $\delta_V(\omega)$  and  $\epsilon^*(\omega)$  is not simple, the shape of the spectra and the temperature dependence of the peak frequencies are qualitatively very similar; a direct analysis of the  $\delta_V(\omega)$  spectra would not change the results given below. The main advantage of this approach is that it yields a facile comparison of the LDS results to conventional dielectric spectroscopy measurements on bulk PVAc.

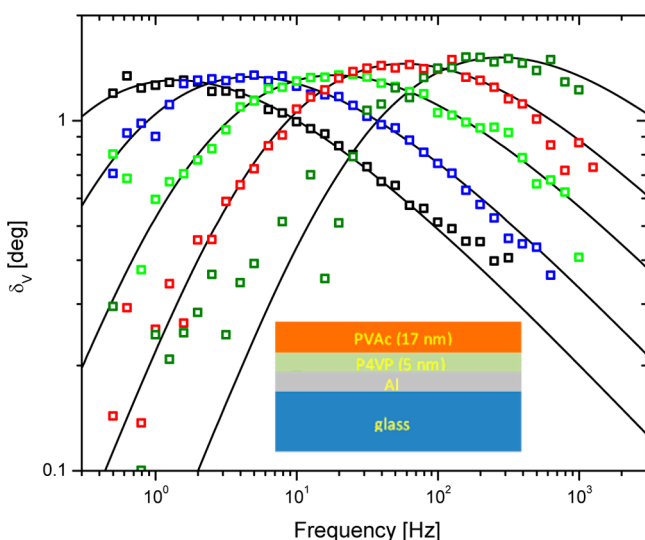
The fits to data measured on a 17 nm thick PVAc film using the procedure described above are shown in Figure 1 as solid lines. We find that for all temperatures  $\beta_{\text{KWW}} = 0.42 \pm 0.01$ , which is significantly smaller than the value of the exponent,  $0.54 \pm 0.01$ , measured for bulk PVAc by conventional dielectric spectroscopy over the same temperature range. In Figure 2 are plotted the peak frequencies,  $f_{\text{max}} = (2\pi\tau_\alpha)^{-1}$ , for both the thin films and bulk PVAc. The segmental dynamics are faster for the former than for bulk, corresponding to a 2K shift to lower temperature. These results are in good agreement with a previous investigations on thin PVAc films.<sup>9,27,28</sup>

**Measurements of Thin Film PVAc on P4VP.** Dynamic measurements were also carried out on a second configuration,



**Figure 2.** Temperature dependence of the peak frequency of the  $\alpha$  process for PVAc in bulk and for PVAc thin film (17 nm) (i) deposited on Al, (ii) deposited on a thin film of P4VP, and (iii) deposited on Al and capped with a thin film of P4VP with holes.

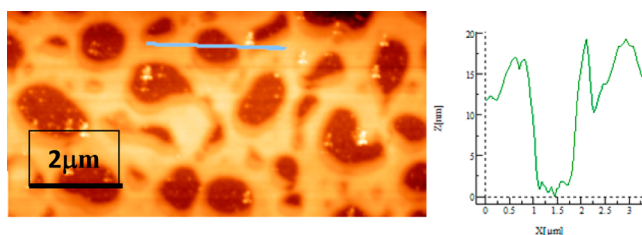
a 17 nm film of PVAc deposited on a 5 nm film of P4VP. The  $\delta_V$  spectra at five different temperatures are shown in Figure 3.



**Figure 3.** LDS phase spectra for PVAc thin film deposited on a thin film of P4VP, with the underlying glass substrate covered with aluminum. The solid lines are the best fit using the procedure described in the text. The spectra were measured at  $T = 318.1, 321.1, 324.1, 327.1,$  and  $330.1$  K (from left to right).

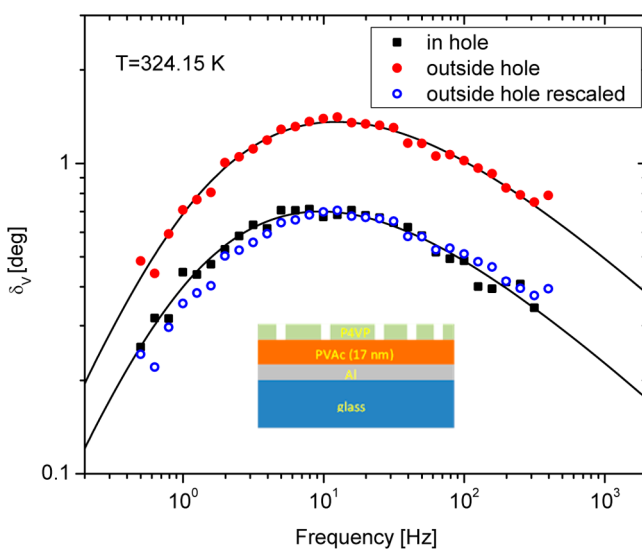
From fitting the data, we obtain  $\beta_{\text{KWW}} = 0.43 \pm 0.01$  for all spectra; the corresponding peak frequencies are included in Figure 2. Neither the spectral shapes nor  $\tau_\alpha$  of PVAc are affected by the presence of a thin layer of P4VP over the aluminum substrate.

