Metal Rubber –
Free-Standing, Mechanically Robust Flexible Conducting Materials

Richard Claus[1,2], Jennifer H. Lalli[2], Andrea B. Hill[1], Bradley A. Davis[2], and Richard M. Goff[2]

Summary

This paper describes a new class of nanostructured materials that exhibit the combined properties of low mechanical modulus and high electrical conductivity. Such "metal rubber" materials are formed by molecular-level self-assembly processes. Material synthesis and properties are described.

Introduction

Molecular-level self-assembly processes offer unique opportunities for the fabrication of novel materials with constitutive properties not generally achievable following conventional synthesis routes. Electrostatic self-assembly (ESA) is one of these processes. It allows the combination of a variety of molecules, including polymers, metal, metal oxide and semiconductor nanoclusters, cage-structured molecules, biomolecules, nanotubes and others, at room temperature and pressure to form thin and thick films. This section briefly reviews the ESA process and demonstrates how it leads to the formation of ordered multilayer films on substrate materials.

The concept behind the basic ESA process for the self-assembly of polymer molecules been discussed in prior work [1- 3]. A substrate surface, such as that shown at the left in Figure 1, is typically cleaned and functionalized so the outermost surface layer has a net negative charge. The resulting negatively-charged substrate is then dipped into an aqueous solution containing water-soluble "cation" polymer molecules that have net positively charged functional groups fixed to the polymer backbone. Because the polymer chain is flexible, it is free to orient its geometry with respect to the underlying substrate so a relatively low energy configuration is achieved.

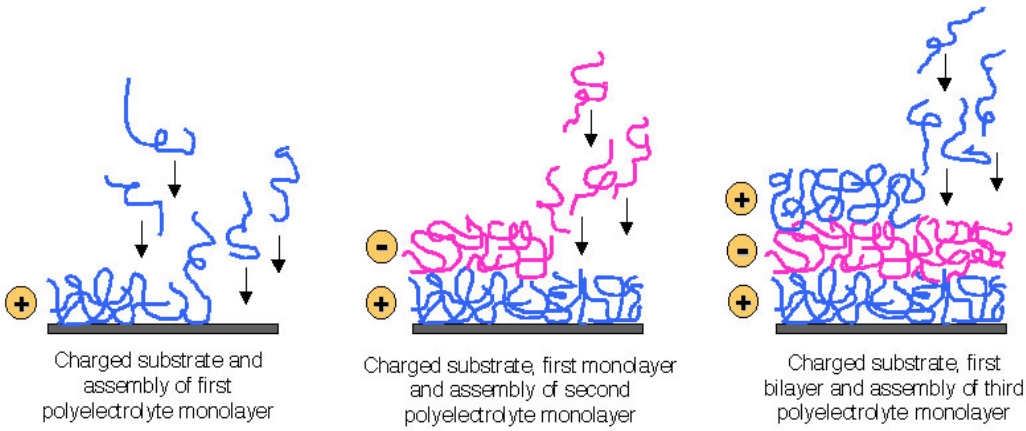

Figure 1. ESA Process for Formation of Multilayered Polymer Thin Films.

[1] College of Engineering, Virginia Tech, Blacksburg, VA 24061, USA
[2] NanoSonic Inc., 1485 South Main Street, Blacksburg, VA 24060, USA

As a result, some of the positively charged functional groups along the polymer chain experience attractive ionic forces toward the negative substrate, and the polymer chain is bent in response to those forces. The net negative charge on the substrate is thus masked from other positive groups along the polymer chain. Those groups feel a net repulsive force due to the fixed positive functional groups at the substrate surface, so move away from that surface to form a net positive charge distribution on the surface of the substrate. Since the total polymer layer is neutral, negative charges with relatively loose binding to the polymer network pair up with positive ions. Subsequent polyanion and polycation monolayers are then added, to produce the multi-layer structure as shown. The properties of the multilayer thin-films fabricated using this method are determined by both the properties of the molecules in each monolayer and the physical ordering of the multiple monolayers through the composite multilayer structure.

Figure 2 shows how the same process may be used to form multiple layers of nanoclusters, again in alternating cation/ion bilayers.

