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Using Nanoparticle Embedding to Probe Surface Rheology and the Length Scale of Surface Mobility in Glassy Polymers

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The near surface properties of glassy polymers continue to be the subject of much interest and debate. While there have been a number of studies that support the idea of enhanced mobility in some region near the free surface,[1−10] it is difficult to define what the length scale of that region is. This length scale has obvious technical importance for such properties as adhesion and impurity diffusion. Of equal importance is the critical information it can give about a correlation length for dynamics in glass-forming materials. Experimental verification of such a length scale may be crucial in developing a detailed understanding of glass formation.

There is mounting evidence that for at least some glassy polymers the surface region exhibits a mechanical behavior that is significantly different from the bulk glass. In particular, for the cases of poly(styrene) (PS) and poly(methyl methacrylate) measured reductions in the glass transition temperature, T_g, for thin films have suggested the existence of enhanced surface mobility.[1,2] A near surface depth dependent T_g reduction was measured by probing thin constituent layers of thick films.[3] Isothermal, dynamic measurements over long time scales similarly revealed a surface relaxation process that would not exist in the glassy state.[4−8] Evidence for a mobile surface layer was proposed on the basis of nanoparticle embedding experiments,[9] but the limited time and temperature range of those experiments allowed for the possibility of multiple interpretations.[10−13] One way of circumventing this ambiguity was the removal of the nanoparticles to produce nanodeformations whose relaxation could be monitored[4,8] as a function of time and temperature. Nanodeformation measurements of glassy PS show evidence for surface relaxation at temperatures as low as 240 K.[4,14]

A number of questions are evident from the surface studies in the literature to date. How can the apparent vitrification of the polymer surface near room temperature in embedding studies[9] be consistent with nanodeformation measurements where relaxation is observed even at temperatures far below room temperature?[4] How does the temperature dependence of compliance and size of the surface region compare with that expected for correlated dynamics in a glass-forming material? Answering these questions can provide a more rapid reaching of consensus in thin film dynamics and also put the measurements in the context needed to develop an understanding of dynamics in glass-forming materials.

To tackle these questions, we extend the nanoparticle embedding experiments to a much larger time and temperature range. This allows us to make robust qualitative conclusions. A key advantage of embedding experiments compared to nanodeformation relaxation is that monitoring relaxation of surface deformations *always* probes a layer very near the free surface and hence has limited use for depth profiling. Embedding, on the other hand, allows for a degree of depth profiling in terms of rheological properties. Embedding is also a much more robust experimental technique because measuring the apparent height of a nanoparticle is not inherently sensitive to the atomic force microscopy (AFM) tip shape.

In this paper we present a detailed study of isothermal nanoparticle embedding onto PS surface at temperatures below the bulk T_g. The data spans over 5 orders of magnitude in time and provides a clear indication of anomalous viscoelastic properties near the free surface. In fact, for temperatures near the bulk T_g both the surface relaxation and relaxation deep into the film are measured.[15] Here we focus on the near free surface region and temperatures well below T_g, where the bulk relaxations are essentially immeasurable on the time scale of the measurements. This allows for a clear determination of surface properties, without interference from bulk relaxation. The results show the nanospheres reach an asymptotic maximum embedding depth after a long period of time. This maximum depth increases as a function of temperature and, consistent with previous measurements,[9] becomes undetectable near room temperature. Within the context of a simple model these results can be interpreted in a way that is completely consistent with previous results on surface relaxation.[4] On the basis of this model, we also provide an estimate for the rheological temperature of the near surface region and upper bounds on the temperature dependent size of correlated dynamics in the near surface region. The results of this process are in quantitative agreement with a model used to describe the measured T_g values for thin freestanding PS films.[2]

