Molecular Design of Low-Density Multifunctional Hybrid Materials

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Final Report
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### 5. ABSTRACT

Low-density hybrid materials, which contain organic and inorganic molecular components, can be engineered over a wide range of length scales to exhibit unique combinations of mechanical, thermal, and optical properties desirable for use in mechanically-robust, multifunctional aerospace applications. In this AFOSR program, we have investigated the effects of molecular confinement in low-density hybrids which provides new opportunities to tailor properties. Our research focuses on the smallest molecular length scales of this confinement, where new mechanisms of strengthening and toughening exist that are not found in traditional composite materials. By focusing on the behavior of molecules confined at length scales of ~1-10 nm, we are able to probe the fundamental limits of strengthening and toughening in nanostructured low-density materials and find new avenues for innovation. We have also demonstrated the possibility of creating hybrids with confined polyimide molecules and have gathered evidence of both the imidization and cross-linking of the polyimide precursors occurring in the highly confined nanoporous matrix. This exciting new direction for our program opens the door to high-temperature, low-density hybrids for next-generation technologies.
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STANFORD UNIVERSITY
Abstract

Low-density hybrid materials, which contain organic and inorganic molecular components, can be engineered over a wide range of length scales to exhibit unique combinations of mechanical, thermal, and optical properties desirable for use in mechanically-robust, multifunctional aerospace applications. In this AFOSR program, we have investigated the effects of molecular confinement in low-density hybrids which provides new opportunities to tailor properties. Our research focuses on the smallest molecular length scales of this confinement, where new mechanisms of strengthening and toughening exist that are not found in traditional composite materials. By focusing on the behavior of molecules confined at length scales of ~1-10 nm, we are able to probe the fundamental limits of strengthening and toughening in nanostructured low-density materials and find new avenues for innovation. We have also demonstrated the possibility of creating hybrids with confined polyimide molecules and have gathered evidence of both the imidization and cross-linking of the polyimide precursors occurring in the highly confined nanoporous matrix. This exciting new direction for our program opens the door to high-temperature, low-density hybrids for next-generation technologies.
This is the final report on our program entitled “Molecular Design and Mechanical Behavior of Low-Density Multifunctional Hybrid Materials”. The report summarizes progress over the course of the program.

**Motivation**

Our AFOSR-supported research addresses fundamental questions related to the mechanical and fracture properties of molecular hybrid materials that have application for emerging aerospace technologies (Fig. 1). Low-density hybrid materials, which contain organic and inorganic molecular components, can be engineered over a wide range of length scales to exhibit unique combinations of mechanical, thermal, and optical properties desirable for use in mechanically-robust, multifunctional aerospace applications. Hybrid materials are therefore ideally suited to a bottom-up materials design where molecular structure and resulting properties can be engineered and tailored to achieve desired property sets.

In this AFOSR program, we have investigated the effects of molecular confinement in low-density hybrids which provides new opportunities to tailor properties. Confinement of the organic phase is a common phenomenon in composite materials, which often use intimately mixed hard and soft components to achieve desired properties. This confinement can occur on a wide range of length scales, from macro-scale polymer confinement in fiber-reinforced composites, to molecular-scale confinement in advanced nanocomposite materials.

![Fig. 1. The bottom-up design of low-density hybrid materials combine organic and inorganic components at molecular to macro length scales, enabling materials with multifunctional property sets. Increasing molecular confinement provides new opportunities to tailor mechanical, thermal, and optical properties.](image-url)
Our research focuses on the smallest molecular length scales of this confinement, where new mechanisms of strengthening and toughening exist that are not found in traditional composite materials (left side in Fig. 1). By focusing on the behavior of molecules confined at length scales of ~1-10 nm (referred to as “hyper-confined”), we are able to probe the fundamental limits of strengthening and toughening in nanostructured low-density materials and find new avenues for innovation, which we describe in this proposal.

In our AROSR program, we have demonstrated the possibility of creating hybrids with confined polyimide molecules and have gathered evidence of both the imidization and cross-linking of the polyimide precursors occurring in the highly confined nanoporous matrix. This exciting new direction for our program (described later) opens the door to high-temperature, low-density hybrids for next-generation technologies.

Our program has thus focused on developing a fundamental understanding of the effects of molecular confinement in low-density hybrids and exploring the limits of strengthening and toughening to create mechanically robust hybrids for aerospace applications. We have also exploited the opportunity of creating high-temperature hybrids that can withstand elevated operating temperatures not compatible with current polymer composites.

