# GEOMETRIC AND INTERFACIAL EFFECTS ON VISCOELASTIC INDENTATION OF CONFINED POLYMER FILMS

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## Introduction

One of the limitations to the development and application of complex interfaces is determining the adhesion of buried interfaces. Fracture methods in various geometries have been used to determine the adhesion and toughness of multilayered materials. These methods usually require destruction of the interface, and one possible measurement technique is the delamination of a buried interface through indentation. During an indentation experiment, a thin film coating is indented with an increasing load, which will cause delamination to occur at the interface [1]. The required delamination load and interfacial crack area both change dependent on the indenter geometry, material properties, and interfacial strength.

In systems where delamination does not occur, the interfacial strength dictates the load required to indent a confined film to a specified depth. Previous modeling work has been developed for indentation of both perfect adhesion and slip interfaces [2-4]. These two cases show a dramatic difference in the indentation contact area, since restrictions at the interface limit the available relaxation modes and stress transfer into other layers. In the case of films with viscoelastic properties or weakly bonded interfaces, an idealized case cannot be assumed since contact area and penetration depth changes the stress field at the polymer-substrate interface. In this work, fixed load indenters were used to investigate interfacial properties in confined polymer films at conditions where delamination does not occur.

## Experimental

Equipment and instruments or materials are identified in the paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology (NIST), nor does it imply the materials are necessarily the best available for the purpose.

For confined indentation, four 12.7 mm diameter chrome steel spheres were arranged in a row on a 3 µm to 50 µm thick polymer film. Experimental geometry is shown in Figure 1. Each sphere indented the polymer surface due to the force load from gravity. The indentation contact areas were imaged with an inverted optical microscope, detecting contact radii from edge detection techniques. Spheres were placed on the surface at the same time through the use of a vertical motion stage.

The gravity indentation load required no monitoring and no indenter drift was seen throughout the length of the experiments. Bulk viscoelastic indentation was performed with a high-throughput technique using an array of 3 mm diameter chrome steel spheres as detailed previously [5]. For bulk indentation, creep compliance is described by Hertzian mechanics. Uncertainty in this work is displayed as standard error at a 95% confidence interval.

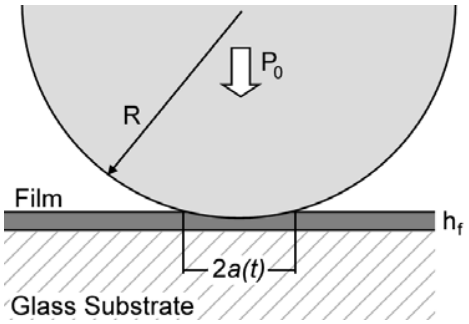


**Figure 1.** Confined spherical indentation of a two layer substrate. A large radius, $R$, sphere with a fixed load, $P_0$, indents a polymer film of a specified thickness, $h_f$. Contact radius, $a(t)$, was measured using optical imaging.

Glass slides were treated with different silane depositions to change the polymer-substrate interface. Glass slides were cleaned with ethanol and toluene, then dried and exposed to ultraviolet & ozone (UVO) for 500 s. Slides were then left in a toluene solution containing 20 mmol/dm$^3$ of the specific silane for 1800 s. Slides were then washed with toluene, dried, and tested for uniformity using water contact angle measurements.

Photopolymer films were cured *in-situ* on silane treated glass slides, using a formulation containing lauryl methacrylate (LMA), isobornyl methacrylate (IBoMA), and hexanediol dimethacrylate (HDDMA). These monomers contained only alkyl and methacrylate moieties, limiting the possible interactions at the interface. Samples were polymerized for 3600 s using an Acticure 2000 mercury arc lamp (EXFO Systems) with a 365 nm bandpass filter at a light intensity of 10 mW/cm$^2$. Hydroxypropyl cellulose (HPC) samples were solvent cast and annealed for 24 h in a dry oven before use.

