



# Elastic modulus and surface tension of a polyurethane rubber in nanometer thick films



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## ABSTRACT

Estane is a polyurethane with thermodynamically incompatible hard and soft segments and behaves like a thermoplastic elastomer. In the present work the mechanical properties of Estane at the nano- and macro-scales have been characterized. The macroscopic viscoelastic properties were found to follow time–temperature superposition. Also we used a nano bubble inflation method to obtain the compliance of the Estane ultra thin films over thicknesses ranging from 220 nm to 22 nm. The results have been analyzed using both a direct stress-strain analysis and an energy balance method to separate the rubbery plateau regime modulus and the surface tension of the ultra thin films. It is found that the rubbery regime modulus stiffens significantly as thickness decreases, while the surface tension is independent of film thickness. The rubbery stiffening dependence on film thickness is found to be consistent with a new analysis that suggests that it is related to the shape of the macroscopic segmental relaxation.

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## 1. Introduction

Segmented polyurethane elastomers have a great commercial importance and wide industrial application as engineering plastics, adhesives, coatings and industrial fibers [1,2]. Material scientists have great interest in this material and a wide range of studies on polyurethanes have been performed to characterize their macroscopic properties [1,3,4]. The domains of the segmented polyurethane are formed from the hard segments which act as physical crosslinks while the soft segments act as the elastic network [1–4]. The large difference between the glass transition temperature of the soft segments and the glass transition temperature of the hard segments results in the material exhibiting a broad rubbery plateau region in this temperature range [5,6]. They behave much as cross-linked rubber, i.e., as thermoplastic elastomers.

The observation that the glass transition of materials is changed by confinement has attracted significant attention [7–10], since the first reports from Jackson and McKenna [11] and Zhang *et al.* [12] showed that confining glass-forming liquids to nano-meter dimensioned pores leads to reduction of the  $T_g$ . Earlier work on nanoparticles and block copolymers had suggested similar behavior [13,14]. The motions of confined polymer molecules are different from those in bulk, and have been studied under different

experimental geometries [15,16], such as nanowire and ultra thin film [17]. The ultra thin film sample provides a straight-forward way to control the interaction between film and substrate. At the same time the film thickness can be readily controlled in the experiment. Thus a significant amount of work has been done to study the glass transition temperature ( $T_g$ ) and segmental dynamics for freely standing films and supported films at the nanometer size scale using different experimental methods [17–27]. However, the behaviors of materials at this scale have been found to not be unique [7,8,22–27], and apparent behaviors can depend on measurement method or condition. For example, freely standing polymer films generally exhibit reduced  $T_g$  as the film thickness decreases, while in supported films, the changes of  $T_g$  have been reported to increase, decrease, or not change. Teichroeb and Forrest [24] performed spherical nano-particle embedment experiments on ultra thin polystyrene films and interpreted the results to be consistent with the existence of a surface liquid layer of only a few nanometers thickness. On the other hand, Hutcheson and McKenna [25] used a viscoelastic contact mechanics analysis for the same particle embedment data and showed that the surface rheological properties were very similar to the bulk. Tsui *et al.* [26] using AFM adhesion force measurements showed that surface viscoelastic properties were similar to the bulk. Ellison and Torkelson [28–30] explored the  $T_g$  gradient in polymer thin films using fluorescence spectroscopy experiments, and they showed both the free surface and surface effect are important in the confined systems. While it seems clear that there is an effect of surface in competition with

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possible finite size effects, the interpretation of the apparent  $T_g$  changes in ultra thin films remains controversial and investigation of confined polymer systems continues to be an important field of investigation.

Regarding to the  $T_g$  reduction in thin polymer films, the first impetus to this field traces back to the work by Keddie *et al.* [17,31,32] when they first [17] reported the reduced glass transition temperature at the nanometer size scale for supported polystyrene films using ellipsometry. They found ultra thin polymer films spin cast onto weakly interacting surfaces could exhibit strong reductions in the glass transition temperature. This was followed by major findings that the effects in freely standing films could be even more dramatic, Dalnoki-Veress *et al.* [33] used transmission ellipsometry to test the glass transition temperature for free standing polystyrene film, reaching up to 80 °C  $T_g$  reductions in high molecular weight polystyrene at approximately 10 nm thickness. Using a bubble inflation method, which was developed by O'Connell and McKenna [34], O'Connell *et al.* [35] found a  $T_g$  reduction of as much as 122 °C for a 3 nm polycarbonate film. Associated with the observation that the  $T_g$  of polymers changes upon confinement, whether increasing or decreasing, there have also been reports that the mechanical properties at the nanometer size scale of polymers can change [34–41]. Of particular interest in the present work is the observation from McKenna and co-workers [34–39] that freely standing ultra thin polymer films exhibit dramatic stiffening in the rubbery plateau regime, following a power law dependence on film thickness that seems to be dependent on the molecular structure.

