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NOTE

Suppression of the T_g-Nanoconfinement Effect in Thin Poly(vinyl acetate) Films by Sorbed Water

Soyoung Kim,[†] Manish K. Mundra,[‡] Connie B. Roth,[†] and John M. Torkelson*[,†,‡]

[†]*Department of Chemical and Biological Engineering and* [‡]*Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208*

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In seminal, ellipsometry-based studies, Keddie et al.[1,2] reported that nanoconfinement reduces the glass transition temperatures (T_gs) of polystyrene (PS) films supported on silica and poly(methyl methacrylate) (PMMA) films supported on gold. In contrast, they found that nanoconfinement increases T_g for PMMA films on silica.[2] They proposed that this arose from a competition between effects of attractive interfacial interactions at the silica substrate with a native oxide layer, which slow dynamics and are absent for PMMA on gold, and free-surface effects[3−6] which enhance mobility and reduce T_g near the surface. They suggested that interactions at the PMMA−silica interface dominate over the free-surface effect, resulting in an increase in average T_g across nanoconfined PMMA films relative to bulk T_g. Priestley et al.[7−9] provided support for this hypothesis via multilayer/fluorescence studies, which, like ellipsometry studies, provide a pseudo-thermodynamic determination of T_g based on a change in the temperature dependence of intensity upon cooling from the equilibrium rubbery state to the nonequilibrium glassy state. They demonstrated that the T_g increase in an ultrathin layer at the PMMA−silica interface is greater than the T_g decrease in a similar layer at the PMMA−air interface. Confinement effects can also be tuned by covalent attachment of polymer to a substrate,[10] modifying polymer structure (isomers, tacticity, and side chains)[9,11−14] or architecture[15] and using free-standing films.[16−18]

In 2004, Ellison et al.[19] reported via fluorescence studies that the T_g-confinement effect in PS films on silica is suppressed by low-molecular-weight diluent. In particular, $T_g - T_g(\text{bulk}) = -37$ K in 13−14 nm thick neat films; this T_g reduction is eliminated by adding 4 wt % dioctyl phthalate (DOP) to PS. This was hypothesized to arise from a "connection between the size scale of cooperative dynamics associated with T_g, which decreases with added diluent, and the size scale of the nanoconfinement effect".[19] Later, Mundra et al.[20] reported that the increase in T_g with nanoconfinement of PMMA films on silica is eliminated in 20 nm thick films by adding 4 wt % DOP. Molecular dynamics simulations by Riggleman et al.[21,22] supported these findings. They stated, "Packing frustration effects...responsible for fragile glass formation[23] can apparently be relieved through confinement or the addition of an antiplasticizer additive... [and] the confinement of a strong (antiplasticized) glass former reduces the length scale over which free surfaces affect the dynamics compared to the confined fragile glass formers...our results substantiate the [hypothesis by Ellison et al.]".[21]

The impact of low-molecular-weight diluents on confinement effects is also important when diluent is naturally sorbed at low levels into polymer. Our group and others have reported that poly(vinyl acetate) (PVAc) sorbs a fraction to several weight percent water from ambient atmosphere, depressing T_g and increasing mobility.[24−28] Here, we show via differential scanning calorimetry (DSC) that with PVAc containing sorbed water, long annealing times at temperatures above the boiling point of water are necessary to obtain dry polymer. "Bone-dry" PVAc exhibited a T_g value ~14 K higher than the T_g value of lab-equilibriated PVAc containing water. We also show via ellipsometry that water in "wet" PVAc films suppresses the T_g-confinement effect relative to "dry" PVAc films supported on silica. As a result, in ultrathin films, "wet" PVAc may exhibit a higher T_g than "dry" PVAc. These results are significant because some synthetic and natural polymers sorb water from ambient atmosphere at levels comparable to that in PVAc.[29,30] Thus, with such materials care must be exercised in confinement studies or applications taking advantage of confinement because the bulk material properties and confinement responses may depend strongly on sample preparation and humidity. Related effects may occur in polymer membranes used for CO_2 separation because sorbed CO_2 can modify polymer properties.[31,32]

Poly(vinyl acetate) (Scientific Polymer Products, reported $M_n = 57\,500$ g/mol, $M_w/M_n = 2.73$, lot 08) is the same sample used in refs 33−37. The bulk (onset) T_g of lab-equilibrated PVAc was measured as a function of annealing time at 393 K by DSC. Ellipsometry was used to characterize the T_g-confinement effect on films spin-coated[38] from PVAc/toluene solutions. Details of sample preparation and conditioning and measurement protocols are given in the Supporting Information.

