

Direct Imaging of Nanoparticle Embedding to Probe Viscoelasticity of Polymer Surfaces

J. H. Teichroeb and J. A. Forrest*

Department of Physics and Guelph-Waterloo Physics Institute, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1
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Atomic force microscopy was used to study the embedding of gold nanoparticles into the surface of polystyrene films. The rate of embedding was determined at temperatures near the bulk glass transition temperature T_g by measuring the apparent nanosphere height as a function of annealing time. In particular, relative height measurements of the adhered particles were made at temperatures below the bulk T_g value. In the absence of enhanced surface dynamics or yield processes no embedding is expected to occur for $T < T_g$. Measurements on 10 and 20 nm particles both indicated that the particles did embed 3–4 nm into the polymer for $T < T_g$. Both the extent and time frame for engulfment appear to be independent of the particle diameter. The results suggest a more mobile surface region on the order of 3–4 nm thick, with a lower glass transition temperature than the bulk.

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A long-standing and important question in the study of polymer surfaces and interfaces can be posed as “Is the surface of glassy polymers also glassy?” [1–3]. In addition to its own intrinsic interest, this problem holds the keys to the solution of other important problems in polymer science. Studies of thin polymer films have provided a number of fascinating and as yet unexplained observations [4]. Perhaps the most striking among these observations are those concerning the glass transition temperature, T_g , of thin polymer films. For the particular case of polystyrene (PS), there have been a number of studies reporting measurements of the T_g value of thin films. Reviews of the literature [5] suggest that for sufficiently thin films of PS on many different substrate materials, the measured T_g values are decreased below the bulk value. This behavior has been observed for other polymers as well [6]. For PS films supported on substrates, the measured values appear only weakly dependent on the substrate properties, and T_g reductions of 15–30 K are observed for films with $h \sim 10$ nm. The T_g values for supported films do not display any discernible M_w dependence suggesting that polymer chain confinement is not a dominant effect [7]. For freestanding polymer films, the results are more striking with T_g reductions as large as 70 K measured for films with thickness of 20 nm or greater [8–12]. For freestanding PS films with $M_w \lesssim 350\,000$ no apparent M_w dependence is observed [9]. In fact for these samples the thickness dependence of the T_g is similar to that observed for supported films. This correspondence between supported PS films and (relatively) low M_w freestanding PS films can be stated more quantitatively [12]: a supported PS film of thickness h has the same measured T_g value as a freestanding PS film of thickness $2h$. This remarkable correspondence suggests that the film properties may simply be determined by the volume fraction of an interfacial region. While some models that have been introduced to explain the thin film T_g values refer to enhanced free surface dynamics

[12,13], others do not [14,15]. Measurements of the dynamic properties of polymer surfaces will be a key element in providing the answer to these fascinating observations. Such measurements will enable us to decide between different classes of models. Even more significant is the fact that many interactions with a polymer material occur by physical contact with the surface. For problems such as wear, adhesion, and lubrication, the interfacial properties can be more important than the bulk properties.

Studies on the viscoelastic properties of polymer surfaces can be divided into two main classes. In the first class, a scanning probe microscope is used to perform a dynamical mechanical analysis. The results of such studies have been inconclusive [16–19]. One notable complication is the interaction between the probe tip and the polymer surface. In any contact measurement the normal force applied to a small diameter probe tip can result in considerable stress on the polymer surface. This may give rise to a nonlinear response or even yield processes. In addition, the probe tip interacts not with just the free surface, but with some near surface region. It is very difficult to quantify this region. Since the dynamics in a film are likely not constant through the entire film, it is not possible to make strong statements about the surface dynamics without the ability to define what the *surface* region is. A second technique that has been used is the introduction and subsequent relaxation of a perturbation on the surface. A prominent example is the relaxation of artificially created surface roughness on the polymer. This has the advantage of being a direct technique, but the results of studies so far have been inconclusive. By measuring the relaxation of micron sized surface relief, Hamdorf and Johannsmann concluded that the polymer surface has bulklike properties [20]. In contrast, Kerle *et al.* templated the surface of PS using a CaF_2 surface [21]. This novel approach leads to a surface with roughness on many different length scales that can be observed

