Comment on “The properties of free polymer surfaces and their influence on the glass transition temperature of thin polystyrene films” by J.S. Sharp, J.H. Teichroeb and J.A. Forrest

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Abstract. Sharp, Teichroeb and Forrest [J.S. Sharp, J.H. Teichroeb, J.A. Forrest, Eur. Phys. J. E 15, 473 (2004)] recently published a viscoelastic contact mechanics analysis of the embedment of gold nanospheres into a polystyrene (PS) surface. In the present comment, we investigate the viscoelastic response of the surface and conclude that the embedment experiments do not support the hypothesis of a liquid surface layer of sufficiently reduced “rheological temperature” to explain reports of very large reductions in the glass temperature of freely standing ultrathin polystyrene films. We also report some errors and discrepancies in the paper under comment that resulted in an inability to reproduce the reported calculations. We present our findings of error in a spirit of clarifying the problem of embedment of spheres into surfaces and in order that others can understand why they may not reproduce the results reported by Sharp, Teichroeb and Forrest. In the comment, we also examine the effects of the magnitude of the forces that result from the polymer surface-nanosphere particle interactions on the viscoelastic properties deduced from the embedment data and we provide a comparison of apparent surface or “rheological” temperature vs. experimental temperature that indicates further work needs to be performed to fully understand the surface embedment experiments. Finally, we comment that the nanosphere embedment measurements have potential as a powerful tool to determine surface viscoelastic properties.

PACS. 64.70.Pf Glass transitions – 65.60.+a Thermal properties of amorphous solids and glasses: heat capacity, thermal expansion, etc. – 68.15.+e Liquid thin films – 68.35.Ja Surface and interface dynamics and vibrations

1 Introduction

In 2003 Teichroeb and Forrest [1] performed experiments in which the rate of embedment of colloidal gold nanoparticles placed onto the surface of a spin cast polystyrene film was measured at different temperatures from above to below the bulk glass transition temperature. Based on the raw embedment depth vs. time data, they interpreted their results as supporting the hypothesis that there is a liquid-like layer on the polystyrene surface [1]. In 2004 O’Connell et al. [2] and Sharp et al. [3] (STF) applied viscoelastic contact mechanics models to these data in order to provide a quantitative comparison between the surface properties and the bulk properties of polystyrene. The results of these and a subsequent work by Hutcheson and McKenna [4] (HM) in 2005 gave conflicting interpretations of the surface behavior. STF interpreted the results as implying that there is a liquid layer at the polystyrene surface and this can partially explain the large reductions observed in the glass transition temperature of ultrathin polystyrene films [5]. On the other hand, HM interpreted the nanosphere embedment experiments to show little difference between surface and bulk viscoelastic properties of polystyrene. The purpose of the present article is to consider differences in interpretation and the significance of the experiments themselves as regards the determination of surface behavior of polymeric materials and to explore some of the reasons for quantitative differences between the STF and HM works.

The work is constructed so that we consider the meaning of the nanosphere measurements and where such measurements may be useful. We discuss the differences between the rheological temperature (\(T_{rheal}\)) or surface temperature that we define subsequently and the experimental temperature (\(T_{exp}\)) and show that, though they are different, the differences are insufficient to explain large changes in the glass transition temperature of ultrathin films as being due to high surface mobility or extremely low glass transition of the surface. We also argue that the nanosphere embedment measurements can be a useful tool to extract surface rheological properties.

Included in our discussion is a section that points out some errors in the STF reference [3]. These are provided
Comparison of 10 and 20 nm embedment data at 378 K

is taken to be the equilibrium PS/Au

... there is a misstatement in

\{R − \}\ is the surface energy of polystyrene

\( P = 0 \) − \( \xi \) \( \phi \) (3)

− \( + \) is the sphere radius and \( P \)\( \sin(\)\( ) \approx 2 \)− \( 1 \) is Poisson’s ratio.

is the load (force), \( \nu \) .

for the 10 nm spheres and 59

\( \nu \) are not. Interestingly,

Figure 1, the data reported in r

... and the STF paper that “... most of this data has been repro-

sets of data are reproduced as

... Both Teichroeb and Forrest [1] and by Sharp et al. [3]. Both

2.2 Embedment data

Figure 1 shows data for the embedment of 10 nm and

20 nm gold spheres into a polystyrene surface at 378 K.

... It is such data that can be used to test equation (1) or

2.3 Integration of the viscoelastic equations

2.3.1 Integration by STF [3]

In order to reproduce the calculations reported by STF in

reference [3] we set-up a program to solve equation (1)

that is based on the Heaviside Calculus (commonly used to

solve such convolution integrals) and using the trapezoidal

rule [8,9]. To do this, one needs the force function from

STF and this is reproduced here:

\[ P = 2\pi R \gamma \sin(\phi) \sin(\theta + \phi) \] (2)

where,

\[ \cos(\phi) \approx \frac{h - R}{R} \] (3)

\( P \) is the load (force), \( \gamma \) is the surface energy of polystyrene

\( \sim 0.035 \) N/m and \( \theta \) is taken to be the equilibrium PS/An

contact angle of 46° for the 10 nm spheres and 59° for

the 20 nm spheres [3], and the angle \( \phi \) is estimated from the

apparent sphere height versus time data for the HM

calculation.

Figure 2 shows the results for both the 10 nm and

20 nm spheres embedded at 378 K. Also shown are the

calculations reported by STF [3] and our calculations us-
ing their force function (Eq. (2)). In principle, the results

should be the same. Clearly, they are not. Interestingly,

our calculations using the STF force function predict that