ADHESION AND MECHANICS OF COMPLEX POLYMER INTERFACES

Christopher M. Stafford, Jun Young Chung, Heqing Huang, Adam J. Nolte, Peter M. Johnson, and Edwin P. Chan

Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

Introduction
The Polymers Division at the National Institute of Standards and Technology (NIST) exemplifies the types of research environments enabled by federal funding of polymer science. Through partnerships with industry and academia, we have built several thematic programs of broad interest to the scientific polymer community. For example, we are developing quantitative metrology tools to elucidate the properties of polymer interfaces in complex systems. The structure and properties of polymer interfaces play an integral role in numerous technological applications, particularly in the areas of coatings and adhesives. These interfacial interactions are dependent on a host of factors, including interfacial energy, roughness, surface chemistry, mechanical properties, and the presence or absence of defects. The goal of this program is to develop measurement approaches that quantify the effects of interfacial chemistry, topography, and mechanical properties on interactions of soft materials at and near hard surfaces. In particular, we are investigating interfacial structure and properties in soft, deformable materials as well as particle-laden networks and coatings. To complement these measurement techniques, we are designing a number of combinatorial libraries that express key factors governing interfacial properties, including surface chemistry, thickness, and composition. These libraries provide a foundation for systematically investigating the effect of these parameters on interface properties.

Discussion
Surface Chemistry. Developing methods to generate surfaces with chemical and morphological diversity is a key step in determining the factors governing adhesion at complex interfaces. Polymer brushes present a versatile, stable route for modulating the properties of a surface through tailored chemistry and architecture. We developed a facile surface treatment of poly(dimethylsiloxane) (PDMS) that enables grafting of polymer brushes from the surface without altering the underlying mechanical properties of the substrate. Our modification scheme uses hydrochloric acid treatment of PDMS to introduce hydroxyl groups without generating a stiff oxide layer on the substrate surface; initiator groups are then covalently attached to the hydroxyl groups for subsequent polymerization, as shown in Fig. 1.

![Figure 1](image1.png)
Figure 1. Scheme for grafting polymer brushes from PDMS. Hydroxyl groups are generated on the surface of PDMS and used to anchor initiator molecules for growing the polymer chains.

We have also generated conformal coatings created by layer-by-layer (LbL) assemblies of polyelectrolytes to chemically functionalize PDMS surfaces. These coatings, created via alternating adsorption of positively and negatively charged polyelectrolyte species from solution, introduce a thin surface layer with mechanical, topological, and chemical attributes that are quite different than the bulk PDMS material. LbL assembly is a flexible technique capable of incorporating a wide variety of macromolecular materials that facilitates measurements of surface interactions with enormous scientific and technical interest; for example, coatings comprising various polycids, polylbases, colloids, DNA, and proteins have all been demonstrated. The ability to precisely control the composition and properties of the resulting coatings makes LbL assembly an attractive technique for modifying the interfacial properties of a surface.

Surface Topography. Surface wrinkling provides a unique method for generating textured surfaces and interfaces that can serve as model rough surfaces. The formation of self-organized wrinkling patterns is a potential route for generating tunable ordered patterns that display long range order and high fidelity across many length scales. We demonstrated that surface wrinkling of polymer films can lead to a variety of surface topographies, including the established stripe, labyrinth, and herringbone patterns. We can also generate intriguing axisymmetric patterns as shown in Fig. 2. Due to the ease with which it can be used to control surface structure, wrinkling could serve as a facile test-bed for studying topography-driven phenomena such as wettability and adhesion and diffusion related processes, as well as facilitate a better understanding of dynamic self-assembly.

![Figure 2](image2.png)
Figure 2. Surface wrinkling patterns display symmetry patterns that are governed by the stress state in the film. (a) Isotropic labyrinth patterns arise from biaxial planar compression. The axisymmetric concentric ring "target" (b) and spoke (c) patterns arise due to solvent diffusion into the film from an engineered point defect.

Property Measurements. With the drive to developing materials incorporating nanoscale structures or nanoparticles, the properties of interfaces are becoming difficult to measure due to the complexity in both their structure and chemistry. We are developing several measurement platforms for assessing the fundamental interactions that develop when surfaces are brought into and out of contact using indentation-based approach (Fig. 3a) to examine the effects of internal interfaces such as those presented by nanoparticles and confined thin films on the thermorheological properties of polymer films and coatings. Another approach employs a cantilever-based peel geometry (Fig. 3b) to investigate the effect of sub-surface patterns on interfacial adhesion. Compared with surface patterns, a subsurface pattern is particularly interesting since it provides a practical means to dynamically change adhesion without directly altering the interfacial properties.

![Figure 3](image3.png)
Figure 3. Two methods for probing the effect of buried interfaces: (a) indenting sphere geometry and (b) cantilever peel geometry.

Conclusions
This presentation provides a snapshot of the on-going efforts in the Polymers Division aimed at probing the effects of interfacial chemistry, topography, and mechanical properties on interactions of soft materials at and near hard surfaces. We are able to measure interfacial interactions that...
develop when two materials are brought into contact, as well as the effect of buried interfaces on the material properties.

Acknowledgements. This work is an official contribution of the National Institute of Standards and Technology; not subject to copyright in the United States. A.J.N. and P.M.J thank the NIST/National Research Council Postdoctoral Fellowship Program for funding.

References