To create a bonded interface, 3-mercaptopropyl dimethylchlorosilane treated glass slides presented methacrylate groups on the glass surface and created covalent bonds at the interface with the photopolymerized film. To create a slip interface, a fluorinated silane surface was created using tridecafluoro-1,1,2,2-tetrahydrooctyl dimethylchlorosilane. Alkyl and carboxylic acid surfaces were formed

in a similar manner using octadecyltrichlorosilane and 10-(carbomethoxy)decyl dimethylchlorosilane, respectively.

## Results and Discussion

Bulk viscoelastic experiments were performed to determine the creep compliance of an unconfined polymer network containing 50/50 LMA/IBoMA by mass percent. Bulk creep compliance was then used to predict the indentation contact radius on a 14 μm thick photopolymer film. Predictions for a slip interface were made with a model formulated by Chadwick [3], while the bonded interface prediction was developed from theory by Chen and Engel [4]. Experiments were performed on confined films for 50000 s, using the methacrylate monolayer interface as a bonded interface, while the slip case was measured on delaminated film from a fluorinated monolayer.

The contact radius at 100 s for the bonded interface was 48 μm ± 1 μm, equivalent to the predicted contact area from the bonded model. The contact radius for delamination sample was 76 μm ± 1.2 μm, which was lower than the slip interface prediction of 80 μm. At all measured times, the delaminated indentation contact radii was lower than the predicted slip condition contact radius. In the case of a fluorinated sample without delamination from the surface, the contact radii at 100 s was 55 μm ± 1 μm, which was between the two ideal cases. Throughout the experiment, the fluorinated sample contact radius remained between the two ideal cases. In all experiments, the indentation force required to delaminate the coating was much higher than the force from the sphere gravity load.

To study the extent of this effect, confined indentation experiments were performed on film thickness gradients of photopolymer films of varying network structure to determine where deviations from an ideal bonded adhesion occur. Film thickness gradients of multiple different photopolymer formulations were polymerized with varying crosslink density and initial modulus. Film thicknesses ranged from 3 μm to 50 μm, and either the methacrylate or fluorinated silane was deposited on the glass substrate prior to polymerization. The contact radii would deviate from the predicted contact radius once the film thickness decreased below a critical value. If these measurements were used in the bonded model, the calculated compliance would begin to deviate from the bulk compliance as the film thickness decreased, appearing higher than expected. The film thickness where this effect was seen was dependent on the polymer-substrate interface and the polymer network structure.

Since the magnitude of the deviation was dependent on the buried interface, four different interfaces were produced to determine if this technique could discriminate between each buried interface. Hydroxypropyl cellulose films were tested with four different interfaces. Carboxylic acid, alkyl, or fluorinated silane glass slides were indented, along with untreated UVO cleaned glass. Interfaces which contained hydrogen bonding moieties at the interface showed a lower apparent compliance than an alkyl or fluorinated interface. HPC contains numerous hydroxyl groups along the backbone, so the ability to hydrogen bond with the glass interface results in an improved interfacial strength in comparison to a treated glass substrate containing no hydrogen bonding groups.

## Conclusions

Confined indentation experiments on viscoelastic materials exhibited a change in indentation contact area due to the buried interface. Interfacial effects only appear at a specific range of film thicknesses, dependent on the network structure of the polymer film. Decreases in modulus or crosslink density increased network mobility and detection of the confined interface is limited to a smaller range of film thicknesses. Measurements of polymer films with different silane interfaces at the polymer-glass surface were able to detect the relative strength of the interface. Since the bulk viscoelastic response of the film remains constant, this technique can be used to measure changes at the interface in a high-throughput manner and determine the viscoelastic responses of different surface treatments. In addition, more complex geometries and interactions can be explored with further modifications of both the polymer and the glass substrate.

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## References

1. J. E. Ritter, T. J. Lardner, L. Rosenfeld et al., *J. Appl. Phys.* 1989, 66, 3626-3634.
2. K. R. Shull, D. Ahn, W. L. Chen et al., *Macromol. Chem. Phys.,* 1998, 199, 489.
3. R. S. Chadwick, *SIAM J. on App. Math*. 2002, 62, 1520-1530.
4. W. T. Chen and P. A. Engel, *Int. J. of Solids and Struct.* 1972, 8, 1257-1281.
5. P. M. Johnson and C. M. Stafford, *Rev. Sci. Instrum.* 2009, 80, 103904.