after annealing. These experiments showed definite relaxation below the bulk T_g . A complicating factor is that the relaxation appeared to depend on the length scale, and that the very small length scale asperities may result in surface tension forces large enough to cause plastic flow [22]. An additional technique involving measuring the interaction of small probe particles with the polymer surface has provided evidence for a surface process below the bulk T_g [18,23]. Studies utilizing particles prepared *in situ* by evaporation of metals onto polymer surfaces [24] have revealed evidence for enhanced surface mobility. Concerns arising from these experiments include the effect that thermal evaporation may have on the near surface layer of the polymer, the indirect nature of the measurements, and the inability to vary the size of the probe particles over an appreciable length scale. It is clear that in any experiment we need to be able to control and quantify the perturbation we introduce on the near surface layer. In this Letter we present the results of a conceptually simple experiment where we use atomic force microscopy (AFM, TM explorer, Veeco) to monitor the time dependent embedding of monodisperse gold nanoparticles into polymer surfaces. This experiment provides a direct semiquantitative measure of surface properties of polymeric materials. The results of the study show that PS surfaces have a layer of at least 3–4 nm that is not glassy at temperatures as low as 10 K below the bulk T_g .

Colloidal gold was purchased (Ted Pella) with particle diameters 10 nm ($9.4 \text{ nm} \pm 10\%$) and 20 nm ($20.2 \text{ nm} \pm 15\%$). The solutions (initially of optical density 1.0 at 520 nm) were diluted to 1 part in 50 with deionized water. The colloid is charge stabilized and so does not contain a surfactant coating, but the exact positions of the citrate ion responsible for keeping it in solution are not fully known [25]. TEM studies showed the particles to be uniform and circular in cross section with a size consistent with that stated by the manufacturer. PS films of thickness ~ 180 nm were prepared by spin casting PS ($M_n = 214\,000$, $M_w/M_n = 1.03$ from Polymer Source Inc.) in toluene onto Si substrates. The films were annealed at 403 K for 20 h and then allowed to cool to room temperature at ~ 1 K/min. Ellipsometric studies of such films give a T_g of 370 K. A drop of the colloid solution was placed on the polymer film and allowed to dry. We have used ellipsometric determination of T_g to study the possibility of polymer plasticization on exposure to ionic solutions, and found no evidence for such an effect on films as thin as 7 nm. The samples were placed on a custom built hot stage with a Linkam TP93 controller. To perform the measurements, an AFM image (containing 15–20 particles/ μm^2 with many diameters spacing between particles) was acquired before any annealing. The AFM head was then removed and the sample temperature was raised to the experimental temperature, T , and held there for some predetermined time. The sample was then cooled to 300 K and imaged again. This process

was repeated until the total annealing time was sufficient to quantify the embedding behavior. The AFM images were acquired in tapping mode with very similar experimental parameters in each run. This ensures as much as possible that we consistently applied the same forces to each sample. The measured lateral dimension of the spheres is a convolution of the real diameter and the tip shape ($R \sim 20$ nm). The height, on the other hand, should be insensitive to the tip radius of curvature as long as it stays constant. The apparent height of each particle in the image was measured and used to calculate an average particle height for each annealing time at temperature T . The use of the hot stage allowed the exact same set of particles to be measured for each scan at a given temperature. This was necessary as the height resolution required for the experiments is the same order as the variation between different particle sizes. Since we are concerned only with differences in the apparent height of each particle between each image, effects such as a possible different tip-sample distance (resulting from a different interaction) between the gold and PS surfaces will not affect the results. We have recently described the application of this technique to PS melts [26]. A key finding of the behavior for the case $T > T_g$ ($= 370$ K) involves a comparison between the embedding behavior of 10 and 20 nm spheres. In particular, the time dependence of the normalized depth (h/h_0) is very similar for both the 10 and 20 nm spheres. This suggests that the system is being driven towards an equilibrium situation where the angle between the polymer surface and the nonsubmerged part of the nanosphere is the Au-PS contact angle. The similarity of the data between the two sphere sizes suggests the absence of nonlinear effects which would be stronger for the 10 nm spheres due to the greater curvature.

A representative series of images obtained is shown in Fig. 1. In this case the spheres are 10 nm in diameter, the experimental temperature is 363 K, and the total annealing times of the three images are 0, 15, and 120 min. As time progresses in this series of images the apparent height of the gold nanospheres becomes smaller. This observation clearly and directly indicates that the particles are becoming embedded into the polymer surface. A remarkable point about this particular set of images is that the sample temperature is 7 K below the bulk T_g value. For a more detailed analysis we average over all of the (~ 20) particles in the image to define a mean apparent height which we can monitor as a function of time. Figure 2 shows the average apparent height as a function of time at various sample temperatures for nanoparticle sizes of 20 and 10 nm. The sample temperatures range from 358 to 378 K which encompasses the measured bulk T_g of 370 K.

