Metal Rubber[TM] Materials

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ABSTRACT

We discuss recent improvements of Metal Rubber[TM] materials formed by electrostatic self-assembly (ESA) processing. Free-standing and mechanically robust sheets of Metal Rubber[TM] have been synthesized with electrical conductivities approximately one order of magnitude lower than those of bulk noble metals and with moduli from 1 to 100 MPa.

1. INTRODUCTION

Advanced polymer, metal and ceramic composite materials that achieve combinations of properties due to their constituents and processing routes have been developed and demonstrated during the past tens of years. Composites that contain constituents of nanometer size are typically termed nanocomposites. The nanometer size of some constituents can lead to interesting constitutive properties typically not obtainable in other materials. Metal Rubber[TM] is such a nanocomposite material, which combines relatively low mechanical modulus with relatively high electrical conductivity. Metal Rubber[TM] is formed from advanced polymers and nanoclusters, but unlike traditional blends in which particles are mixed with host materials, it is synthesized using layer-by-layer (LBL) processing. This paper briefly reviews the processing method and then describes representative resulting material properties and macroscopic behavior.

2. LAYER-BY-LAYER PROCESSING OF METAL RUBBER[TM]

The layer-by-layer or electrostatic self-assembly (ESA) approach used to fabricate Metal Rubber[TM] is based on the combination of metal nanoparticles and polymers in free-standing materials. The process involves the alternate adsorption of net negatively charged and net positively charged molecules from liquid solutions onto electrically charged substrates to form multilayered thin film materials. The macroscopic properties of the resulting films are a function of the properties of the individual molecules, as well as their order and structure within the film thickness. Here we have specifically used this process to grow thin nanocomposite films, alternately containing specialized polymers and metal nanoclusters, molecular layer-by-molecular layer.

The concept behind the basic ESA process for the self-assembly of polymer molecules alone has been discussed extensively in prior work but is included here for completeness [2, 3]. A substrate surface, as shown in Figure 1, is typically cleaned and functionalized so the outermost surface layer has a net negative or positive charge. Then, a net surface-charged substrate is dipped into a solution containing water-soluble "cation" (or "anion") 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 substrate so a relatively low energy configuration is achieved [3-7].
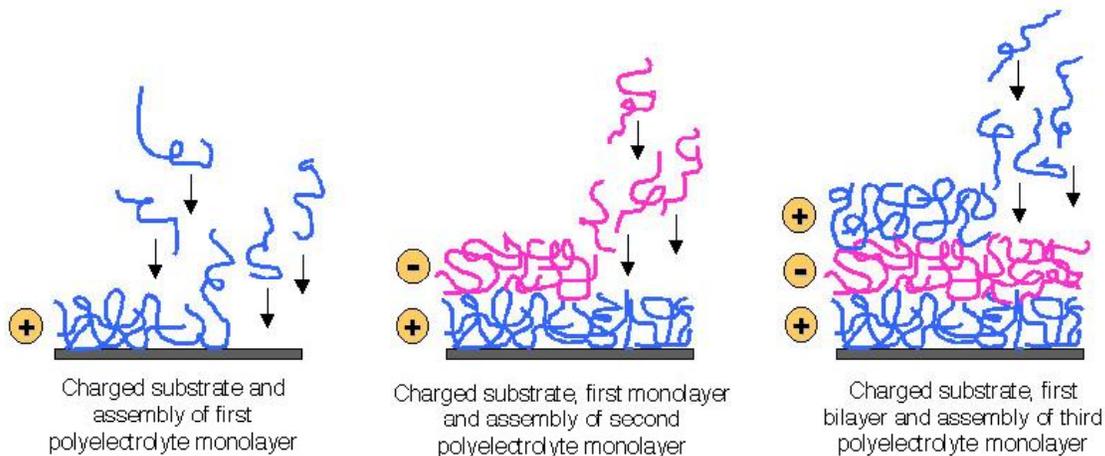
Figure 1. ESA Process for Formation of Multilayer Polymer Thin Films.

