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Hierarchically Structured Soft Polymer Composites and Non-Aqueous Polymer Gels for Multifunctional Materials

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INTRODUCTION

In defense and security related applications, materials and devices must often function under unusually harsh environmental conditions including: a broad range of operational temperatures; a long service lifetime; extreme radiation, electrical, and chemical environments; and severe mechanical stress. These stringent requirements, coupled with current drives to reduce size, weight, power, and cost, while still providing improved capabilities, necessitates novel and multifunctional materials solutions.

Hierarchical construction of composite structures at length scales varying from millimeters to nanometers has immense opportunity for multifunctional materials with a broad range of practical applications from actuators, to structural components, to coatings technology. Synthetic composites composed of continuous fiber reinforcements impregnated with nano-particle reinforced resins is an example of man-made hierarchical structures with multifunctional capability such as simultaneous structure and thermal or electrical conductivity (1,2). Nature presents an inspiring example of hierarchical, self-organizing assemblies that can perform diverse task including structural support, mass transport control, chemical detection, self-healing capability, etc (3). Many researchers have focused on exploiting self-assembly and processing approaches to mimic nature's ability to form intricate structures for applications including tissue engineering scaffolds, sensors, membranes, and nano-reactors (4-7).

Multifunctional materials are invaluable to Army applications, and recent work has focused on developing soft polymer composites and polymer gels with hierarchical structure and multifunctional properties. A specific example of how soft polymers would enable future Army technology is in the area of robotics. Figure 1 shows a schematic of the Army's desire to move from large hard robotics, composed of rigid materials, to small milli-to-micro scale biomimetic-robotics composed entirely of soft-flexible materials. The soft robots could obtain covert access to spaces through confined openings and over difficult terrain. Soft materials advances are critical for enabling soft robotics including a) the development of a flexible and elastic body that is tough and durable, b) the incorporation of controlled adhesion mechanisms for traversing difficult terrain, c) the design of soft actuators or artificial muscles that can move the robot reliably with low power input, and d) the integration of flexible sensors and electronics into to robot to provide information gathering capability, environmental recognition, and stimuli-responsiveness. The multi-scaled structure of the robotic soft tissue would enable a broad range of functionality including durable body; controlled transport; chemical sensing; integrated communications, sensors, and power technology; etc. While the schematic in Figure 1 is conceptual and has not been fully realized to date, it provides a useful framework to guide the development of multifunctional composites with controlled hierarchical structures.

This talk will present initial research in several areas that illustrates how multifunctional polymer composites can be realized through the judicious selection of materials and processing approaches. The research is currently focused on the materials physics and structure-property relationships, rather than specific applications towards actuators and stimuli-responsive materials. However, the relevance to these technologies will be discussed. The topics include 1) soft polymer gels with enhanced toughness and broad temperature performance (8,9); 2) extrusion processable conductive polymer composites for manufacturing functional multilayered structures; and 4) radiation tolerant organic films through the incorporation of small molecule electron trapping dopants (10-13).

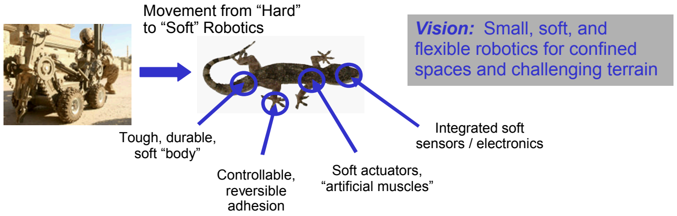

Figure 1. An example of how soft polymer development would enable future missions in soft robotics.

RESULTS

A common problem with soft polymers and polymer gels is poor toughness, fatigue resistance, and durability. Figure 2 shows mode I tear testing data for polydimethyl siloxane (PDMS) based gels with various fractions of non-reactive PDMS sol. The gels that contain a high molecular weight and highly entangled sol fraction (30 or 50 vol% of 308K sol) exhibit higher tear toughness (G J/m^2) than the gels that have the small molecular weight unentangled sol fraction (30 or 50 vol% of 1K sol). Multi-scale modeling approaches are currently being incorporated to investigate the impact of physical entanglements and sol architecture on the gel mechanical properties. Multifunctionality can be introduced in these soft gels by incorporating particulate fillers into the matrix. For example a radiation shielding composite was recently developed by incorporating high density particulate fillers into the PDMS matrix. The composites had equivalent electron shielding ability to traditional metallic shields with 20-40% less density. The hierarchical nature of the composite (molecular scale sol additive to improve toughness, and sub-micron to micron scale particulates to provide radiation shielding) can provide the multifunctionality including simultaneous coating performance, high voltage protection, and radiation shielding capability.