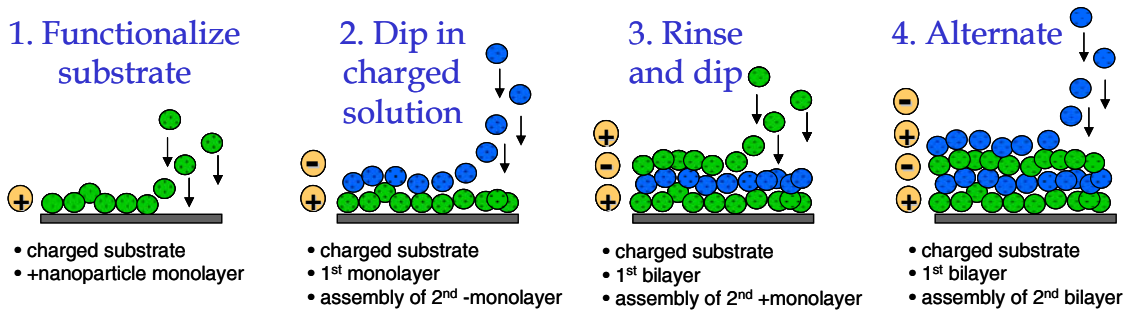

Figure 2. ESA May Be Used to Build Polymers, Nanoclusters and Other Molecules Into Multilayer Films.

Experimental Analysis of ESA Fabrication Process

The physics of this simple process may be demonstrated using several different analysis methods. First, for example, the surface energies of the alternating molecular layers may be determined by measuring the water contact angle after each layer is deposited. Figure 3 shows

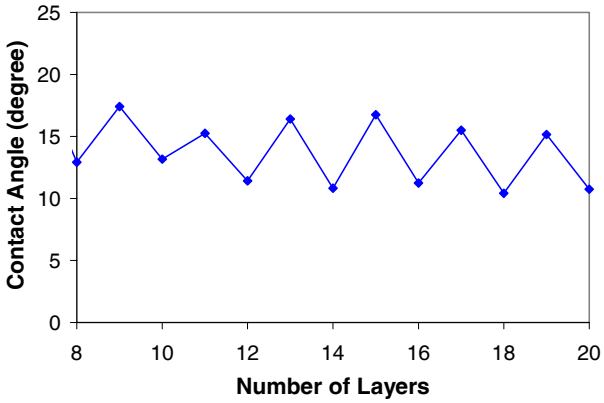

Figure 3. Water Contact Angle for Successive Deposited Layers Supports Model Assumptions of ESA Processing of Multilayer Films.

alternating water contact angle for a 20-layer structure formed by ESA. As additional support fo this model, Figure 4 shows the linear increase in the optical absorption of a representative film as multiple layers are deposited. The linearity of the absorption increase shown at the right in this figure additionally suggests that the deposition process is stable, and that the size of the molecules added with each layer are constant.

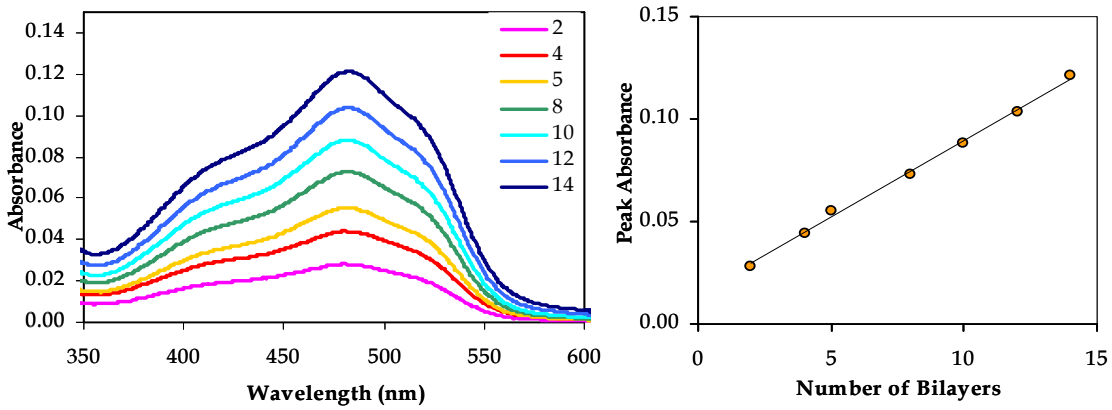

Figure 4. UV-Visible Absorption Indicates Linear Build-up of Multilayer Films.