PS (Polymer Source Inc., $M_w = 641$K and $M_w/M_n = 1.11$) films of thickness $h \simeq 100$ nm are spin-cast out of toluene solution onto silicon substrates and annealed in dry N_2 at $T_g + 28$ K for at least 16 h in a home-built oven before being cooled to room temperature. Such thick films are considered bulk-like as all measured film properties are consistent with bulk values. Citrate-stabilized gold nanoparticles with diameter 19 nm were synthesized[16] and spin-cast onto the PS surface using a spin-coating speed 800 rpm. One drop of ethanol in 10 drops of gold colloidal solution was used to enhance PS−Au affinity during gold sphere casting. To determine the isothermal time dependent gold sphere embedding at a given temperature T, more than 10 nanoparticle-decorated PS samples were placed onto a solid aluminum block in an oven that is purged with dry nitrogen gas. After a time t, one of the samples is removed, quenched to 287 K, and then imaged at this temperature using tapping-mode AFM. The image size (typically $5\,\mu m \times 5\,\mu m$) is enough to determine the average apparent height of more than 100 spheres.

Figure 1 shows the average apparent height of gold nanospheres as a function of time for all temperatures between 287 and 366 K. A qualitative distinction between this work and previous studies is the extension to much lower temperatures and to much longer times. It is obvious that on the time scale of these experiments there is embedding observed at temperatures as low as 309 K, but not for 287 K. The lower temperatures of these experiments are such that the observed embedding cannot possibly be described by bulk viscoelastic properties. This qualitative improvement over previous studies[10] allows for more robust conclusions than were possible with the previous measurements. As the annealing temperature is increased, the lifetime of

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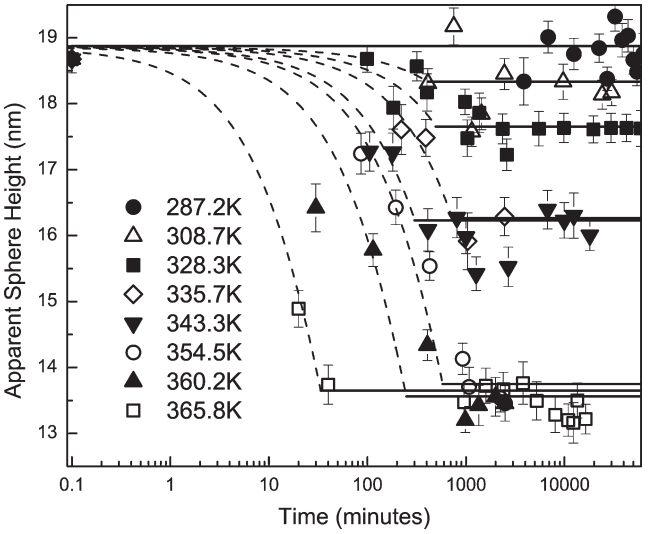

Figure 1. Apparent height of gold nanospheres as a function of time for temperatures in the range 287 K < T < 366 K measured using AFM. Each data point is the average of at least 100 spheres. Dashed lines are calculations based on ref 17.

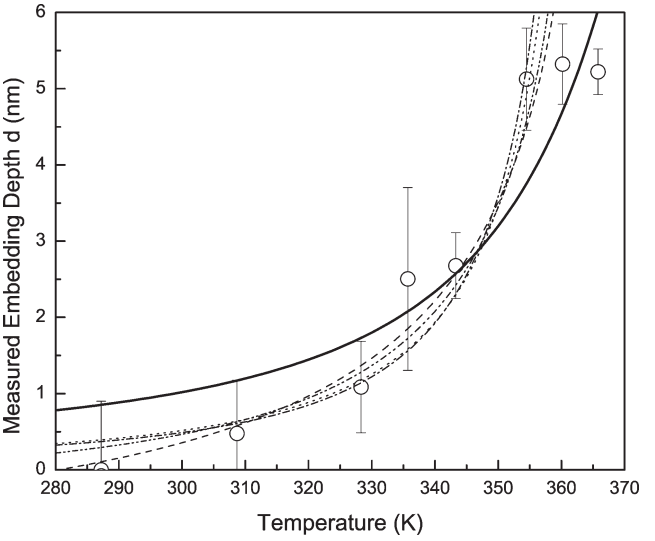

Figure 2. Asymptotic maximum embedding depth as a function of temperature (open circles) and the fit using the linear model described in the text (solid line). Also shown are fits using the Gaussian (dashed line), exponential (dotted line), stretched exponential (dash-dotted line), and compressed exponential models (dash-dot-dotted line).