AFRL Interactions

A particularly relevant new direction for this AFOSR program has been based on an active collaboration with Dr. Jeffrey Baur (Organic Matrix Composite M&P, Wright-Patterson Air Force Base) to synthesize low-density high-temperature hybrids with molecularly-confined AFRL polyimide precursors. The combination of our high-temperature low-density hybrid nanoporous matrix together with the inherently superior temperature capabilities of polyimides has the potential for an entirely new class of high-temperature hybrids for aerospace applications. In addition, these polyimide-based hybrids provide an excellent platform for studying the fundamental polymer science and reaction kinetics of polyimides under molecular-scale confinement, which has not previously been attempted.

Objectives and Approach

The objective of our program was to explore the fundamental limits of hybrid material strengthening and toughening, especially as it relates to the mechanical and fracture properties of highly confined organic phases in low-density hybrids. We employed a synergistic combination of materials synthesis, experimental characterization, and molecular modeling to realize new classes of hybrids with unique property combinations.

Our research was concentrated in two related Focus Areas most relevant to the AFOSR Low-Density Materials program:

- **Focus Area 1**: High-Toughness Low-Density Hyper-Confined Hybrids
- **Focus Area 2**: High-Temperature Molecularly-Confined Polyimide Hybrids
Research Accomplishments

This program has brought together an interdisciplinary research team with a unique combination of internationally recognized hybrid materials synthesis, nanomechanical characterization and modeling capabilities, along with established collaborations with several AFOSR Labs and Investigators, and a number of additional academic and industry partners. Research was conducted by 2 Stanford graduate students working in each of the two Focus Areas, as well as our partners at WPAFB, IBM, and Princeton.

Research Accomplishment 1: High-Toughness Low-Density Hyper-Confined Hybrids

The nanoporous “matrix” for our hyper-confined hybrids are made from an organosilicate material, itself an organic/inorganic hybrid, that we have engineered to be strong, tough, and chemically stable. They have high operating temperature capabilities above 400 °C in inert environments and above 280 °C in air.

To make low-density hyper-confined molecular hybrids, we have focused on a strategy that involves “backfilling” the nanoporous matrix through molecular diffusion of a polymer phase **Fig. 4(a)**. A large potential “library” of polymer fill molecules are possible as we discuss below and *remarkably uniform filling of the layer can be achieved to any desired level of fill (Fig. 4(b))*.

Such molecular impregnation into the connected nanoporosity of the low-density hybrid matrix has several advantages, including the exceptional nanometer-precision control of the confinement and volume fraction of polymer molecules. This derives from the well-established routes to creating the defined nanoporosity with porogen or templating species and then filling with a second polymer phase after the hybrid matrix has been vitrified or cured. Internal layer stresses related to differential curing shrinkage can also be greatly mitigated.

In our current AFOSR program, we have begun to use the pore structure of nanoporous hybrids to confine polymers to dimensions much smaller than their bulk radius of gyration (equilibrium molecular size). This confinement provides a means to rationally alter the conformations and intermolecular interactions of the polymer phase, thus leveraging the full breadth of macromolecular science in the design of hybrid materials.

We developed the capability to uniformly fill nanoporous hybrids with polymers ranging in molecular weight from $10^3$ to more than $10^6$ Da. This enables unprecedented levels of molecular confinement, in which *chains are up to ten times larger than the pores in which they are confined* (Fig. 5). We used these materials to perform the first-ever measurements of the fracture and mechanical properties of polymers in molecular-scale confinement.
In our recent work published in *Nature Materials*, we showed that incorporation of high molecular weight polymers into a nanoporous hybrid matrix leads to an outstanding five-fold improvement in cohesive fracture properties while maintaining a low density ([Fig. 6](#)) [1]. This dramatic enhancement in toughness is enabled by a novel “molecular bridging” toughening mechanism in which individual confined polymer chains are stretched and pulled out of a nanoporous matrix behind an advancing crack tip. In essence, this mechanism translates the successes of traditional macroscale fiber reinforcement down to molecular length scales, allowing for unprecedented control over the interactions between phases. Our recent work has focused on discovery and characterization of this new toughening mechanism, and we expect significant optimization of the hybrid’s mechanical and fracture properties will be possible through improved polymer chemistry, incorporation of higher molecular weight chains, and tuning of the polymer/matrix interaction.

