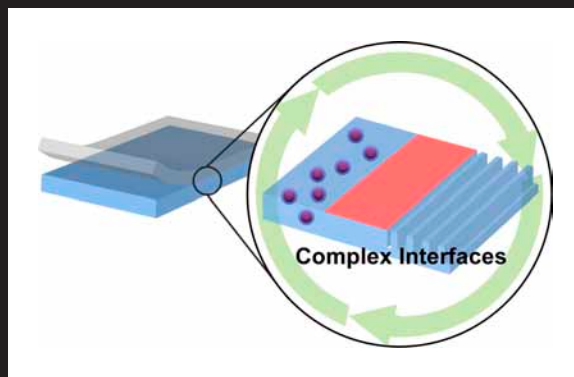


# Mechanics of Complex Interfaces

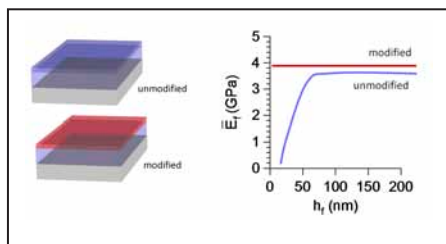
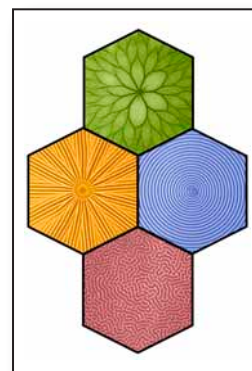
## Objective

The goal of this project is to develop measurement methods that correlate the structure and dynamics of materials at surfaces and buried interfaces to their macroscopic mechanical properties. These measurements are needed to develop predictive modeling of material lifetime and the effects of degradation on performance. The measurement methods developed here are transferable to industry and will enable them to develop sustainable practices through reducing or restoring polymer coatings and adhesives.



## Impact and Customers

- Polymer coatings and adhesives serve to modify critical properties of surfaces and interfaces, such as appearance, corrosion resistance, and wettability.
- Detailed measurements of the structure and dynamics of these materials is critical for accurate prediction of performance and failure modes, as well as to provide the framework for designing higher level function into these materials, such as self-healing, self-cleaning, or controlled degradation/release.
- Improved coatings and adhesives technology extends the service life of critical infrastructure, including buildings, pipelines, transportation vehicles, marine and military equipment.



- Our work in the area of mechanical properties in ultrathin polymer films via surface properties in ultrathin polymer films via surface wrinkling revealed that the modulus of these films is much lower than in bulk. In addition, we have shown that the relaxation dynamics in ultrathin films are faster than their thick film counterparts.
- Many of our measurement techniques have been developed in partnership with and adopted by companies such as Intel, IBM, Dow, National Starch, and Vistakon.

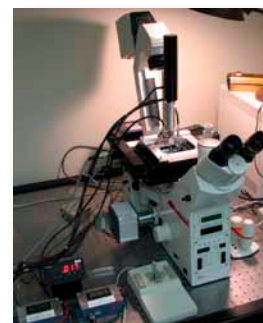
## Approach

Both contact and non-contact techniques are employed to measure the structure and dynamics of thin coatings and structured or confined materials. Relaxation processes play a critical role in determining the lifetime and potential failure of coatings and adhesives. We measure relaxation processes in polymer films using two complementary techniques: indentation of spherical probes to measure creep in thick films, and surface wrinkling to measure viscoelasticity and dynamics in thin films. The kinetics of self-healing over small length-scales also provides a measure of the chain dynamics and flow of polymer films.



The structure and chemistry of a buried interface are also key in determining properties such as adhesion and failure of coatings. We utilize a cantilever peel method to elucidate the effect of surface roughness and surface patterns on the adhesion and release of polymer films to various substrates. We are also employing thermally-responsive materials to examine substrate-enhanced deprotection reactions as a function of coating thickness.

We have focused on measurement approaches that can easily be adopted or adapted into industrial R&D workflows across the diverse applications of sustainable coatings, adhesives, and composites.