the process decreases (dashed lines) and the extent of embedding increases (solid lines). The lifetimes were fit using several methods. The dashed lines in Figure 1 are fits to a numerical integration of the viscoelastic spherical indenter problem.[17] This model incorporates a depth dependent driving force on a sphere into a viscoelastic half-space and is desribed in detail in ref 10. Alternatively, a complete finite element (FE) simulation of the spherical indenter problem using the commercial FE software ABAQUS[15] as well as WLF parameters from ref 18 give similar results. The embedding data could also be described well by *single exponential relaxations*. Independent of the fitting method, the measured lifetimes were substantially shorter than the bulk α relaxation time. Figure 2 shows the size of the surface region of enhanced mobility, as given by the extent of embedding. In particular, the values in Figure 2 are the difference between the measured initial and asymptotic apparent heights. The temperature dependent depths from Figure 2 describe the size of a near surface region where the viscoelastic properties are such that nanoparticle embedding can be observed. These values are similar to those suggested in ref 1. While perhaps encouraging, this observation brings up other questions. The notion of cooperative dynamics first discussed in detail by Adam and Gibbs[19] has proven to be an enduring description of glassy dynamics. In this description, the structural relaxation dynamics in glass-forming materials becomes highly cooperative at temperatures near the measured T_g value. This leads to the idea of a temperature dependent length scale, over which the dynamics are correlated. This length scale increases in size as the temperature is lowered. This concept has been discussed in the literature in terms of both detailed simulation studies of a glass-forming material[20] and models for the measured T_g values of thin films.[2] In both cases there is a strong case made for a monotonically decreasing correlation length as a function of temperature. This temperature dependence seems difficult to reconcile with the data shown in Figure 2. Related to this difficulty is the comparison between the results presented above, especially at lower temperatures, and those obtained for nanodeformations relaxation on glassy PS surfaces.[4] In that case relaxation was observed for temperatures as low as 240 K.[14] Clearly, this apparent contradiction needs to be resolved if there is any hope of using this data, or any other data on surface dynamics in polymer glass formers, to advance our knowledge about the physics behind glassy dynamics.

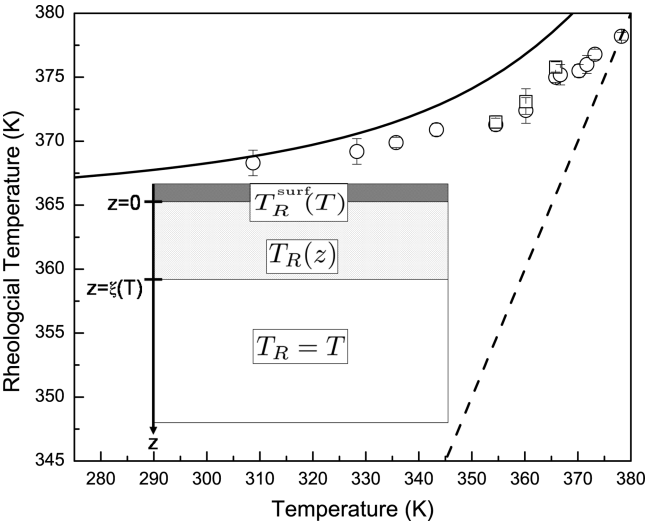

Figure 3. Rheological temperature of the fitted average rheological embedding temperature T_R^{avg} from a numerical integration (circles) and a finite element simulation (squares) as described in the text. The solid line is a hyperbolic function that numerically very accurately describes the nanodeformation data from ref 4, and the dashed line is the bulk behavior. The inset shows a sketch of the simple layer model.

To facilitate meaningful comparison between different lifetimes, we transform our fitted lifetimes into an average rheological temperature, T_R, by means of the WLF relation for bulk PS.[18] The rheological temperature is the temperature at which the bulk material would have the same lifetime as the measured lifetime. For embedding, the rheological temperature has a weaker temperature dependence than the bulk (Figure 3) and is similar to the previously determined nanodeformation relaxation measurements.[4] We also make a distinction between the *very near* surface region, which is described by the relaxation of nanodeformations in ref 4, and the *near* surface region, which is probed in the current nanoparticle embedding studies.