![Graph showing RMS end-to-end distance vs. molecular weight](image1)

**Fig. 5.** The local environment of polymer chains in the matrix changes considerably with molecular weight. (a) Polystyrene chains with $M_w \geq 11$ kDa are larger than the pore diameter and experience an increasing degree of confinement at higher molecular weights. The molecular weights and end-to-end distances of the polystyrene used in this study are shown as filled squares. (a) The scaling of the end-to-end distance of confined polymers remains the same as in the bulk until $M_w \approx 1210$ kDa.
Throughout this work we have pioneered new molecular mechanical models and simulation techniques that provide insight into nanomechanical processes occurring on the length scale of individual polymer chains and describe the fracture behavior of the nanocomposites over almost three orders of magnitude of polymer molecular weight (Fig. 6). The combination of these models and the unique nature of the confined molecular bridging process has allowed us to measure the pullout force, pullout length, and even the tensile strength of individual polymer chains (Fig. 7). In addition to their relevance to high-toughness hybrid materials, these measurements also represent a significant advance in the field of mechanochemistry, where the measurement of polymer backbone strength has proven challenging.

We verified the physical plausibility of these molecular strength measurements by developing a new molecular simulation technique that estimates the strength of confined polymer chains based on backbone bond strength and the presence of inter-chain entanglements (Figs. 7). The limits of molecular strength as measured by our mechanical models and our molecular simulations are in excellent agreement, lending further credibility to the novel confined molecular bridging toughening mechanism.

**Fig. 6.** Cohesive fracture energy of hybrid nanocomposites with varying confined polymer molecular weights. A dramatic five-fold over the matrix fracture resistance is observed where the strength of individual polymer chains ultimately limits the fracture energy. The solid curves are predictions of molecular strength-limited bridging models (inserted equation).
A particularly relevant new direction for our AFOSR program has been to demonstrate the possibilities for creating heat-resistant hybrids capable of high temperature service for several AFOSR applications (Fig. 8). As previously noted, the short chain reinforced organosilicate nanoporous matrix we employ has demonstrated continuous high-temperature capabilities to above 400°C in inert environments and above 280°C for continuous operation in air. This is due to the short chain (ethylene or methylene) carbon reinforcement bridge in the silicate molecular structure which imparts significant mechanical, chemical and heat resistance [2, 3]. The key then is to seek a similar high-temperature-capable polymer that can be used as the backfilling material to create a very low-density but temperature resistant hybrid.

To this end, we have recently begun a collaborative effort with Dr. Jeffery Baur and his team at Wright-Patterson Air Force Base in the design, fabrication, and characterization of high-temperature hybrids backfilled with heat-resistant AFRL polyimide precursors. Thermosetting polyimides are of course the ideal choice due to their known thermal stability, chemical resistance and impressive mechanical properties in the bulk or as thin films (best example is Kapton, produced by the condensation of pyromellitic dianhydride and 4,4’-oxydianiline).

**Research Accomplishment 2: High-Temperature Molecular-Confined Polyimide Hybrids**

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In this very promising new direction for our AFOSR program, we have adapted our proven hybrid synthesis techniques (Fig. 3 and 4) to a variety of polyimide precursor materials in order to create low-density hybrids capable of withstanding high operating temperatures. The approach, however, has several associated challenges, including the poor solubility of most polyimides, the relative stiffness and size of the polyimide molecular backbone (contributing to low molecular mobilities), and the completely unknown effects of extreme molecular confinement on the imidization and crosslinking reactions.

To mitigate these risks, we have undertaken some preliminary studies to address these challenges. We have received several AFOSR polyimides and polyimide precursors from the Baur Organic Matrix Composite M&P group at Wright-Patterson Air Force Base (Fig. 8). The basic chemical structure of the precursors are shown in the figure together with an estimate of the molecular size of the AFR-PE-4 precursor. We reiterate the challenge related to the relative stiffness of these molecules compared to other polymer molecules we have studied as well as estimates of their size (~7 nm) that is comparable to the nanopore size. Despite these concerns, our initial attempts at fabrication of polyimide backfilled hybrids have been successful, and preliminary characterization of these materials described below has been extremely promising.