**Measurements of Thin Films of PVAc Sandwiched between Aluminum and P4VP.** A third configuration was 17 nm PVAc film deposited on Al, with a thin P4VP film deposited on the top. The thickness of this top layer of P4VP was intended to be 7 nm; however, AFM imaging (Figure 4) revealed that the deposition of the P4VP solution did not



**Figure 4.** (Left) AFM height of PVAc thin film capped with P4VP. The P4VP thin film is not uniform, having many large holes. (Right) Representative cross section along the direction indicated in the image.

produce a uniform film; rather the top layer has a “Swiss cheese” character, with irregular holes 1–3  $\mu\text{m}$  in diameter. The thickness was  $\sim 16$  nm, corresponding to roughly 50% coverage. This unexpected morphology enables measurement of the dynamics of a thin film of PVAc both capped by P4VP (LDS away from any holes) and with a free surface (LDS within the hole). The  $\delta_V$  spectra at  $T = 324.1$  K for the AFM tip in a hole (directly on PVAc) and away from the holes (dynamics of PVAc covered by P4VP) are shown in Figure 5. Scaling the



**Figure 5.** LDS phase spectra for PVAc thin film sandwiched between an aluminum-coated glass substrate and a thin film of P4VP. The solid lines are the best fit using the procedure described in the text. The temperature was 324.1 K.

ordinate to make the peak maxima coincide, it can be seen that the two spectra have the same peak frequency and peak shape. From the fit (solid line), we find  $\beta_{\text{KWW}} = 0.43 \pm 0.01$ ; the peak frequencies are plotted in Figure 2. The conclusion is that the dynamics of PVAc are unaffected by a top layer of P4VP.

Most polymers are immiscible due to a negligible combinatorial entropy, in combination with unfavorable interactions between monomers. The magnitude of this excess enthalpy driving phase separation can be assessed from the Flory–Huggins parameter,  $\chi$ . For  $\chi N \gg 1$ , where  $N$  is the degree of polymerization, a phase-separated morphology with negligible interfacial mixing is expected. Although  $\chi_{\text{PVAc-P4VP}}$  is not known, we expect  $\chi_{\text{PVAc-P4VP}} \geq 0.4$ , since, for polystyrene/P4VP,  $7.5 \geq \chi_{\text{PS-P4VP}} \geq 0.4$ ,<sup>29</sup> and the Hildebrand interaction parameters for PVAc and PS are quite close ( $\delta_{\text{PVAc}} = 19.5 \pm 0.3$  MPa<sup>0.5</sup>,  $\delta_{\text{PS}} = 18.3 \pm 2.5$  MPa<sup>0.5,30</sup>).



A large (positive) interaction parameter for the present pair of polymers indicates the interpenetration between the films will be very small. For the case of strongly interacting polymers with very small or negative mixing enthalpies, such as polycarbonate and polymethylmethacrylate, the interface can be as large as a few nanometers, with commensurate large changes in the glass transition temperature.<sup>31</sup> For PVAc/P4VP, however, the interface exerts a negligible effect on the dynamics. This lack of interfacial constraint by P4VP means that a top layer of the latter functions equivalently to a free surface, such as air. This expectation is indeed realized in the results herein. Interestingly, the PVAc thin film dynamics are also unaffected by deposition on an aluminum substrate; that is, deposited on Al, the PVAc behaves similarly to a freestanding thin film of PVAc. This result is in agreement with previously reported mechanical measurements on freestanding ultrathin PVAc films, which showed similar changes of the glass transition temperature.<sup>32</sup> For all configurations, the PVAc 17 nm films exhibit dynamics that are faster by roughly a factor two than for bulk PVAc. Our results for aluminum are consistent with molecular dynamics simulations for motion near a “smooth wall” without attractive interactions.<sup>33</sup> We note that recently it has been proposed that rigid surfaces can also induce nonequilibrium density gradients, with material near the interface having lower density and thus faster dynamics.<sup>34–36</sup> On annealing at high temperatures for long times, the system equilibrates, and the density gradient is diminished.<sup>17,37</sup>

In this work we applied the LDS technique in a novel way to probe directly the effect of surface conditions on the segmental dynamics of PVAc thin films. We find that layering with either aluminum or the incompatible polymer P4VP increases the mobility in an equivalent manner to that obtained with a free (air) interface. This dynamics enhancement is due to mitigation of local constraints on segments in close proximity to the interfaces, with consequent asymmetric broadening of the distribution of relaxation times. These results are specific to thin films, since only the PVAc segments in the near surface region are affected by the interface. Likewise, the speeding up in bilayers with P4VP is not a general phenomenon; polymers more compatible with PVAc would have more extensive interfacial mixing and, consequently, exert more constraints on the local motions. The sensitivity of thin film polymer dynamics to the nature of the interface affords a means to control the myriad properties, in particular those mechanical properties governed by the local segmental relaxation. This method of using very incompatible polymers can be applied generally to resolve some of the controversies that have been found concerning the effect of nanoconfinement in capped versus free-standing thin films.<sup>24</sup>

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### Notes

The authors declare no competing financial interest.

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