

Nanosphere Embedding into Polymer Surfaces: A Viscoelastic Contact Mechanics Analysis

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Teichroeb and Forrest [Phys. Rev. Lett. **91**, 016104 (2003)] image gold nanosphere embedment into a polystyrene surface and imply the existence of a liquid surface layer. We use a viscoelastic contact mechanics model of their results to give a contrary interpretation. The surface interactions between gold and polystyrene and the indentation depth determine the loads on the nanospheres. Using bulk properties, quantitative agreement between the model and the data is obtained, implying little or no depression in the glass temperature or existence of a liquid layer at the polystyrene surface.

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A full understanding of glass formation and glassy behavior remains an important issue in polymer and materials physics [1,2]. A possible answer to assist us in understanding these phenomenological questions comes from the observation of changes in the behavior of glass-forming liquids at the nanometer size scale [3–18]. Polymeric systems make excellent models for studying size and constraints on the behavior of complex fluids in the glass formation regime because they can be made into ultrathin films (nanometer thicknesses) that maintain their integrity and can, therefore, be studied in ways not available to small molecule glass formers. In addition, the observation of this changing behavior is important for the processing and use of polymer elements in applications such as microelectronics and nanoelectronics in which sizes at the nanoscale are already being approached. Importantly, in thin films the reduction of the glass temperature T_g has been reported to be very large for polystyrene (PS) and the depression has been interpreted as being due to a liquid surface layer in many cases [4,11–14]. It should be noted, there is work using x-ray reflectivity and x-ray photoelectron spectroscopy that studies embedment of metal nanoclusters with differing results of the magnitude of the glass transition depression at the surface of thin films [15–17].

Previous work in thin polymer films has often been performed using a “pseudothermodynamic” approach where a change in the slope of a property with temperature is interpreted as the glass transition temperature [18]. In these instances, the film properties have been examined with either two free surfaces, one free surface and one constrained surface, or both surfaces constrained. Here we examine quantitatively measurements performed by Teichroeb and Forrest [19] in which colloidal gold particles with diameters of approximately 10 nm ($9.4 \pm 10\%$) and approximately 20 nm ($20.2 \text{ nm} \pm 15\%$) were placed onto the surface of a spin cast polystyrene film (~ 180 nm thick, T_g by ellipsometry of 370 K) and their rate of embedding into the surface was followed with an atomic force microscope after subsequent annealing treatments both above

and below the bulk glass transition temperature. Teichroeb and Forrest claim that their results support the hypothesis that there is a liquidlike layer on the polystyrene surface.

In our analysis, we use a viscoelastic contact mechanics equation and include the surface interactions between the polystyrene and the gold particles to calculate the reported embedding data. We hypothesize that the viscoelastic solution provides a quantitative explanation for the data without invoking a liquidlike layer at the surface.

The contact mechanics problem of the response of a loaded rigid sphere in contact with a viscoelastic surface of a material with a constant Poisson’s ratio (ν) and a monotonically increasing contact radius has been solved by Lee and Radok [20–26]. Ting further considered the idea of a variable Poisson’s ratio [23]. Here we consider a complete solution of the Lee and Radok [26] solution based on Ting’s solution [23]. In addition, unlike those solutions, we consider the forces due to the surface tension (energy) interactions between the polystyrene and the gold particle. The relation between the indentation depth $h(t)$ into the surface, the applied load $P(t)$ and $\phi(t)$, a viscoelastic function including the creep compliance and Poisson’s ratio, is given by

$$[h(t)]^{3/2} = \frac{3}{8\sqrt{R}} \int_0^t \phi(t - \xi) \left(\frac{dP(\xi)}{d\xi} \right) d\xi. \quad (1)$$

The viscoelastic function $\phi(t)$ has the form of [24]

$$\phi(t) = \int_0^t \{1 - [\nu(t - \xi)]\} \left[\frac{dJ(\xi)}{d\xi} \right] d\xi, \quad (2)$$

where J is the creep compliance.