**Motivation**
- higher temperature
- thermal transport
- chemical resistance

**Hybrid challenges**
- high temp. organic phase
- stiff molecular backbones
- poor solubility
- reactions in confinement

**Synthesis of state-of-the-art hybrids for 650°F use in next-gen fighter engine**

![Diagram of hybrid synthesis](image)

*Fig. 8.* We will explore the possibility of making heat-resistant low-density polyimide hybrids with an unprecedented combination of low-density and high operating temperatures. Several AFOSR polyimide precursors will be evaluated in a collaborative effort with the WPAFB Baur composites group.
Based on evidence from XPS depth profiling through the film thickness, we now have conclusive evidence that AFR-PE-4 polyimide precursor molecules can be made to infiltrate and fill the nanoporous matrix (Fig. 9). *This is the first demonstration that this type of filling process is compatible with materials that are not readily soluble in common solvents, opening the door to an even wider array of filler materials.* Using FTIR spectroscopy and selected fill and curing temperatures, we have found the very interesting result that imidization of the precursors are possible under such nano-confinement (Fig. 10). FTIR peaks indicative of the imidization reaction products were clearly apparent. A detailed analysis of FTIR peaks has allowed us to characterize the reactions of polyimides in confinement in greater detail, including approximating reaction rates and monitoring side product formation (Fig. 11).

**Fig. 9.** XPS depth profile of a hybrid nanocomposite film filled with AFR-PE-4 polyimide. The plateau at ~50% carbon concentration is evidence of uniform and complete filling (T\textsubscript{fill} = 260 °C). Partial filling has been observed at the crosslinking temperature (T\textsubscript{fill} = 370 °C) and even at room temperature (T\textsubscript{fill} = 25 °C).

**Demonstrated Nano-Confined Imidization of Poly(amic ethyl ester) in 7 nm Pores**

poly(amic ethyl ester) → 260 °C → EtOH → polyimide

**Fig. 10.** FTIR spectra provide evidence that imidization of the AFR-PE-4 polyimide poly(amic ethyl ester) precursor can be achieved in under nanoscale confinement in the hybrid nanoporous matrix. Characteristic peaks at 1850 and 1780 cm\(^{-1}\) that appear after thermal curing provide unambiguous evidence for cyclized polyimide formation. Clear increases in the carbonyl (1725 cm\(^{-1}\)) and C–N (1360 cm\(^{-1}\)) peaks are also consistent with the desired reaction.

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Furthermore, we now have additional FTIR evidence of the polyimide crosslinking reaction under the same nanometer scale confinement. We are able to track the concentration of carbyne endcaps, enabling an estimate of the rate and extent of crosslinking reactions in confinement (Fig. 12). We have found that after 370 °C heat treatments, the concentration of carbyne groups is higher in confined polyimide nanocomposites than in neat polyimide films, suggesting that confinement limits the maximum extent of the crosslinking. To our knowledge, this is the first time that hybrids with a molecular-confined polyimide second phase have been fabricated. These exciting early results significantly mitigate the anticipated challenges associated with both backfilling the nanoporous matrix with polyimide precursors and reacting them under nanoscale confinement.

In addition to chemical characterization, we have recently begun measuring the fracture properties of these polyimide molecular hybrids. Preliminary studies have shown that crosslinked polyimide in nanoscale confinement can effectively toughen nanoporous matrices (Fig. 13). Besides their technological significance, these measurements build upon our earlier studies on the fundamentals

Fig. 11. Imidization reaction and associated FTIR spectra for AFR-PE-4 polyimide. The green spectrum is the result of a 260 °C, 1 hour heat treatment in nanoscale confinement (7 nm pores).

Fig. 12. Remaining concentration of carbyne groups after various heat treatments.

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of the molecular bridging energy dissipation mechanism and provide the foundation for further improvements of polyimide nanocomposite strength and toughness.

With the synthesis process for high-temperature polyimide hybrids proven, we have begun a systematic study involving both synthesis and characterization to create a new polyimide-based platform for stable high-temperature hybrids. Of chief interest is the measurement and optimization of the mechanical strength, modulus, and fracture toughness of these materials with respect to fill level, degree of crosslinking, polymer chemistry, and polymer-pore interactions. Due to their combination of low density, high thermal stability, and potential for high toughness, these polyimide hybrids hold extraordinary potential for numerous aerospace applications.

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**Fig. 13.**

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Other Significant Research Accomplishments

Several research areas are common to both Focus Areas and these are described below. In addition to our interests in strengthening and toughening behavior, the hyper-confinement of polymer molecules in our hybrids engenders other fundamentally interesting properties relevant to our proposed research and these are also briefly reviewed below.

