Formation of Nanowrinkles on Varied Polymers Using Reactive Ion Etching

The optical and mechanical properties of many materials can be altered by forming nanoscale structures on their surfaces, such as wrinkles, without altering the bulk properties of the materials. Such nanowrinkled materials have important applications in many fields, including the production of photodetectors and solar cells. Wrinkles are formed when compressive strain is applied to a stiff skin bonded to a softer, elastomeric main material, or substrate, causing the skin to buckle in a periodic fashion. The most commonly used method involves bonding a thin layer of metal to the substrate to create the skin. This method has trouble forming wrinkles with large amplitudes relative to their wavelengths, a trait that is desirable for many applications. A recently discovered method, however, forms nanowrinkles through altering the surface of the substrate, and has shown increased control over the average wavelength, amplitude, and orientation of the wrinkles. This is accomplished through reactive ion etching (RIE), in which the substrate is treated with plasma formed from various gases, such as argon (Ar), carbon tetrafluoride (CF₄), and trifluoromethane (CHF₃), creating a stiff skin. Applying this method to various polymers with different properties would be highly beneficial, with applications ranging from biomechanical work such as brain and cardiac monitors to flexible electronics for deformable transparent displays and microlens arrays.

The use of RIE in the formation of a stiff skin on polymers for nanowrinkle applications has only been tested on polystyrene (PS), commonly known as the material used for Shrinky Dinks. There has been some research into the effects of Ar, oxygen (O₂), and CF₄ plasmas on polydimethylsiloxane (PDMS)³,⁴,⁵, which is often used to produce contact lenses, on polyurethane⁶, which is commonly used to make rollerblade and skateboard wheels, and on PS for other characteristics. However, the effectiveness of this method of wrinkling across a range of substrates has not been investigated. As such, I will test this technique on multiple substrates with differing characteristics in order to determine the compatibility of the nanowrinkling method with different polymers, providing insight into nanowrinkle formation and the polymer/plasma interaction.

I will be working in the Odom lab while performing this experiment. I will spend one to two weeks familiarizing myself with the relevant techniques by performing the procedure on PS, attempting to reproduce the previous results, effectively making PS the control polymer. For the experimental polymers, I will test the following polymers: (1) polyolefin, which has been shown to shrink more than PS when heated above its glass transition temperature (Tᵥ)⁸, (2) polyvinylchloride (PVC), which has been shown to shrink less than PS when heated, and (3) PDMS, which has the ability to be stretched, treated, and allowed to shrink at room temperature, producing the wrinkles below its Tᵥ as opposed to above for the other polymers.

The polymers will be treated with Ar, CF₄, and CHF₃ plasmas, as they have been shown to form the skin through crosslinking, saturated fluorination of a constant-thickness layer, and saturated fluorination of a layer of increasing thickness as time increases, respectively. I will first clean samples of each polymer with solvent to remove contaminants that would interfere with the treatment. Each sample will then be treated with Ar gas using RIE in order to form the skin. I will treat the polyolephin and PVC samples and then heat them above their respective Tᵥ, while
the PDMS sample will be stretched, treated, and allowed to shrink at room temperature. I will then repeat this procedure using CF$_4$ plasma and CHF$_3$ plasma.

All samples will be coated with a thin layer of gold and palladium in order to image them using Scanning Electron Microscopy (SEM), visualizing the wrinkles that form and the manner in which they are oriented. The images will then be analyzed using Fast Fourier Transform (FFT), in order to determine the average wrinkle wavelengths. This process should take approximately three to four weeks. With the remaining time, I will then investigate the effect of increasing the temperature further over the T$_g$ during the shrinking process, using similar methods.

Although it is not known precisely how the different polymers will react to the nanowrinkling method, it is likely that the greater possible shrinkage in polyolephin will result in wrinkles with larger average amplitude, due to the increased strain release, whereas the lesser possible shrinkage in PVC will likely result in wrinkles of smaller average amplitude. It is possible that the PDMS will form wrinkles of smaller average amplitude, as previous experiments with PDMS treated with oxygen gas plasma have shown it to have a tendency to produce multiple generations of wrinkles with progressively larger wavelengths when treated. These secondary wrinkles reduce the strain forming the original small wavelength wrinkles, resulting in smaller amplitudes. This experiment will provide information about the compatibility of this method of nanowrinkle formation with different substrate properties and therefore its applicability to larger scale production of nanowrinkled materials. In addition, it will provide insight into the interaction between the substrates and the plasma, directing the course of future research.

In order to prepare myself for this research experience, I am currently participating in the Science Research Workshop program, and by the end of spring quarter 2013 I will have completed organic chemistry 212-1,2, and 3. I will also have taken Chemistry 360, Nanopatterning, in which I will learn and practice many of the techniques that I will utilize in my experiment. I have been working closely with Cliff Engel, a graduate in the Odom group, on developing this project, and I plan to attend group meetings and work more with the Odom group in spring quarter in preparation for my summer research. The Odom lab is the group that discovered the method for nanowrinkling that I will be utilizing in my experiments, and as such they have the most experience with the method. This experiment will help me to gather skills and experience that I can utilize upon graduation to pursue a PhD in Chemistry.

References