In order to make a more quantitative comparison, we use a simple model to describe the near surface region. We treat the sample in terms of a layer model which is shown schematically in the inset of Figure 3. The very near surface region is described by

a parametrization of the relaxation times from Figure 4 of ref 4. Those relaxation times are then converted to a temperature dependent rheological surface temperature $T_R^{surf}(T)$ as described above. In using that data, *this model necessarily incorporates the idea that the very near surface region does not vitrify*. Since thick films are used, there exists a (possibly temperature dependent) distance $\xi(T)$ from the free surface, beyond which bulk dynamics are recovered. In the region $0 < z < \xi(T)$ the rheological temperature $T_R(z,T)$ could have many forms, and in what follows we assume a linear interpolation of the surface and bulk rheological properties

$$T_R(z,T) = T_R^{surf}(T) + \frac{z}{\xi(T)}(T - T_R^{surf}(T)) \qquad (1)$$

It is clear that there is some value of T_R (denoted as $T_{vitrify} \lesssim T_g$) where there will be no embedding in the time frame of the experiment. On the basis of the measured embedding times in the bulk of the film, $T_{vitrify} \approx 363$ K. For $T < T_{vitrify}$ the surface will appear to have vitrified. The depth d where $T_R(d,T) = T_{vitrify}$ will define the extent of embedding observed in a particular experiment. This is different from the nanodeformation experiment where the mobility probed always includes that of segments very near the free surface. Previous work has shown that simply removing a coating layer can cause T_g reductions in thin films,[21] and it is very likely the surface mobility is similarly affected by the presence or absence of the gold nanoparticles. As one probes the dynamics further from the surface and more into the bulk of the sample, the characteristic rheological temperature would approach the bulk temperature and the relaxation time would change by many orders of magnitude. In probing the relaxation through embedding, we may expect to see a significantly broadened relaxation. The fact that embedding data seems to follow a single exponential is remarkable. However, this could be compared with and related to the fact that in free-standing PS films, even though there are indications of a broad range of dynamics, a single sharp T_g is measured. Because the time dependence of embedding exhibits single exponential relaxation, we can characterize the near surface region $0 < z < d$ where T_R varies from $T_R^{surf}(T)$ to the bulk temperature T by a single average rheological temperature T_R^{avg} from Figure 3.

The fact that the surface rheological temperature varies much weaker than linearly with T means that *even if $d(T)$ is monotonically decreasing as T is lowered, $\xi(T)$ does not have to be*. The success of this approach will enable us to provide an estimate of an upper bound for $\xi(T)$. The maximum embedding depth d depends *only* on the value of $T_{vitrify}$, which is fixed within a few degrees by the maximum time frame of the embedding experiment, and the values of $\xi(T)$. As an ansatz we take $\xi(T) = \xi(T_g) + \alpha(T_g - T)$ which is a two-parameter fit. These two parameters are then varied to fit to the $d(T)$ values obtained from the experimental data. The fit using this model is shown as the solid line in Figure 2. The linear interpolation between the surface and bulk rheological temperatures assumed in eq 1 is certainly not the only functional form that can be used. In order to make as strong a conclusion as possible, we tried several functional forms for this interpolation (described in Figure 4). The bound on $\xi(T)$ indicating the domain where reasonable solutions can be obtained is shown as the shaded area in Figure 4. While not able to provide information about lower limits of $\xi(T)$, the procedure does provide a reasonable upper bound on $\xi(T)$. Our confidence in the bound of this length scale comes from the strength of the hypotheses used in the model. We use the observations of enhanced surface mobility in ref 4, the fact that the rheological temperature far from the free surface must be the sample temperature, and the reasonable assumption of monotonic change in rheological temperature from surface-like to bulk-like.