Glass Transition Behavior of Confined Molecules: Our hybrids are ideally suited for fundamental studies of confined molecule glass transition behavior as they incorporate low-polydispersity and high molecular weight polymers with equilibrium size far in excess of the nanometer pores (~7nm) into which they are confined, leading to extraordinary levels of molecular confinement. Preliminary data has shown that confined polymers in our hybrids exhibit glass transition temperatures that are markedly different from those of the bulk (Fig. 12). Such confinement appears to stabilize the glass transition temperature of polymers with respect to their molecular weight. We hypothesize that this is due to the combined influence of adsorption and confinement effects on the polymer chains. We have initiated a collaboration with Professor Rodney Priestley (Princeton University) who has been recognized by the AFOSR for his pioneering studies of the glass transition and non-equilibrium dynamics of confined polymeric materials. Our hybrids provide a much higher level of molecular constraint than they have previously been able to study and his group is currently probing the glass transition temperature and structural relaxation of our hybrids below the glass transition.

Optimizing Polymer/Matrix Interactions: In nanoporous hybrids the internal pore surfaces occupy a disproportionately large surface to volume ratio (compared to macroscopic porosity). We have previously reported on how the internal pore surfaces themselves play a very important role in mechanical properties and interactions with environmental species [4-7]. For our polymer filled hybrids, the polymer/matrix interaction should then clearly be expected to play a significant role on molecular mechanisms of strengthening and toughening, although these have not yet been characterized or exploited.

Controlling the internal pore chemistry by functionalizing with polar, non-polar, or conjugated groups therefore provides a simple and potentially tunable way to control the interactions between the matrix and the polymer phase (Fig. 15). The concept is of course similar to what is now routine materials chemistry and manufacturing in macroscopic fiber-reinforced composites where the matrix-fiber interface is carefully tuned to allow controlled debonding. We are applying this concept at the level of single molecules. When the nanoporous hybrid matrix is imbibed with large polymer molecules, we have seen that one fundamental limit for toughening involves the strength of individual bridging polymer molecules. By controlling the polymer/matrix interaction, we have the potential of decreasing the maximum molecular pullout force, while at the same time increasing the pullout distance. The resulting molecular stress-separation relation is shown in Fig. 15(b) and indicates that much larger energy dissipation may be possible.
Hybrid Degradation and Fracture in Hostile Environments: Our research involves not only fundamental studies related to the role of hybrid molecular structure and constraint on mechanical and fracture properties, but also the synergistic interactions of reactive chemical and simulated solar UV environments with the hybrid film which leads to unexpected mechanical and fracture behavior. Our research has demonstrated that reactive chemical environments including moisture can, depending on composition, have dramatic effects on fracture properties. The kinetics of crack growth are sensitive to gaseous and aqueous environments where solution pH, electrolyte type, and other organic components (like surfactant molecules) can result in marked effects on the fracture process [4, 5, 8-10]. We have even provided the first quantitative characterization of a “true” mechanical fatigue phenomena in the hybrid films where we used a combined experimental and molecular modeling approach to characterize and describe the molecular mechanisms responsible for susceptibility to fatigue [11]. Inclusion of the organic phase makes the fatigue-insensitive organosilicate matrix prone to fatigue like any other polymer.

However, inclusion of the hyper- or ultra-confined polymer molecular phase can also be used to great advantage to reduce the sensitivity of fracture in hostile operating environments. For example, we have recently demonstrated how ultra-confined adhesive hybrid layers at the interface between a toughened epoxy (TUF) and a metal-oxide (in this case SiO₂ on a Si substrate) in the presence of hot and humid environments improves the debond threshold four-fold.

**Fig. 15.** Tuning polymer/matrix interactions for enhancements of strength and toughness by a) changing the chemical functionality of the pore surfaces with single covalently-bound monolayers to b) carefully control the maximum stress experienced by the molecular bridges, which in turn influences the total amount of energy dissipated by each chain. c) A variety of surface chemistries will be used to tune matrix-filler interactions.

**Fig. 17.** Subcritical debonding of epoxy/Si interfaces with and without the presence of a hybrid adhesion film layer exposed to hot and humid environments. The presence of the hybrid films improves the debond threshold four-fold.
of hot and humid (70°C/85%RH) environments [12, 13]. The hybrid layer dramatically improves the threshold strain energy release rate (G) values for the debonding of the epoxy/Si interface by a factor of four from ~20 J/m² to ~80 J/m² (Fig. 17). The resulting interface is significantly more reliable than one formed with current silane-adhesion promoters.

