

# ADHESION AT LAYER-BY-LAYER SURFACES IN AQUEOUS ENVIRONMENTS

*Adam J. Nolte, Jun Young Chung, Marlon L. Walker, and Christopher M. Stafford*  
*Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD, USA*  
*chris.stafford@nist.gov*

## Introduction

Adhesion between materials is often governed by the ambient environment, which can mediate or change the types of molecular interactions present at an interface. Biological interactions, for example, can be mediated by factors such as temperature, ionic strength, and pH. In light of these considerations, we have been developing an in situ aqueous adhesion test based on Johnson, Kendall, and Roberts (JKR) contact mechanics.<sup>1</sup> Here we present results from measuring the pH-dependent adhesion of poly(dimethylsiloxane) (PDMS) hemispheres coated with layer-by-layer assemblies of polyelectrolytes to silane-functionalized glass. Our results suggest a comprehensive understanding of all surface properties is necessary for understanding and predicting adhesion at such interfaces.

Our adhesion experiments involved pushing a hemispherical PDMS lens ( $\approx 1$  cm diameter) quasi-statically into a functionalized glass substrate to a force of  $\approx 0.5$  mN, after which time the lens was quasi-statically withdrawn. The energy release rate ( $\mathcal{G}$ ) was calculated by monitoring the contact radius ( $a$ ) of the lens with the substrate and the force ( $P$ ) during loading and unloading, and calculated from the equation given by JKR theory:<sup>1</sup>

$$\mathcal{G} = \frac{\left(4Ea^3/3R - P\right)^2}{8\pi Ea^3}, \quad (1)$$

where  $E$  is the plane-strain Young's modulus of the lens (assuming a rigid substrate) and  $R$  is the radius of curvature of the PDMS lens. Following Dillow et al.,<sup>2</sup> our figure of merit is the adhesion hysteresis ( $\mathcal{G}_{HYS}$ ), which is defined as the difference between  $\mathcal{G}$  as measured during the unloading ( $\mathcal{G}_{UL}$ ) and loading ( $\mathcal{G}_L$ ) portions of the experiment:

$$\mathcal{G}_{HYS} = \mathcal{G}_{UL} - \mathcal{G}_L. \quad (2)$$

$\mathcal{G}_{HYS}$  should therefore reflect specific adhesion interactions that develop while the lens is in contact with the substrate.

## 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 Technol-

ogy (NIST), nor does it imply that the materials are necessarily the best available for the purpose.

PDMS lenses were prepared by mixing Sylgard 184 PDMS according to the manufacturer's specifications, degassing the mixture under vacuum, and curing at 75 °C for 2 h. Uncrosslinked chains were removed by extraction with toluene.

Layer-by-layer (LbL) films composed of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) were assembled onto PDMS lenses at pH 2.5 to yield coatings rich in carboxylic acid functionality<sup>3</sup>—both 3 bilayer and 6 bilayer samples were prepared. The approximate LbL film thicknesses for 3 bilayer and 6 bilayer films were 16 nm and 40 nm, respectively. Glass slides having primary amine functionality (positively charged in solution) were prepared by immersing clean slides in a solution of 3-aminopropyltriethoxysilane (APTES) in anhydrous toluene (1 % volume fraction) for 1 h. The adhesion of LbL-coated and uncoated PDMS lenses to the treated slides was determined using JKR mechanics as discussed in the Introduction, either in laboratory air (relative humidity  $\approx 45$  %) or in aqueous solution (either pH 3.0 or pH 5.5, adjusted using hydrochloric acid and sodium chloride (NaCl)) in a custom-built in situ cell.

Coatings were further characterized to determine their Young's modulus (using wrinkling instabilities<sup>3</sup>), their surface roughness (using atomic force microscopy (AFM)), and their chemical composition (using X-ray photoelectron spectroscopy (XPS)). Some coating samples were treated with a solution of 0.1 mol/L NaCl for 1 h to decrease their surface roughness—XPS results suggested that this procedure had a minimum effect on the surface chemistry of the coatings.