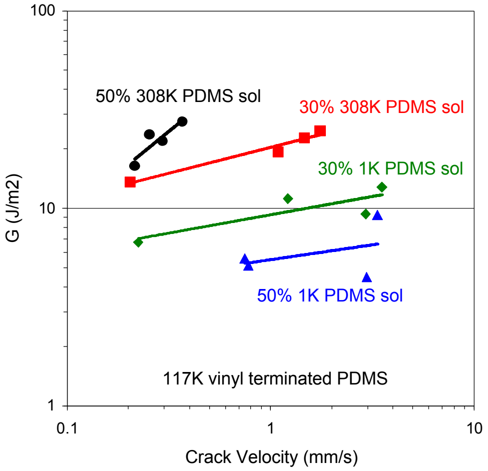

Figure 2. Toughness (G J/m^2) as a function of crack velocity for tear testing of PDMS gels. The gels were prepared by crosslinking a 117K vinyl terminated PDMS with a tetrafunctional silane crosslinker in the presence of non-reactive trimethyl terminated PDMS sol fractions of various molecular weights.

We have recently developed an extrusion processable conductive polymer composite. Conductive polymers are typically difficult to process with traditional approaches due to the conjugated backbones of typical intrinsically conductive polymers that lead to high melt processing temperatures, or the high composite viscosity near electrical percolation in particulate filled systems. Our approach was to melt process a polymer composite composed of a polymer matrix, conductive nickel particulates, and a eutectic alloy. The eutectic alloy melts during processing leading to a low composite viscosity. Upon cooling the eutectic forms a network of connective bridges between the nickel particulates leading to low resistivity values. Figure 3 shows initial conductivity data for the composites with various volume fractions of Ni and the eutectic alloy. High conductivity values greater than 100 S/cm length were achieved, and the composites were extrusion processable even at 60% metal loading. The inset is an SEM micrograph of the 10/40 composite, illustrating uniform Ni / eutectic dispersion.

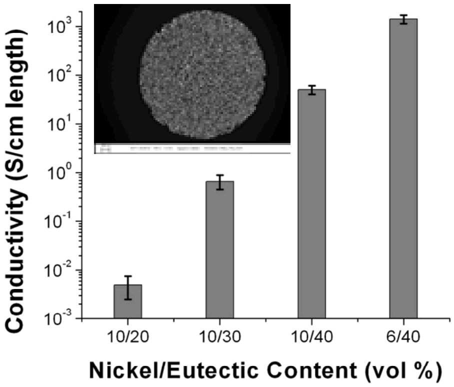

Figure 3. Conductivity values for polymer / Ni / Eutectic composites with various metal loadings.

While seemingly different research areas, tough silicone elastomer composites and conductive extrusion processable composites are potentially relevant to actuator technology for soft robotics. For example, dielectric elastomer actuators (DEAs) are often pursued as artificial muscle technology. DEAs are basically soft capacitors where the actuation is generated by electrostatic attraction between flexible electrodes separated by a soft dielectric. Upon capacitor charging, the attraction between the electrodes can squeeze the compliant soft dielectric. Practical implementation of DEAs is limited by several factors including the dielectric constant and breakdown voltage of the soft dielectric film; the flexibility and durability of the dielectric film and the conductive electrodes; and the ability to reliably process defect free layered structures with the appropriate properties.

By engineering hierarchically ordered soft composites we can improve DEA performance. For example, the extrusion processable conductive composite can be modified to exhibit elastomeric behavior, by dispersing the Ni and an extremely low temperature eutectic alloy into PDMS. Both the PDMS dielectric film and the conductive electrode toughness and durability can be improved by the appropriate choice of molecular additives, such as high Mw sol or branched materials. The breakdown strength of the dielectric can be increased by including small molecule electron traps that scavenge electrons and interrupt the electron cascade process that precipitates high voltage breakdown. Recently a similar approach was taken to reduce radiation induced conductivity in polymer dielectrics by incorporating electron trapping molecules into the formulation (11-14). Hierarchical structures composed of these materials can be generated through a process called multilayer coextrusion. Figure 4 shows a schematic of the process, where two polymers are extruded through a feedblock, generating alternating layers of polymer A and polymer B. The initial layering is determined by the dimensions of the feedblock. However, multiplication can be achieved by splitting the extruded flow vertically and recombining the split flow by stacking them horizontally (14). The relative thickness of these layers can be adjusted by either the relative flow rates or the feedblock design. Alternating the electronic, optical, mechanical, and chemical properties of the layers can be exploited to generate hierarchical structures with multifunctional properties, having applications in actuator and stimuli-responsive device technology.

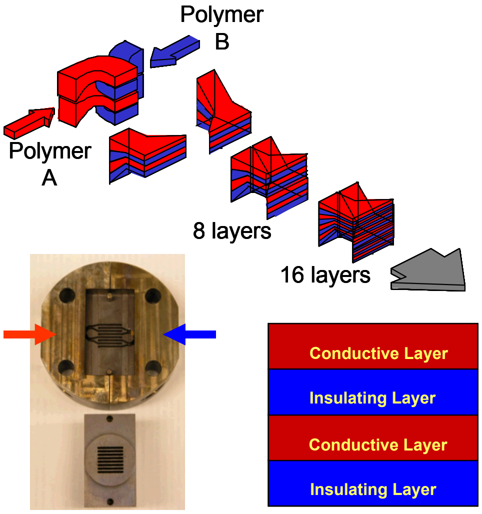

Figure 4. Schematic of multilayer coextrusion processing for engineered hierarchical layered structures having potential applications for actuator and responsive materials technology.

ACKNOWLEDGEMENTS

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