The forces on the colloidal gold sphere are assumed to be similar to a Wilhelmly Plate calculation given by [27]

$$P(t) = (\rho_p - \rho_s)gV_{\text{disp}} + WP(t)\gamma_{LV} \cos\theta, \quad (3)$$

where WP is the wetted perimeter [determined from the spherical geometry and $h(t)$] and γ_{LV} is the surface energy of the polymer. The gravitational and buoyant forces are negligible ($\sim 10^{-11}$ nN) and, using Young’s equation,

$$\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL}, \quad (4)$$

the force acting on the sphere is fully defined:

$$P(t) = 2\pi(\gamma_{SV} - \gamma_{SL})\sqrt{R^2 - [R - h(t) - h_m]^2}, \quad (5)$$

where R is the radius of the particle, $\gamma_{SV} = 1.35$ N/m [28] is the surface energy of gold, $\gamma_{SL} = 0.3$ N/m [28] is the interfacial energy between gold and polystyrene, $h(t)$ is the indentation depth as a function of time, and h_m is the meniscus height defined next.

We dealt with the fact that a meniscus will form upon initial contact between the gold sphere and the polystyrene substrate using the equation developed by Tabor [29] and referred to by Rimai *et al.* [30–32] for a rigid particle in contact with an elastic material. The height of the meniscus h_m can be approximated using

$$h_m = \{[R(w_A/2)^2]/E^2\}^{1/3}, \quad (6)$$

where R is the particle radius, w_A is the thermodynamic work of adhesion ($w_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} = 1.091$ N/m [28,30–32]), and E is Young's modulus of polystyrene. E was taken to be the average of the values reported in [33] ($E = 2.8 \times 10^9$ Pa). The meniscus height for both sphere diameters was assumed to be constant in the calculation for the force profile for each set of temperatures since the spheres were applied to the surface at room temperature. This meniscus height was used to determine the initial force exerted on the film and not as part of the embedment depth. The meniscus height was calculated to be 0.549 and 0.843 nm for the 10 and 20 nm spheres, respectively. Figure 1 shows a representative curve of the load profile.

Before proceeding to our results, we remark that there are similar data to that of Teichroeb and Forrest [19] but for embedding of copper and gold clusters into polymer surfaces rather than spheres [15–17]. These data gave only

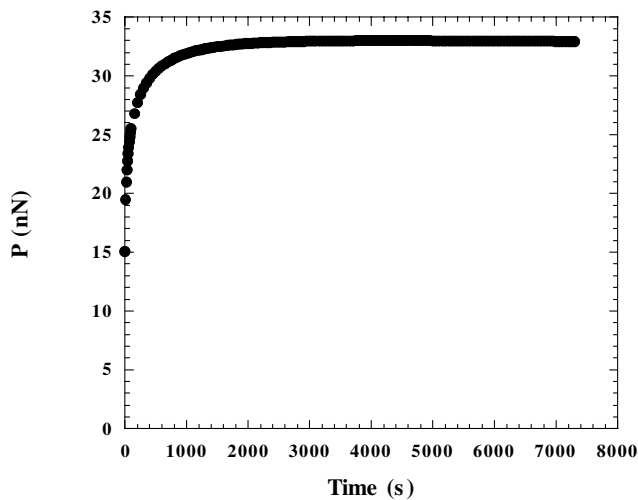


FIG. 1. Force history $P(t)$ vs t calculated from apparent height (t) experimental data collected at 368 K by Teichroeb and Forrest [19], including effects of the meniscus height.

modest depressions in T_g and were analyzed using a viscous fluid model for the polymer surface. Because polymers are viscoelastic fluids, the present model provides a more complete accounting for the material behavior.

We used the creep compliance data from Plazek [34,35] for a polystyrene of similar molecular weight to that used by Teichroeb and Forrest [19] and calculated the $h(t)$ vs t curve for the colloidal gold particles with diameters of 10 and 20 nm. The solutions to the viscoelastic contact models in the literature [20–26] assume constant Poisson's ratio (ν); however, it is known that Poisson's ratio is a time dependent property just as is creep compliance. The polystyrene film is going from a glasslike to rubberlike material during the experiment leading to Poisson's ratio changing from approximately 0.3 to 0.5. We modeled the time dependent Poisson's ratio using a stretched exponential model of the form

$$\nu(t) = 0.3 + 0.2\{1 - \exp[-(t/\tau)^\beta]\}, \quad (7)$$

where τ is the retardation time and β is the shape parameter. These values were assumed to be the same as those for the creep compliance. It should be noted that, in the experimental data from Teichroeb and Forrest collected at 378 K, the surface force goes through a maximum when the particle embeds past halfway into the surface. The complete model used here is only valid to this “half-way” point [26].