Figure 1 shows the T_g in bulk PVAc, initially lab-equilibrated regarding sorbed water,[39] as a function of annealing time at 393 K. The initial (0 min at 393 K) T_g was measured via DSC by heating to 323 K for 10 min, quenching at 40 K/min to 233 K, and heating at 10 K/min, with $T_g = 298.4 \pm 1.0$ K. When PVAc was annealed for 5 min at 393 K, T_g increased to 302.6 ± 1.0 K. With further cumulative annealing at 393 K exceeding 300 min, PVAc exhibited a "bone-dry" $T_g = 312.6 \pm 1.0$ K. These data show that lab-equilibrated PVAc can contain sufficient water to reduce T_g by ~14 K relative to bone-dry PVAc. The extreme annealing conditions (in absence of vacuum) needed to achieve bone-dry PVAc are presumably because of hydrogen bonding between water molecules and the ester unit in each PVAc repeat unit. The 312.6 K bone-dry (onset) T_g agrees with our group's previous report on (onset) T_gs from DSC:[25] 312.6 K for bone-dry PVAc and 307.6 K for PVAc with ~0.7 wt % water. (When in contact with liquid water at ~296 K, PVAc absorbs ~4.5 wt % water at equilibrium.[27,28]) Thus, unless a stringent drying procedure is used in preparing samples and determination of T_gs confirms no change with additional drying, PVAc should be understood to contain a fraction to several weight percent water.

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*To whom correspondence should be addressed. E-mail: j-torkelson@northwestern.edu.

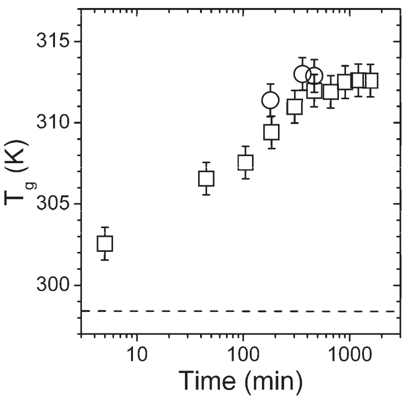

Figure 1. PVAc onset T_gs measured by DSC as a function of annealing time at 393 K. The squares are values measured in cumulative annealing cycles in which a single sample is heated to 393 K for a given time frame (initially 5 min) and then quenched at 40 K/min to 233 K. The T_g is measured on second heat at a rate of 10 K/min. This cycle was repeated with a number of successive annealing cycles (40, 60, 80, 120, 160, 200, 240, 300, and 360 min) at 393 K. Thus, square symbols correspond to the cumulative annealing times from these cycles: 5, 45, 105, 185, 305, 465, 665, 905, 1205, and 1565 min. The circle symbols are the onset T_gs of three PVAc samples measured after a single annealing step (180, 360, or 465 min) at 393 K. The horizontal dotted line corresponds to the T_g of lab-equlibrated PVAc without annealing.

Figure 2 displays normalized thickness as a function of temperature for 600 nm thick and 23 nm thick "wet" and "dry" PVAc films. "Wet" refers to films that were annealed in vacuum at 323 K for 5 h after spin-coating and then lab-equilibrated for 24 h to achieve equilibrium water sorption. These films were then held at 333 K for 20 min (to erase thermal history) in the ellipsometer immediately before measuring the temperature (T) dependence of thickness (1 K/min cooling). "Dry" refers to films that were annealed in vacuum at 323 K for 5 h after spin-coating and then annealed for 3 h under vacuum at 393 K. These films were held at 393 K for 20 min in the ellipsometer immediately before measuring the T dependence of thickness (1 K/min cooling). ("Wet" and "dry" are relative terms and do not equate to limiting water sorption or bone-dry films.) The T_g is determined from the intersection of the fitted linear T dependences of thickness in the rubbery and glassy states,[40] yielding 305.8 ± 0.8 and 306.7 ± 1.0 K for 600 and 23 nm thick "wet" films, respectively, and 309.0 ± 0.8 and 303.4 ± 1.0 K for 600 and 23 nm thick "dry" films, respectively. Thus, based on our group's earlier report that bulk PVAc with ~0.7 wt % water exhibits T_g = 307.6 K, the "wet" film contains somewhat more and the "dry" film slightly less than ~0.7 wt % water.