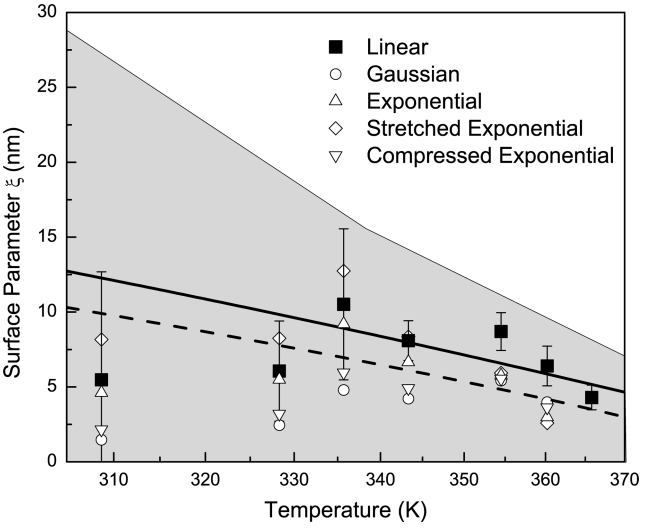

Figure 4. Fitted surface correlation length $\xi(T)$ at the surface for this work (solid line) compared to results from T_g measurements in free-standing films from ref 2 (dashed line). The $\xi(T)$ determined directly from the embedding depth are shown for various assumptions on the functional form of $T_R(z,T)$. Included is the linear assumption from eq 1, but also other functional forms which follow $T_R(z,T) = T + (T_R^{surf}(T) - T)\exp(-(z/\xi(T))^\beta)$ with $0 < \beta < 1$ for stretched exponential, $\beta = 1$ for exponential, $1 < \beta < 2$ for compressed exponential, and $\beta = 2$ for Gaussian. The region bounding the different functional forms is shown as the shaded gray area.

The validity of our conclusions rests on the validity of these assumptions. This is the first determination of a surface correlation length to come from dynamical measurements rather than measurements of T_g and as such is a good starting point for other experimental attempts to measure depth dependent dynamics as well as any theoretical studies. Since there is a significant reason to suspect a relation between enhanced surface dynamics and observed anomalies in the glass transition temperature of thin films,[1,21] it is worth exploring to what extent the above calculation can be compared to similar layer models used to describe glass transition data. Figure 4 compares the measured surface correlation lengths directly. The solid line is the result from this work of applying eq 1, and the dashed line is that obtained in the simple layer model used in ref 2 to describe T_g values in free-standing films. It is extremely encouraging that the two approaches, describing very different observations, both give rise to very similar values of $\xi(T)$. We can also compare the ideas presented here to the study of T_g in labeled layers from ref 3. In that work, the 14 nm nearest the free surface of PS had a glass transition of 32 K lower (at roughly 340 K) than the bulk T_g. The upper bound provided from Figure 4 suggests that at 340 K the 14 nm measured layer is part of a correlated region, exhibiting a dynamic behavior quite similar to that of the free surface. The rheological temperature of the surface at 340 K (from Figure 3) is approximately the bulk glass transition temperature (T_R^{surf} (340 K) $\approx T_g$), so one might expect the glass transition of this 14 nm correlated region to occur at 340 K. This shows an agreement between a direct measurement of dynamics and a measurement of the glass transition temperature near the free surface. Finally, it is worth noting that while the model has been developed with the concept of a dynamical correlation length scale, it is not possible to use this to determine the root physical cause of this length scale. It may be that this is related to cooperative motion or other ideas of model glass-formers, but there may be other physical reasons for such a surface layer. While we have confidence in the existence of a region of correlated dynamics near the free surface of the film with a temperature dependence bounded by Figure 4, it is not possible to

assign a definite physical reason. Our results should provide a driving force for future theoretical work in this area.

In summary, we have used a very simple model to describe observations of nanoparticle embedding in polystyrene. This picture allows a consistent description of embedding, relaxation of nanodeformations, and thin film T_g studies with a common set of parameters. The description leads to a bound on the length scale of dynamics near the free surface. This concurrent agreement suggests very strongly that there is a real physical meaning to this length scale.

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