Creep compliance data for a polystyrene of 189 000 g/mol M_v with a polydispersity index of 1.01 from Plazek [34,35] was fit using a stretched exponential model of the form

$$J(t) = J_G + J_N\{1 - \exp[-(t/\tau)^\beta]\}, \quad (8)$$

where $J(t)$ is the creep compliance as a function of time, J_G is the glassy compliance, J_N is the rubbery plateau compliance, τ is the retardation time, and β is the shape parameter. There was no viscosity term used in the model because the material response probed here was far from the viscous flow regime. The stretched exponential model values from the fit to the bulk data, referenced at 373.2 K, are as follows: $J_G = 8.50 \times 10^{-10}$ Pa $^{-1}$, $J_N = 6.109 \times 10^{-6}$ Pa $^{-1}$, $\tau = 9.44 \times 10^5$ s, and $\beta = 0.7708$. Using this model for the creep compliance and knowing the force profile as a function of time, Eq. (1) can now be solved for an indentation depth. The model indentation depth was compared to the original data obtained by Teichroeb and Forrest [19] and the retardation time τ was adjusted until the model predicted an indentation depth bounding the error of the measurement supplied by Teichroeb and Forrest. In some cases the model predicted a slower indentation at the beginning of the annealing experiments; for these occurrences, the data was bounded for the longer times. The retardation times and temperature shift factors were compared to the bulk data obtained for the 189 000 g/mol molecular weight polystyrene [34,35].

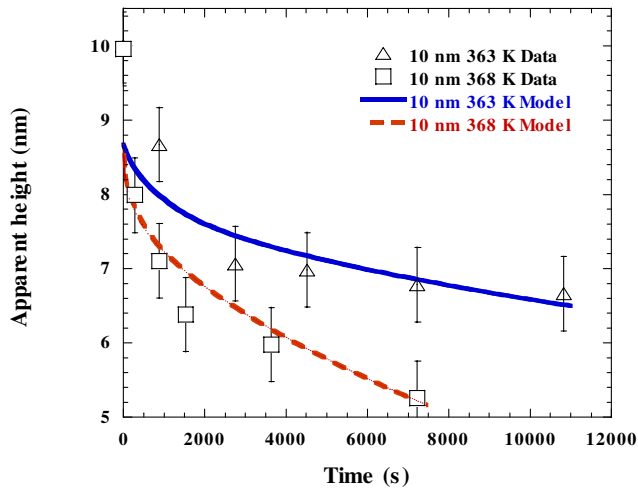


FIG. 2 (color online). Comparison of calculated and measured 10 nm sphere embedment into polystyrene surface. Model h values estimated using creep compliance data of bulk polystyrene of 189 000 g/mol M_w , collected by Plazek *et al.* [34,35]. The retardation times for 363 and 368 K data are 1.0×10^9 and 2.6×10^8 s, respectively.

Figure 2 depicts the indentation data for the 10 nm spheres embedding into the polystyrene at 363 K and the data are well represented with the viscoelastic contact model when using a retardation time of 1.0×10^9 s. The retardation time used in the model corresponds to the bulk behavior at ~ 367.1 K, which is 4.1 K above the temperature of the test. [This is based on a bulk retardation time of $\tau = 9.44 \times 10^5$ s at $T = 373.2$ K and the known shift factors for polystyrene [34,35]. We further note that this time is longer than often used 10^2 or 10^3 s at the glass temperature. This is due to the form of equation used to fit the Plazek [34,35] data [Eq. (8)] and it represents the time to achieve the rubbery plateau.] The shift factor relative to the Plazek bulk data implies that the glass temperature is depressed by 4.1 K. Similar calculations and comparison with the data for the 10 nm spheres embedding at 368 K is within ~ 0.1 K of the actual experimental temperature.