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 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 [4]. Similar ESA processing may be realized where appropriately charged inorganic nanoclusters, typically metal nanoclusters [3], may be substituted for either or both of the polymer layers to provide a wider range of possible coating and material properties. Specifically, for Metal Rubber[TM] we have combined gold nanoclusters and polymers using this basic approach to form materials that have properties typically associated with each, namely, high electrical conductivity and low mechanical modulus.

Further, we have automated the layer-by-layer coating process to reduce the amount of time required to make many-layer films. Using a chemical release layer that is applied to the

substrate prior to thin film growth, free-standing sheets of material may be formed. The ESA process is used to form films of desired thickness, then the release layer is chemically etched away, and a sheet of material separate from the substrate is formed. Figure 2 shows a representative piece of Metal Rubber[TM] and suggests that it may be easily bent and stretched.
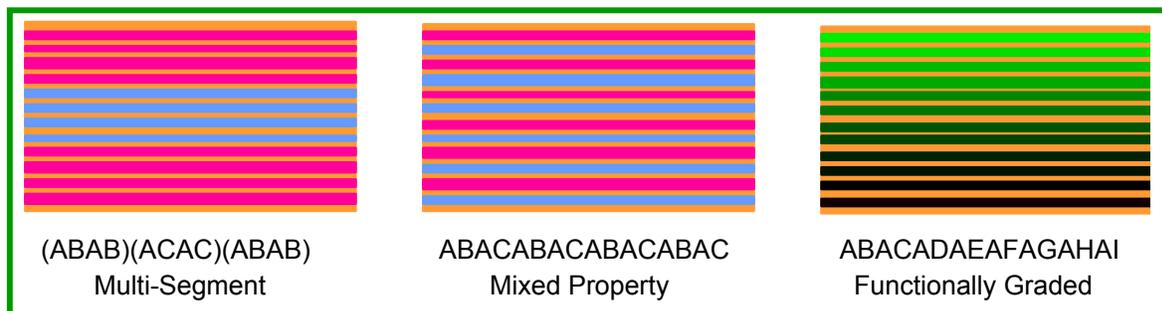

Figure 2. Flexible Metal Rubber[TM] Nanocomposite Material.

3. METAL RUBBER[TM] MATERIAL PROPERTIES

Sheets as large as several feet square may be formed in this way. Some of the resulting constitutive properties have been evaluated. For example, maximum electrical conductivities up to 10^{-5} Ω·cm (or approximately one order of magnitude less than that of bulk metals), and Young's modulus between 1MPa and 100MPa have been measured. The low modulus materials may be elongated up to several hundred percent strain, and relax back to their original shape elastically while retaining their electrical conductivity.

These materials also may be designed to exhibit strain-dependent resistance by incorporating a percentage of nanoclusters so the material lies near the conductivity percolation threshold. A simple model is that unloaded, the high electrical conductivity of such materials is due to the sequential hopping electrical conduction between adjacent metal nanoclusters. When the materials are strained, these nanoclusters gradually move apart, the cluster-to-cluster transport efficiency decreases, and the macroscopic resistance increases. This forms the basis of the use of Metal Rubber[TM] as a strain sensor.

The properties of the materials may also be designed to vary as a function of position within the sheets formed, and thus be either approximately isotropic or highly anisotropic. For example, Figure 3 shows three different materials designs for self-assembled materials.

(ABAB)(ACAC)(ABAB)	ABACABACABACABAC	ABACADAEAFAGAHAI
Multi-Segment	Mixed Property	Functionally Graded

Figure 3. Self-Assembled Materials Designs.

Each of these designs is based on the assumption that multiple layers of different materials may be formed together to create coatings that have uniform properties through their thickness. At the left is shown a multi-segment material based on the stacking of multiple layers of different materials, the center shows a mixed property design in which multiple materials are combined within the coating by simply changing the constituents on each bilayer, and the sketch at right suggests that properties may be graded through the thickness of a material by gradually changing materials during deposition. Metal Rubber[TM] is similar to this last generic design, in that its electrical conductivity varies anisotropically through the thickness while being uniform versus dimensions parallel to the plane of the sheet, and its Young's modulus is approximately isotropic.

3. SUMMARY

We have demonstrated the design, synthesis and performance of Metal Rubber[TM] materials and discussed recent improvements and characterization.

4. REFERENCES

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