Additional confirmation of this process is shown in Figure 5. Here, a multi-segmented film of the form ABAB/ACAC/ABAB has been formed, and the thickness of the deposited layers has been measured after each bi-layer deposition. A, B and C are used to represent different molecules. From the thickness plot shown, the AB bilayer thickness is less than the AC bilayer thickness. This also demonstrates that segments of materials with different properties may be formed using the ESA processing technique.

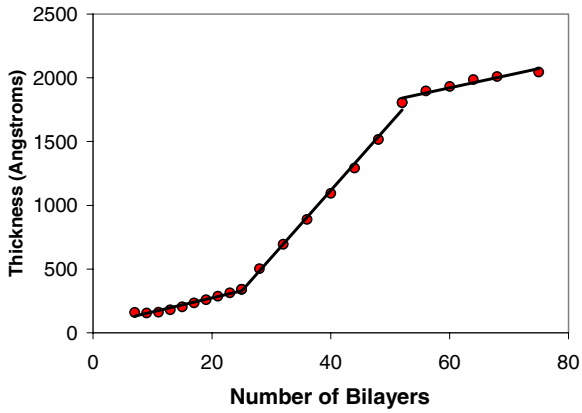

Figure 5. Segmented ESA-Formed Thin Film Thickness Versus Number of Deposited Layers.

Design and Synthesis of Metal Rubber Materials

The ESA process may be extended to the formation of think films by continuing the method described above. Materials as thick as one centimeter have been formed, with properties controlled by the molecules used to form each of the subsequent monolayers. Such materials may be removed from the substrate on which they are formed by depositing a chemical release layer

prior to the desired molecular layers, and chemically removing this layer to free the material once deposition is completed. Of specific interest here, gold nanoclusters and polymers have been used to form millimeter-thick coatings on substrates treated with such release layers. The resulting self-assembled metal/polymer nanocomposite material exhibits combined mechanical modulus and electrical conductivity not easily measured while attached to the substrate.

Examples of such free-standing, mechanically-robust and electrically conducting materials are shown in Figure 6. At the left is shown a piece of gold nanocluster/polymer free-standing material where the concentration of gold is low enough that the material is semi-transparent. Dogbone samples of the material have been cut to allow standard ASTM analysis of modulus and fatigue properties. In the center and at the right are shown other sampels that exhibits good optical reflection and mechanical flexibility.

Figure 6. Metal Rubber Materials Formed by ESA Processing.

Representative properties obtained for these materials are Young's modulus on the order of 10 MPa and electrical conductivity on the order of 10^6 $\Omega^{-1}m^{-1}$, although these values may be varied through control of the precursor molecules used to form the initial film on the substrate surface. For example, Figure 7 shows a representative measurement of the sheet resistance of one nanocluster/polymer free-standing films.

Figure 7. Metal Rubber Displays High Electrical Conductivity and Low Modulus.

Discussion

It has been demonstrated that free-standing materials that combine high electrical conductivity and low Young's modulus may be formed using ESA methods. The resulting metal rubber materials are mechanically robust and exhibit properties not anticipated from observations of ESA-formed thin films on rigid substrates through prior work.

Applications of the developed materials include use as conducting and highly flexible electrodes for actuators and sensors, where the modulus of conventional metal electrodes physically inhibit actuator or sensor motion. Other applications will be presented at the conference and described in future publications.

References

[1] G. Decher, Fuzzy Nanoassemblies: Toward Layered Polymeric Multicomposites, Science 1997, 277, 1232-7.

[2] Y. Liu, A. Rosidian, K. Lenahan, Y-X. Wang, T. Zeng and R. Claus, Characterization of ESA nanocomposite thin films, Smart Mater.Struct. 8 (1999), p. 100-105.

[3] J. H. Lalli, B. Lepene, J. Huie, D. Wood and R. Claus, Proc. SPIE vol. 4991, paper 77, 2003.