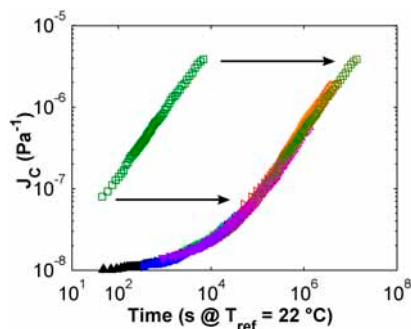




## Accomplishments

### Creep Compliance

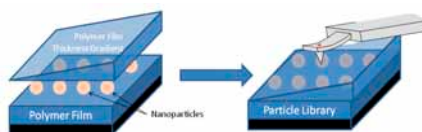
Relaxation processes factor into polymer performance and stability throughout an application lifetime. These processes are controlled by the polymer network structure and dynamics and span a wide spectrum of time scales. In FY09, we demonstrated that an independent array of surface indenters can measure the creep compliance at multiple points on a polymer substrate. Samples with gradients in composition and temperature were used to illustrate this technique's ability to measure viscoelastic properties under unique conditions for each indentation. Methacrylate photopolymer systems were measured simultaneously at different compositions and crosslink densities within an indenter array to increase the measurement throughput. The measured creep compliance ranged from  $10^{-9}$  Pa $^{-1}$  to  $10^{-5}$  Pa $^{-1}$ . Our measurement technique can be used as a predictor of different product applications, operating windows, and lifetime. Temperature gradients allow acquisition of large data sets for time-temperature superposition, enabling accelerated tests on materials and films that aid in predicting property changes over long times.



Compliance master curve

### Detecting Nanoparticles

Detecting buried features, particles, and voids at the nanoscale level is critical for many applications but remains challenging. In FY09, we began developing a measurement technique for detecting buried nanostructures in compliant nanocomposite films. Using contact resonance force microscopy techniques, subsurface features can be evaluated in a nondestructive manner.

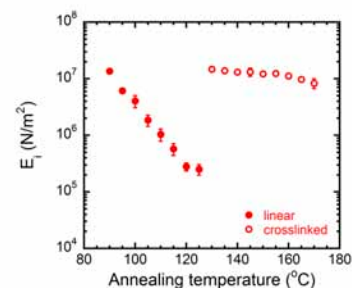


Depth detection of nanoparticles and voids

The fabrication of gradient library samples allows us to calibrate depth detection for quantifying particle depth in real samples. Recent accomplishments include detecting silica nanoparticles below 75 nm in a polystyrene matrix. We plan to extend this technique to the detection of nanovoids at different depths within a coating or composite. This will be instrumental for the characterization of crack formation and propagation as well as fabrication defects that could ultimately lead to material failure. Future work will include varying the modulus of the polymer matrix as well as particle size and distribution. Additionally, we will refine the approach to detect not only the location of the nanoparticles within the film but also the adhesion of the nanoparticles with the matrix material. This advance in measurement science will facilitate tailored design and reliable manufacturing of nanocomposite films and coatings.

### Viscoelasticity

As polymeric materials degrade during service life, the properties of the material can change from elastic to viscoelastic as a result of chain scission and other processes. This transition in properties can adversely affect the performance of the material and thus necessitate replacement. We have developed a measurement strategy based on surface wrinkling to quantify changes in the rubbery modulus of thin coatings as a function of temperature. In FY09, we demonstrated that this technique can accurately differentiate subtle changes in the network structure of a film (e.g., degradation), which causes the film to shift from an elastic response to a viscoelastic response.



Effect of crosslinking on rubbery modulus

Future work includes studying molecular mass effects on the mechanical properties of thin films as well as changes in substrate/coating adhesion. Additionally, our measurement approach could also probe the viscoelastic property changes upon degradation of one phase within a two-phased composite film, as well as the effect of humidity and light exposure on the mechanical properties of renewable materials and coatings.

## Learn More

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## Publications

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Chan EP, Page KA, Im SH, Patton DL, Huang R, Stafford CM, *Viscoelastic properties of confined polymer films measured via thermal wrinkling*. Soft Matter 5: 4638-4641 (2009)

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