The key issue to address is the question of whether the surface of the PS sample exhibits any liquidlike characteristics at temperatures where the bulk of the sample is glassy. This was shown in Fig. 1 to be the case, but the

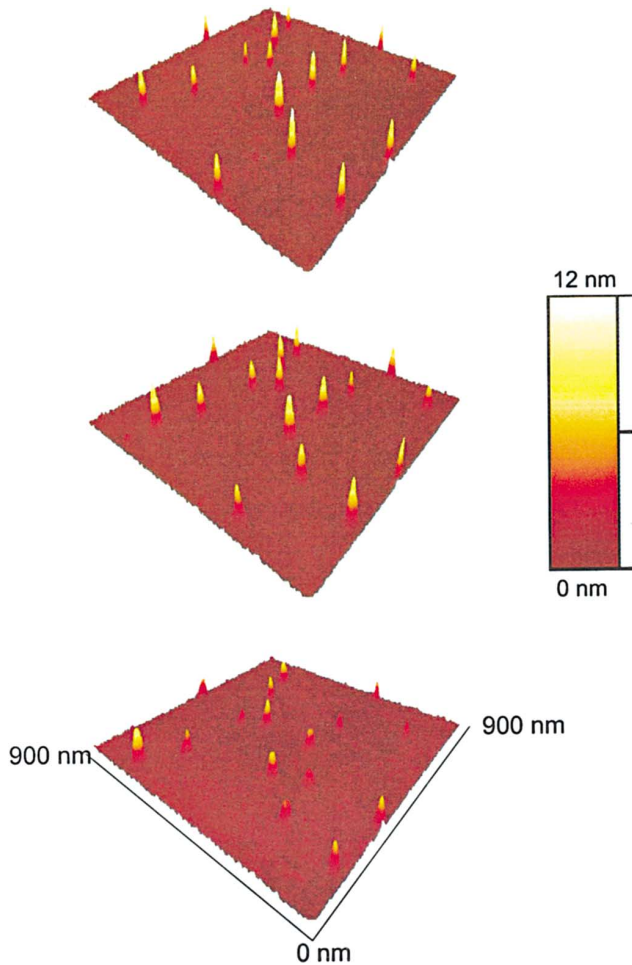


FIG. 1 (color). A series of AFM images for 10 nm Au spheres embedding into a 180 nm PS film at $T = 363$ K. The image size is 900×900 nm, and the same set of particles is imaged each time.

effect can be further quantified. Figure 2 shows a collection of data for the 10 and 20 nm spheres at a number of temperatures. The data can be grouped into two different classes, one with $T > T_g$ and one for $T < T_g$. The case for $T > T_g$ was discussed above. For $T < T_g$ the behavior is quite fascinating in that even for the glassy samples, there is a degree of embedding into the polymer surface. In Fig. 2(a) we see that for temperatures of 363 and 368 K (all less than the measured bulk T_g value), the particles become embedded to a depth of about 3.8 nm. In all cases the rate of embedding is such that this depth is attained in a time of about 50 min. After this initial behavior the particles remain at that depth. In some cases ($T = 363$ K) we have followed the embedding for times > 1000 min with no change in the apparent particle height. In order to rule out time dependent changes in the properties of the nanoparticles that could possibly produce such effects, we performed measurements on (both 10 and 20 nm) nanoparticles on bare Si at $T = 363$ K. These measurements, also shown in Fig. 2, indicate that there is no discernible change in the apparent