For 23 nm thick films, "wet" PVAc exhibits a higher T_g than "dry" PVAc. On first inspection, this result is nonintuitive because low-molecular-weight diluents that act as plasticizers or antiplasticizers reduce T_g as more diluent is added to polymer.[19−21] However, this result is consistent with results by Ellison et al.,[19] who found that nanoconfined PS exhibits a T_g below that of nanoconfined PS containing 4 wt % DOP. This was explained by diluent-induced elimination of the T_g-confinement effect in nanoconfined polymer. The data from our "dry" and "wet" 23 nm thick PVAc films can be similarly explained, with increasing water levels resulting in greater suppression of the T_g-confinement effect.

Figure 3 shows the thickness dependence of $T_g - T_g$(bulk) for "wet" and "dry" films. "Wet" films exhibit a thickness-independent T_g. With "dry" PVAc, a 60 nm thick film exhibits a measurable reduction in T_g, with T_g decreasing with increasing nanoconfinement, yielding $T_g - T_g$(bulk) = −6 K in a 23 nm thick film. The modest T_g reduction with confinement in "dry" PVAc is consistent with results for poly(ethyl methacrylate), which also contains ester side groups that can hydrogen bond with hydroxyl groups on the silica substrate surface.[7]

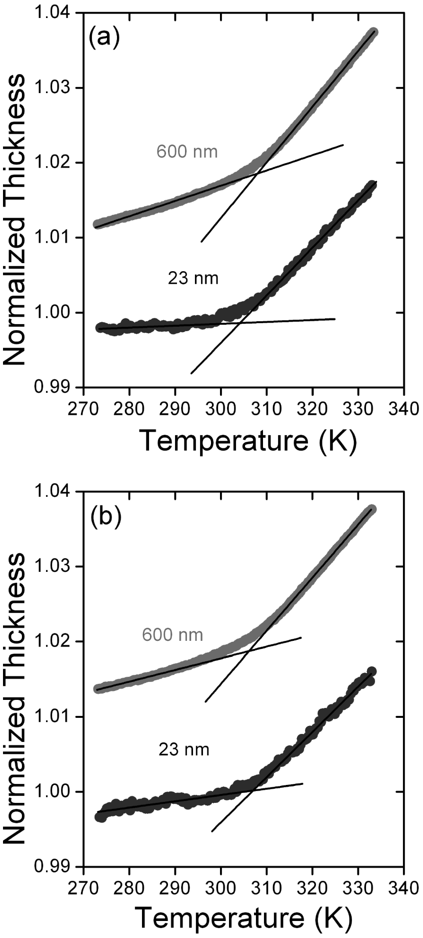

Figure 2. Temperature and thickness dependences of the normalized thickness of 600 nm thick (gray) and 23 nm thick (black) (a) "dry" and (b) "wet" PVAc films as measured by ellipsometry. The data have been normalized to the value at T_g and shifted vertically for clarity.

Previous studies of PVAc confinement effects have reached a range of conclusions, with none explicitly considering the impact of water sorption. Fukao et al.[41] characterized T_α, the peak temperature in the T dependence of the imaginary part of the complex dielectric constant, at 100 Hz. Using films annealed at high temperature in vacuum, they found reductions of T_α of ~2 K for 60 nm thick films and ~5 K for 23 nm thick films, consistent with our "dry" films. In contrast, Serghei et al.[36] reported in dielectric spectroscopy study of PVAc films with a free upper interface that T_α, measured at a frequency of 0.75 Hz, was independent of film thickness between 10 and 300 nm. However, as T_α does not account for possible changes in the breadth of the relaxation distribution, which affect *average* relaxation times that define a dynamic T_g, these studies cannot be considered definitive in regard to T_g-confinement effects in PVAc films. Furthermore, the frequencies employed with these studies correspond to relaxation times that are much smaller (that is, relaxation dynamics that are much faster) than normally ascribed to T_g values (with *average* cooperative segmental relaxation times often being ~100 s at T_g[42]). Thus, care should be taken not to over interpret the T_α data in refs 36 and 41 in terms of T_g-confinement effects.