## Results and Discussion

The adhesion hysteresis of unmodified PDMS and LbL-coated PDMS was measured against APTES-glass slides in air and in aqueous solutions of pH 3.0 and pH 5.5. For LbL-coated samples, XPS confirmed a surface abundance of free carboxylic acid groups. In aqueous solution, these groups were more highly charged at pH 5.5 than at pH 3.0, while the degree of positive charge on the primary amines present at the APTES-glass surface remained essentially unchanged over that pH range. Thus, the LbL adhesion was expected to increase with pH due to a higher number of possible acid-base interactions. The adhesion hysteresis for uncoated and LbL-coated PDMS is given in Figure 1.

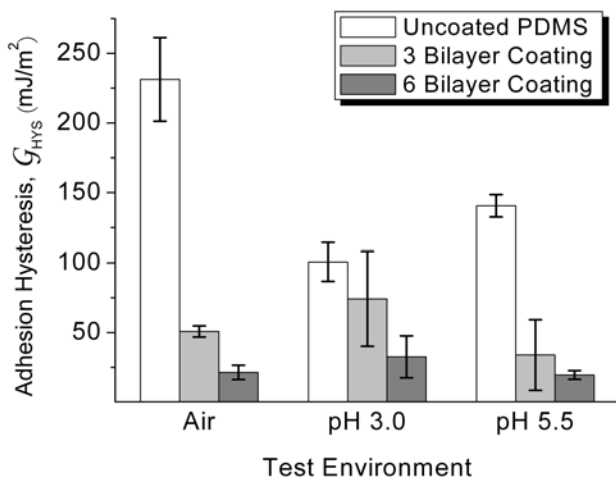


Figure 1. Adhesion hysteresis for uncoated, 3 bilayer-, and 6 bilayer-coated PDMS lenses against amine-functionalized glass. Samples were tested in air and in aqueous solutions of pH 3.0 and pH 5.5. The uncertainty in the measurement is taken as one standard deviation from a set of at least 3 samples.

As illustrated in Figure 1, the adhesion of uncoated PDMS was highest in air, and decreased upon testing in aqueous solutions. This is due to PDMS adhesion competing with the energetically favorable wetting of water on the hydrophilic APTES-glass surface. Uncoated lenses tested in aqueous solution showed higher adhesion at pH 5.5, possibly due to the charging of residual silanol groups at the PDMS surface that participated in acid-base interactions with the APTES-glass.

The adhesion of LbL-coated PDMS was less than uncoated PDMS overall, but showed no statistically significant decrease from dry state values when tested under aqueous conditions. For all coated samples, the adhesion of 3 bilayer-coated samples was greater than the 6 bilayer samples, and greater adhesion was found at pH 3.0, contrary to our expectations for increased acid-base interactions at pH 5.5. Further characterization of the coated surfaces revealed three important points for consideration:

1. LbL assembly increases the surface roughness ( $R_a$ ) of the PDMS a factor of 5 for 3 bilayer coatings and a factor of 20 for 6 bilayer coatings,
2. The Young's modulus of LbL coatings changes with pH, and is twice as high at pH 5.5 (1.8 GPa  $\pm$  0.8 GPa) than at pH 3.0 (0.7 GPa  $\pm$  0.2 GPa), and
3. Annealing LbL-coated samples in 0.1 mol/L solutions of NaCl decreased their surface roughness by approximately one-half and increased their adhesion hysteresis a factor of two.

Based on the above observations, we concluded that a combination of surface roughness and high coating modulus acted to decrease adhesion for LbL-coated PDMS, and that a pH-modulated change in coating stiffness was the predominant mechanism controlling adhesion at the

LbL-APTES interface. These findings agree with the conclusions of Fuller and Tabor regarding adhesion at rough interfaces.<sup>4</sup>

## Conclusions

We have investigated the adhesion of uncoated and LbL-coated PDMS to amine-functionalized glass slides in air and in aqueous solutions of pH 3.0 and pH 5.5. PDMS shows increased adhesion at the higher pH, possibly due to charging of silanol groups that can participate in acid-base bonding with the APTES-glass. LbL-coated samples as assembled showed lower adhesion than bare PDMS due to an increase in surface roughness. Despite the expected increase in ionized carboxylic acid groups for LbL-coated PDMS at pH 5.5, the LbL samples actually showed higher adhesion at pH 3.0. This finding was attributed to the lower Young's modulus of the coating at pH 3.0, which allowed the interface to establish more intimate contact. Our results demonstrate that a comprehensive understanding of all coating properties is important to elucidate the mechanisms governing adhesion at polymer interfaces.

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