The 20 nm sphere data were analyzed in the same way. Figures 3 and 4 show model calculations and data for the 20 nm spheres embedding into the PS surface at temperatures of 363, 368, and 378 K. At 363 K, the bulk compliance corresponding to a temperature of 365.8 K gives height estimates that agree well with the data, hence implying a glass temperature depression of only 2.8 K. For the 368 K data, the model gives results for a corresponding bulk behavior at 366.8 K leading to a possible increase in T_g of 1.2 K for the 368 K data. These results are in good agreement with the 10 nm sphere data. The 378 K data provided an interesting result. The model results would imply that there is an increase in T_g of ~ 7.2 K. It should be emphasized that the 378 K data were only analyzed up to a time of 1000 s. This is due to the limitation of the viscoelastic contact model being valid only for a monotonically

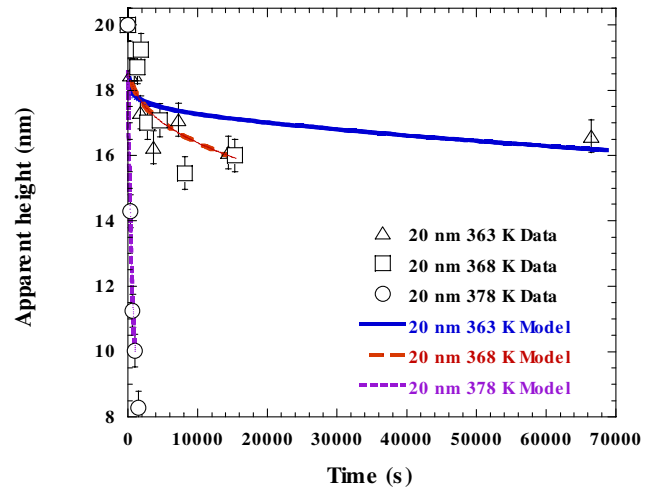


FIG. 3 (color online). Similar to Fig. 2, comparison of calculated and measured 20 nm sphere embedment into polystyrene surface. The retardation times for 363, 368, and 378 K data are 7.0×10^9 , 1.5×10^9 , and 9.5×10^6 s, respectively.

increasing contact radius, i.e., until the ball sinks more than halfway into the substrate [26].

In conclusion, embedment of gold nanospheres into polystyrene surfaces occurs spontaneously due to the large surface attraction (wetting) of PS on gold. The rate of embedment can be calculated using a viscoelastic contact model. Quantitative agreement between the model and results of Teichroeb and Forrest [19] is obtained using the bulk properties of PS (Plazek) [34,35] and with little change in the reference or glass temperature. Our results argue against the existence of a surface liquid layer in polystyrene at or near the bulk glass temperature. Given that the reported depressions in T_g in extremely thin films can be as great as 65–70 K, these results suggest that a free

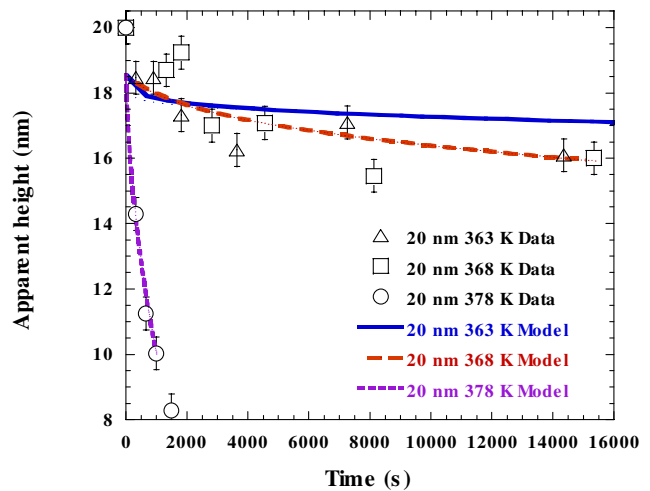


FIG. 4 (color online). Rescaling of early time data from Fig. 3 for measured and calculated 20 nm sphere embedment into polystyrene surface.

surface of lowered T_g is not responsible for these reductions. Experiments to replicate those of Teichroeb and Forrest [19] are in the design stage and the analysis is being extended to embedment beyond the halfway point.

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