We have demonstrated similar behavior for hyper-confined hybrids where, in addition to identifying and exploiting the molecular mechanisms of toughening that we described in the preceding sections, we have also observed just how markedly the constrained polymer molecules can increase the resistance to cracking in reactive moist environments, where the low-density matrix is prone to moisture assisted cracking. Crack growth thresholds can again be increased by four-fold over the unreinforced matrix (Fig. 18).

Note that tailoring nanostructures at molecular dimensions introduces exceptionally high internal surface to volume ratios between the matrix and polymer phases that can result in enhanced diffusion of environmental species [5, 6, 8, 14, 15]. The ability demonstrate improved resistance to the potentially deleterious effects of reactive environmental species like moisture is therefore important for low-density hybrids which will be exposed to reactive operating environments.

**Ultra-Confined Hybrids:** In our AFOSR program we have also made significant progress in developing a new understanding of ultra-confined hybrid materials (far left Fig. 1), which contain organic phases subjected to even stronger confinement than in the hyper-confined hybrids discussed previously (< 1 nm). The adhesive and cohesive strength of these hybrid materials are strongly dependent on precursor materials, sol-gel processing parameters, cure time and temperature [9, 16, 17]. They form a compositionally-graded high-performance hybrid adhesive film that, when deposited onto an underlying substrate, is ideal for bonding to adjacent hybrids or epoxy resins. We have demonstrated significantly higher adhesive properties and moisture resistance compared to traditional silane-based adhesion promoters and have shown how their fracture properties scale inversely with the isoelectric point (IEP) of the underlying surface (Fig. 19). If the IEP of the substrate surface (e.g. metal oxide) or sol-gel solution ion is less than the solution pH, the surface will take on a net negative charge; conversely, for IEP values greater than the solution pH, a net positive charge will exist. By carefully controlling solution pH, favorable electrostatic interactions can be encouraged resulting in the development of hybrid networks that possess a unique compositionally graded structure with strong interfacial connectivity with the top and bottom substrates [18]. For example, we have demonstrated graded hybrid compositions with strong oxide interactions with an underlying oxide surface and with
organic epoxy rings segregated towards the top surface that bond covalently to a top epoxy layer [9, 17, 19].

**Broader Implications**

Engineering of molecular hybrids at the level of individual molecules has broad implications for hybrid materials design and discovery. We have already begun to show that novel toughening mechanisms can be activated when molecules are confined at nanometer length scales. As noted above, other properties including glass transition temperatures, high-temperature resistance and chemical stability are all similarly affected. The possibility of engineering unique mechanical, thermal and optical property combinations in such low-density materials are therefore possible, and have yet to be exploited.

The experimental and computational tools we will develop for bottom-up hybrid materials design will have application beyond the target low-density hybrids for aerospace applications. Related applications include hybrid coupling layers for high-performance structural adhesive bonds. The hybrid materials significantly increase the resistance to moisture degradation and we already have a very successful program with several microelectronic companies demonstrating how these hybrid materials can be used in future high-density microelectronic packages and 3D device structures.

Hybrid film technologies can similarly be directly applied to embedded sensor networks for structural health (damage evolution and diagnosis) and performance (temperature, surface pressures, etc.) monitoring of high performance aerospace systems. A crucial aspect of embedding the sensor network is to ensure optimized adhesion to the epoxy or reinforced polymer composite layers to ensure that the sensor network does not become a *source* of damage initiation. The hybrid processing, screening and optimization capabilities we are developing are particularly well suited to designing the optimal hybrid interphase region for enhanced adhesion and thermomechanical reliability in such multifunctional device structures.

Finally, we note that the versatile property combinations of hybrids make many other technologically important applications possible including microelectronic interlayer dielectrics, antireflective coatings for solar cells, optical waveguides, size-selective membranes, biosensors, micro-fluidic structures, and membranes in fuel cells. A critical aspect for all of these applications is that the hybrids must be mechanically robust and able to operate reliably in harsh mechanical, chemical and thermal environments. That is the focus of our program. The program will therefore have broad implications for the successful integration with high yield of low-density hybrid materials into a range of technologies and ensure that the fundamental hybrid materials science is available to optimize hybrid material mechanical reliability in complex service and processing environments.