Characterizing creep compliance in microbubble experiments, O'Connell and McKenna[33,34] concluded that there was little or no T_g-confinement effect in free-standing films as thin as 27 nm. Because they floated films on water prior to experiment, their

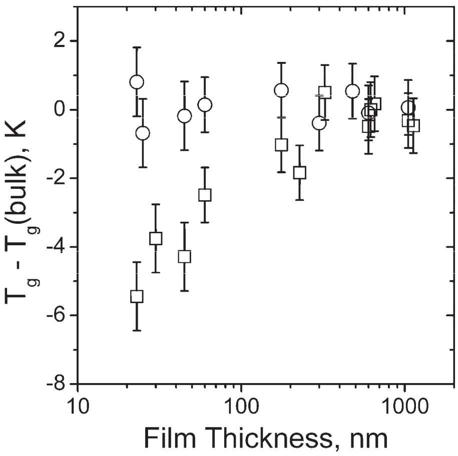

Figure 3. Thickness dependences of $T_g - T_g$(bulk) of "wet" (circle) and "dry" (square) PVAc films as determined by ellipsometry.

films should be considered "wet". Understanding that, their results are consistent with our data presented in this study.[43]

In a dielectric spectroscopy study, Serghei et al.[35] interpreted that their results agreed with those of O'Connell and McKenna[33] for similar thicknesses. In this dielectric study, Serghei et al.[35] characterized the average relaxation time at 322 K of a strictly dried PVAc sample, which is different in character from the "wet" sample employed in the creep compliance study by O'Connell and McKenna. As 322 K is 9−10 K above the T_g value of bone-dry PVAc determined by DSC in our study, we may conclude that the dielectric study was characterizing considerably faster dynamics than would normally be present at the calorimetric T_g. This is supported by the fact that Serghei et al.[35] reported an average relaxation time for bulk PVAc of 0.22 s. Only when film thickness decreased well below 20 nm did they report evidence of a reduction in average relaxation time relative to bulk response. They described the origin of this confinement effect as an asymmetric suppression of the relaxation modes. The fact that confinement effects were not observed via dielectric spectroscopy at thicknesses (e.g., 23 nm) observed in our ellipsometry-based study might, among other reasons, be explained by the fact that the dielectric measurements were taken under conditions in which the average relaxation dynamics are faster than those typically encountered at the T_g determined under typical DSC or pseudo-thermodynamic measurement protocols. In fact, Fakhraai and Forrest[44] have shown via variable cooling rate ellipsometric measurements that T_g-confinement effects that are evident in PS films at slow to moderate cooling rates (1−3 K/min) are strongly suppressed at high cooling rates (~100 K/min).

In summary, because of water sorption, PVAc presents challenges in characterizing the effects of nanoconfinement; these challenges are absent in polymers such as PS and PMMA that absorb much less water.[28,30] The current study demonstrates that if confinement effects are undesirable in applications where nanoscale confinement is inherent, then using polymers such as PVAc that naturally absorb sufficient levels of water may suppress these effects. This study and another recent study of plasticized PVAc[45] also suggest an opportunity to investigate the potential correlation of diluent size and species to the suppression of the T_g-confinement effect by diluent.

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Supporting Information Available: DSC analysis; PVAc drying procedure, ellipsometry; fitting procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

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(39) Experimental data were taken during the winter in suburban Chicago, IL, in a lab at a temperature of ~293 K and relative humidity of ~10%.
(40) Water sorption also impacts the thermal expansion behavior of ultrathin PVAc films in the glassy state, especially in the region below ~290 K. As can be seen in Figure 2b, the thickness change of a 23 nm thick dry PVAc film as a function of temperature in glassy state becomes almost negligible, indicating the reduction of thermal expansivity toward zero in the glassy state with decreasing temperature. We suspect that this originates from water absorption upon cooling: as already mentioned, the sample environment is not perfectly dry, so PVAc films can absorb small amounts of water

upon cooling. Similar behavior was not seen in a detailed study [Kim, S.; Hewlett, S. A.; Roth, C. B.; Torkelson, J. M. *Eur. Phys. J. E* **2009**, *30*, 83−92] of thermal expansion coefficient in confined PS films, presumably because PS sorbs almost no water from the atmosphere.

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(43) We also note that O'Connell and McKenna reported from their creep compliance measurements that a 28 nm thick PVAc free-standing film at $<0.1\%$ RH exhibited a T_g that was ~4.5 K higher than that of a PVAc free-standing film of the same thickness at ~40% RH.[34] This is counter to our ellipsometry-based results for nanoconfined, silica−substrate-supported PVAc films. Further study will be needed to determine whether these differences may be associated with the different nature of the films (silica−substrate-supported vs free-standing), the different experimental methods for determining T_g, or other differences in experimental protocol or analysis.

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