016104-3

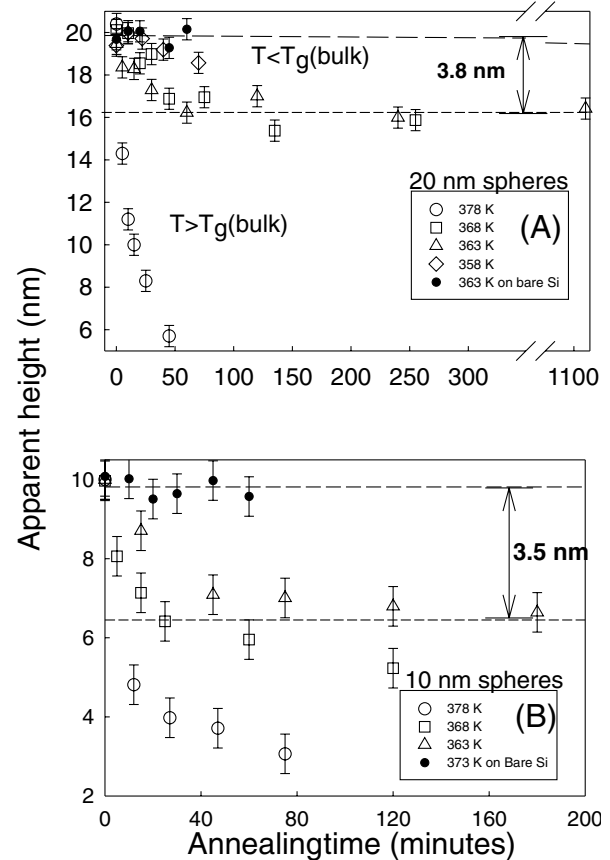


FIG. 2. Time and temperature dependence of the apparent height of gold nanospheres as a function of time for temperatures from 358 to 378 K for the 20 nm spheres (a), and for 363 to 378 K for the 10 nm spheres (b).

height of the Au nanoparticles on the hard Si surface. With this check, it is clear that the measurements indicate an embedding of the nanoparticles. This observation may indicate a layer of increased mobility in the top 3–4 nm of the polymer free surface, but it also may be a result of large surface stresses forcing plastic flow [22]. If the driving force is indeed the interfacial tension, then the most straightforward test is to increase the driving force by using smaller spheres which necessarily have a greater curvature. The results for 10 nm spheres are shown in Fig. 2(b). In this case we see the same behavior described above for $T > T_g$. For the 373 K data the behavior is quantitatively similar to that for the 20 nm spheres. For the case $T < T_g$, the particles become embedded to a depth of 3.5 nm, and the time it takes to do so is ~ 40 min. This level of agreement between the 10 and 20 nm sphere embedding does suggest that the initial 3–4 nm embedding is due to the existence of a liquidlike surface layer. It is hard to make comparisons between the viscosity of the surface layer and the bulk materials based on the time frame for embedding because the flow in the case for $T < T_g$ is affected by many factors not affecting bulk flow. For instance, it is obvious that the polymer flow occurs only in a very thin layer. In addition, the molecules

016104-3

in any surface layer are entangled with molecules in a more glassy underlayer. This also must have some effect on the flow properties. In Fig. 2, the data for $T = 368$ K (2 K below the bulk T_g value) show a behavior intermediate between that of the glass and that of the melt. This may be a result of the fact that in this particular case, the material modulus is low enough at this temperature that the surface stress is enough to induce flow in the case of 10 nm spheres, but not in the case of 20 nm spheres. Generally, the observation of a liquidlike layer even in glassy PS films seems to be an intrinsic surface property rather than one induced by large surface stresses.

The very fact that we are using gold nanoparticles means that the surface the particles actually embed into is not a free surface anymore. This may affect what conclusions can be drawn from the results. The most basic question to address is whether the surface layer has enhanced mobility or is glassy. If the surface is glassy, then the expected observations are quite obvious — absolutely no motion is possible and there will be no embedding of any particles for $T < T_g$. This is not what is observed, so we can conclude with certainty that the *surface region immediately underneath the Au nanospheres is not glassy*. Since the Au spheres do not cause enhanced mobility, any enhanced mobility must be due to the proximity to the free surface. If we consider a region underneath the nanoparticles, it is reasonable that its dynamics will be influenced by the free surface if the region can be connected to the free surface with *any* line of some length λ_{FS} describing the length scale of any free surface region with enhanced dynamics. We could estimate this length scale (when the whole film is influenced by the effects of the free surface) by considering the onset of reduced T_g values in either freestanding or supported films. This suggests a length scale, $\lambda_{FS} \sim 10$ nm [5]. We also have to consider the effect of the solid surface. This will have the effect of negating any free surface effect for some other length scale λ_{sub} . A previous analysis [12] suggested that the length scale associated with the substrate influence was ~ 2 – 3 nm. Thus we should expect that a region near the free surface but covered by the nanoparticles will have an enhanced mobility if it is within λ_{FS} of the free surface but *not* within λ_{sub} of the nanoparticle surface. These conditions are fulfilled in the present experiment. This modifies how the results should be interpreted. The fact that the nanoparticles embed 3–4 nm means that there is a more mobile surface region with a characteristic size with a *lower bound* of 3–4 nm.

In conclusion we have introduced a simple way to directly measure qualitative dynamical properties of the near surface layer in polymeric materials. By design, the technique allows effects at different length scales to be differentiated and is able to provide a definition of the surface region probed. Experiments performed on melt and glassy PS reveal strong evidence for a meltlike layer of at least 3–4 nm at the surface of glassy PS films at a

temperature at least 7 K below the bulk T_g . Extension to even lower temperatures may allow us to define when the surface becomes glasslike.

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*Corresponding author.

Email address: jforrest@uwaterloo.ca

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