# JKR Adhesion Measurements at Layer-by-Layer and Polymer Brush Functionalized Surfaces

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## INTRODUCTION

In developing and screening new materials, researchers are often interested in how factors such as the roughness, surface energy, and the chemical composition of material surfaces govern critical adhesion interactions.  In this work, we examine two surface modification methods to chemically functionalize surfaces for use in contact adhesion tests: layer-by-layer (LbL) deposition of polyelectrolytes, and polymer brush layers.  Our results suggest that not only the types of chemical moieties present, but also the method of chemical functionalization are important factors governing adhesion as measured via an axisymmetric contact adhesion test.

Our measurement platform is based on the contact mechanics theory of Johnson, Kendall, and Roberts (JKR),[1] which describes the contact between two spheres or a sphere and a flat under an applied load.  By measuring the difference between the applied load, $P$, and that expected from Hertzian contact, $P'$, the energy release rate, $\mathcal{G}$, can be calculated over an entire loading and unloading curve.  The energy release rate typically deviates from the thermodynamic equilibrium work of adhesion, especially during the unloading portion of the experiment, as a result of surface-specific bonding events.  Thus, we use the adhesion hysteresis, $\mathcal{G}_{HYS}$, defined as the difference between the calculated $\mathcal{G}$ values upon unloading and loading, to quantify adhesion interactions in our systems.  Figure 1 provides a schematic of the experimental setup.
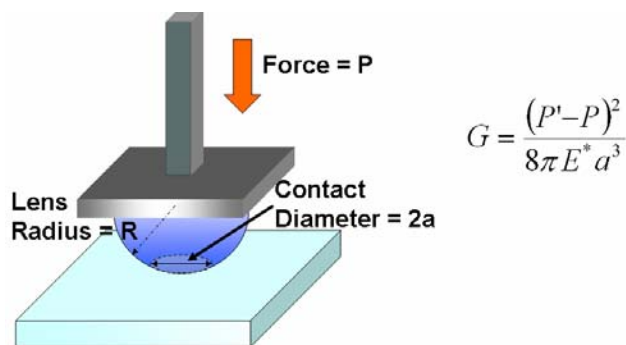


$$G = \frac{(P'-P)^2}{8\pi E^* a^3}$$

**Figure 1.**  Schematic of a typical JKR experiment.  A semi-hemispherical lens with radius $R$ is pushed into a flat substrate with force $P$.  A contact circle with radius $a$ is formed at the interface between the materials.  $E^*$ is the system modulus, calculated from the lens and substrate mechanical properties.  The energy release rate, $\mathcal{G}$, is calculated from these parameters using JKR contact mechanics.

## EXPERIMENTAL

Equipment and instruments or materials are identified in this work 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 that the materials are necessarily the best available for the purpose.

**Lens Preparation.**  Molds for lenses were constructed using 1 cm diameter hemispherical glass lenses.  Poly(dimethylsiloxane) (PDMS, Sylgard 184) was mixed at a 10:1 ratio by mass of base to crosslinker and degassed under house vacuum for approximately 1 h, after which it was poured into the mold and cured in a 75 °C oven for 2 h.  Cured lenses were extracted overnight in toluene using a Soxhlet extractor,

and then dried in air for a few hours, followed by a longer (≈ 1 d) drying step under house vacuum.

**Multilayer Preparation.**  Aqueous solutions of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) were prepared from Milli-Q DI water at concentrations of 0.01 mol/L per repeat unit.  Solutions were pH-adjusted to 7.5 (PAH) and 3.5 (PAA) with 1.0 mol/L hydrochloric acid or sodium hydroxide.  Polyelectrolyte multilayers were assembled from aqueous solutions of PAH and PAA using protocols similar to those published previously.[2]  Multilayers were adsorbed onto both detergent-cleaned glass slides and PDMS lenses.

**Polymer Brush Preparation.**  Poly(2-hydroxyethyl methacrylate) (PHEMA) brushes were synthesized on PDMS lenses according to a published procedure.[3]  Conversion of PHEMA to $COO^-$ or $SO_3^-$ polyelectrolyte brushes was achieved by exposure of PHEMA-PDMS to a solution of dimethylformamide containing 0.1 mol/L of succinic anhydride or 2-sulfobenzoic acid cyclic anhydride and 0.05 mol/L of pyridine for 24 h.  PDMS substrates with polyelectrolyte brushes were thoroughly cleaned with methanol in an ultrasonic bath.  Complete conversion was confirmed by the disappearance of the –OH band at 3340 $cm^{-1}$ using attenuated total reflection infrared spectroscopy.

**JKR Adhesion Tests.**  JKR adhesion tests were conducted using a custom-built axisymmetric system comprised of an inverted microscope, a linear stepping motor, and a 10 g load cell.  Images were captured using a digital camera and the contact area was found using a custom-written macro in the image software.  Tests were conducted by advancing the lens in 2 µm steps into the substrate to a maximum force of 0.75 g.  Force data and contact images were collected after an equilibrium period following each step (30 s on loading, 120 s on unloading).  The lens was held at the maximum force position for 10 min.

Linear regression was performed on the loading data (using the equation in Fig. 1) to yield $E^*$ and $\mathcal{G}_L$.  One-parameter linear regression was then performed separately on the unloading data (keeping $E^*$ constant) to yield $\mathcal{G}_{UL}$.  The adhesion hysteresis is defined as $\mathcal{G}_{HYS} = \mathcal{G}_{UL} - \mathcal{G}_L$.

## RESULTS AND DISCUSSION

Our results suggest that both LbL and polymer brush modification are promising methods of functionalizing PDMS lenses to examine specific chemical interactions when conducting JKR adhesion experiments.  We performed adhesion experiments in both dry (ambient air) and aqueous environments.  Our findings indicate noticeably higher values of $\mathcal{G}_{HYS}$ when a contact between surfaces involved the interaction of an acid and a base, as opposed to, for example, interactions between two acid-functionalized surfaces.  Though LbL and polymer brush chemistry could both be used to introduce carboxylic acid groups onto the lens surface, LbL-modified lenses in the dry state exhibited adhesion behavior dominated by the LbL film thickness, presumably due to the previously reported high Young's modulus for (PAH/PAA) LbL films.[2]  The same effect was not observed for polymer brushes. Measurements conducted in solution revealed increased adhesion between LbL-modified surfaces due to plasticization of the film, and thereby a lower required energy to deform the lens and form adhesive contacts with the substrate.

## REFERENCES

1.  Johnson, K.L.; Kendall, K.; Roberts, A.D.  *Proc. R. Soc. Lond. A.* **1971**, *324*, 301.
2.  Nolte, A.J.; Cohen, R.E.; Rubner, M.F. *Macromolecules* **2006**, *39*, 4841.
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