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**Fig. 18.** Markedly increased resistance to moisture-assisted subcritical cracking of molecular-confined hybrids with higher molecular weight polymers with increased levels of molecular constraint.
References


Personnel Supported on AFOSR Program

Marta Giachino (Ph.D. graduated) Graduate Student Research Assistantship
Jeffrey Yang (Ph.D. graduated) Graduate Student Research Assistantship
Scott Isaacson (Ph.D. current) Partial Support (AFOSR and Kodak Fellowship)
Can Wang (Ph.D. current) Graduate Student Research Assistantship

Prof. Reinhold H. Dauskardt (Principal Investigator)

Publications resulting from current AFOSR program


Conference talks resulting from current AFOSR program


R.H. Dauskardt, "Adhesion and Reliability of Hybrid Molecular Materials in Nanoscience and Energy Technologies," invited colloquium Department of Microelectronics, School of Information Science and Engineering, Fudan University, Shanghai, China.

R.H. Dauskardt, "Fracture in Hybrid Molecular Glass Films: Experiments and Computational Models,” invited presentation at the International Materials Science and Technology Conference 2011, Columbus, OH.

R.H. Dauskardt, "Fatigue and Fracture in Thin-Film Devices and Hybrid Laminates,” invited presentation at the International Materials Science and Technology Conference 2011, Columbus, OH.


Interactions
During this AFOSR program we have initiated a fruitful collaboration with Dr. Jeffrey Baur and Dr. Hilmar Koerner (Organic Matrix Composite M&P, Wright-Patterson Air Force Base) to synthesize low-density high-temperature hybrids with molecularly-confined AFRL polyimide precursors. Our research also involves a strong with Dr. Geraud Dubois at IBM Almaden Research Center in many aspects of porous and hybrid materials synthesis and characterization. We have recently begun a collaboration with Professor Rodney Priestley (Princeton University) – who is also supported by the AFOSR – to measure the glass transition and physical aging properties of polymers in unprecedented levels of molecular confinement.

Consultative Functions
None

Transitions
None

Awards Received
Dauskardt received the following awards:

2013: Appointed the Ruth G. and William K. Bowes Professor, School of Engineering, Stanford University.

2011: The Henry Maso Award for fundamental contributions to the advancement of cosmetic and skin science, The International Federation of Societies of Cosmetic Chemists.

2011: The IBM Shared University Research Award in recognition of scientific and technological research achievements.
1.

1. Report Type
Final Report

Primary Contact E-mail
Contact email if there is a problem with the report.
dauskardt@stanford.edu

Primary Contact Phone Number
Contact phone number if there is a problem with the report
6507256079

Organization / Institution name
Stanford University

Grant/Contract Title
The full title of the funded effort.
Molecular Design of Low-Density Multifunctional Hybrid Materials

Grant/Contract Number
AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".
FA9550-12-1-0120

Principal Investigator Name
The full name of the principal investigator on the grant or contract.
Reinhold Dauskardt

Program Manager
The AFOSR Program Manager currently assigned to the award
Dr. Joycelyn S. Harrison, DR-IV

Reporting Period Start Date
04/01/2012

Reporting Period End Date
10/31/2015

Abstract
Low-density hybrid materials, which contain organic and inorganic molecular components, can be engineered over a wide range of length scales to exhibit unique combinations of mechanical, thermal, and optical properties desirable for use in mechanically-robust, multifunctional aerospace applications. In this AFOSR program, we have investigated the effects of molecular confinement in low-density hybrids which provides new opportunities to tailor properties. Our research focuses on the smallest molecular length scales of this confinement, where new mechanisms of strengthening and toughening exist that are not found in traditional composite materials. By focusing on the behavior of molecules confined at length scales of ~1-10 nm, we are able to probe the fundamental limits of strengthening and toughening in nanostructured low-density materials and find new avenues for innovation. We have also demonstrated the possibility of creating hybrids with confined polyimide molecules and have gathered evidence of both the imidization and cross-linking of the polyimide precursors occurring in the highly confined nanoporous matrix. This exciting new direction for our program opens the door to high-temperature, low-density hybrids for next-generation technologies.

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Archival Publications (published) during reporting period:


Changes in research objectives (if any):

Change in AFOSR Program Manager, if any:

Extensions granted or milestones slipped, if any:

AFOSR LRIR Number
LRIR Title
Reporting Period
Laboratory Task Manager
Program Officer
Research Objectives
Technical Summary

Funding Summary by Cost Category (by FY, $K)

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