Regarding the behaviors of materials in nano-scale confinement, a variety of concepts have been developed to explain this phenomenon. One possibility is that the change in observed properties upon reaching the nano-scale dimensions is induced by free surfaces [42,43]. For example, Wang *et al.* [15] in a study of pure bending of Al nanowires properties, presented the surface elasticity based on the Lagrangian and the Eulerian descriptions. They found that the effective Young's modulus decreased as surface tension decreased, and the effective Young's modulus decreased as the nanowire thickness decreased or the aspect ratio increased. In other work, Cuenot and coworkers [16] measured the apparent elastic modulus of suspended silver nanowires and polypyrrole nanotubes using atomic force microscopy (AFM). In their work the measured modulus increased as the diameter decreased, but the observed behavior was attributed to the surface tension dominating the response as diameter decreased [16]. However, the reported surface tension values extracted from the mechanical analysis were approximately twice the values reported for the material reported at the macroscopic level.

In work on thin polymer films using a bubble inflation method, McKenna and coworkers [36–39] have reported results for the mechanical and rheological properties and, through characterization of the film rheological responses found both a reduction of the  $T_g$  and an extremely high stiffening in the rubbery plateau regime. They have demonstrated that surface tension is not the exclusive cause of the observed stiffening and concluded that the rubbery stiffening behavior arises from both a nano-confinement effect and surface tension effects [36,39].

In the prior work using the bubble inflation experiment results were reported for polystyrene(PS) [35,36] and polycarbonate(PC) [34] for temperatures that were generally close to the (reduced)  $T_g$  of the thin films, while results for poly(vinyl acetate)(PVAc) [33,35] and poly(*n*-butyl methacrylate)(PBMA) [39] films were investigated in the region near to but above the macroscopic  $T_g$ . The PVAc was found to have little dependence of the  $T_g$  on film thickness, while the  $T_g$  behavior of the PBMA, could not be determined as the  $T_g$  was near ambient or below. Hence, it is of interest to examine

systematically the behavior of a material which is known to be well above the macroscopic  $T_g$  and to add new information for both the PS and PVAc at temperatures above the macroscopic  $T_g$ . For this purpose we examine a polyurethane elastomer (Estane) that has not been previously investigated using the bubble inflation method and with this material explore the mechanical behavior in the temperature region far above the macroscopic  $T_g$ . Also, unlike prior work in which linear uncross-linked polymers were examined, Estane is a block copolymer and is a physically cross-linked elastomer at the temperature investigated here. In what follows we show the macroscopic rheological properties of this material as characterized using conventional rheometry and applying time temperature superposition. For the bubble inflation experiments, all results are for ambient temperature, which is far above the macroscopic  $T_g$ , i.e., in the elastic state. Surface tension and confinement stiffening effects are separated and the results are compared with the previous findings. We also provide new data for PS and PVAc above their macroscopic  $T_g$  and show that these materials are different in behavior from the Estane. Finally, we evaluate the film stiffening results in the context of the recent suggestion by Ngai *et al.* [44] that the rubbery stiffening observed is related to the shape of the macroscopic retardation spectrum in the segmental regime.

## 2. Experimental procedures

### 2.1. Material

The poly(ester urethane) (Estane<sup>®</sup> 5703) [45,46] thermoplastic elastomer was provided in pellet form and is a product made by the BF Goodrich Co. Estane<sup>®</sup> 5703 contains approximately 23wt% hard segments which are composed of 4,4'-methylenediphenyl 1,1' diisocyanate and a 1,4 butanediol chain extender. The soft segments are comprised of poly(butylene adipate) with molecular weights in the vicinity of 1000units. The other two materials used are a polyvinyl acetate (PVAc) [ $M_w = 157,000$  Da, PDI = 2.73, Scientific Polymer Products, Lot#08] and a polystyrene (PS) [ $M_w = 994,000$  Da, PDI = 1.07, Sigma–Aldrich, Product # 32780-8].

### 2.2. Calorimetry

The glass transition temperature  $T_g$  of this Estane sample was measured by differential scanning calorimetry (DSC) (Q20 from TA Instruments) using a heating and cooling scan range from –70 °C to 150 °C at rates of 10 °C/min. The limiting fictive temperature  $T_f^l$  was calculated from the heating scan after cooling rates of 10 °C/min. The  $T_f^l$  value obtained using Moynihan's area matching method [47] was –26.7 °C ± 0.7 °C. Because the lowest temperature achievable in our present AFM configuration is –10 °C, which is above the  $T_g$  of the Estane, all bubble inflation tests were run at room temperature 25 °C, hence approximately 50 °C above the macroscopic  $T_g$ .

### 2.3. Rheological measurements

The sample used for the rheological measurements was compression molded using a hot-press in a disk-like geometry of 8 mm diameter and 1.6 mm thickness. The dynamic mechanical measurements were performed using a parallel plate geometry with an ARES rheometer from TA Instruments.

Dynamic frequency tests (0.1 rad/s to 100 rad/s) were performed in isothermal conditions at temperatures from –40 °C to 110 °C. The real and imaginary components of the complex shear modulus ( $G'$ ,  $G''$ ) and the  $\tan(\delta)$  were collected. All measurements were corrected for instrument compliance following the procedure of Hutcheson and McKenna [48].

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