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FINAL TECHNICAL REPORT

**Nanotribological and Nano mechanical Testing
Equipment multifunctional Nanocomposites for Air
and Space Tribology**

FA9550-07-1-0518

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Abstract

Defense University Research Instrumentation Program

Nanotribological and Nanomechanical Testing Equipment in Support of the AFOSR MURI: Multifunctional Nanocomposites for Air and Space Tribology

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 Thierry Blanchet Rensselaer Polytechnic Institute

HIERARCHICAL POLYMER NANOCOMPOSITES have great potential for solving tribological challenges associated with vehicles and equipment used in space. The ability to tailor composite properties at several length scales is leading to materials with unprecedented low wear rates and coefficients of friction combined with environmental insensitivity. To optimize properties, a fundamental understanding of the mechanisms operating at each length scale is required. Our current understanding suggests that the nanomechanical response and nanoscale morphology control the macroscopic tribology. Therefore, to gain further fundamental understanding of these promising materials, it is critically important to evaluate their nanotribology and nanomechanical response more completely. The proposed equipment will provide the unique opportunity to:

- Reach a fundamental understanding of the role of the nanofillers in tailoring polymer morphology and controlling local mechanical response.
- Study the interfacial interactions between nanofillers and polymers and their influence in tribology.
- Ensure the successful space-based operation of next generation tribological materials.

The equipment requested is a Hysitron Triboindenter with (1) indentation, (2) scratch, (3) wear, (4) complex modulus, and (5) Atomic Force Microscopy capability at temperatures ranging from -10°C to 200°C . This equipment directly supports the scientific and technical goals of the MURI entitled "Multifunctional Nanocomposites for Air and Space Tribology", and will provide the opportunity to pursue some of the grand challenges identified by this MURI team and the tribology community: a) predicting the mechanical and tribological behavior of materials from first principles, and b) bridging the gap between nanotribology and macrotribology. The total cost of the system is \$386,365, we are requesting \$322,365 in the budget since the institute is providing \$45,000 in cost sharing, the company is providing a discount of \$19,000 and \$15,000 will be funded from other federal sponsors.

This equipment will significantly enhance the collaboration between the University of Florida and Rensselaer Polytechnic Institute. Rensselaer's ability to further contribute small scale tribological characterization and nanomechanical understanding will strengthen the ability of both institutions to move the project forward.

Research Proposal

1.0 Program Introduction

We believe the multifunctionality required by the challenges of space can be best achieved by creation of hierarchically structured composite coatings in which the nanoscale structure is carefully tailored. This includes tailoring of the nanoscale building block surface and interface, organization of the fillers at the submicron and micron scale, and grading of materials at the submillimeter and millimeter scale (Figure 1). Members of this team are currently engaged in this research and have created polymer nanocomposites with near 1 million fold reductions in wear rate, nanocomposites that

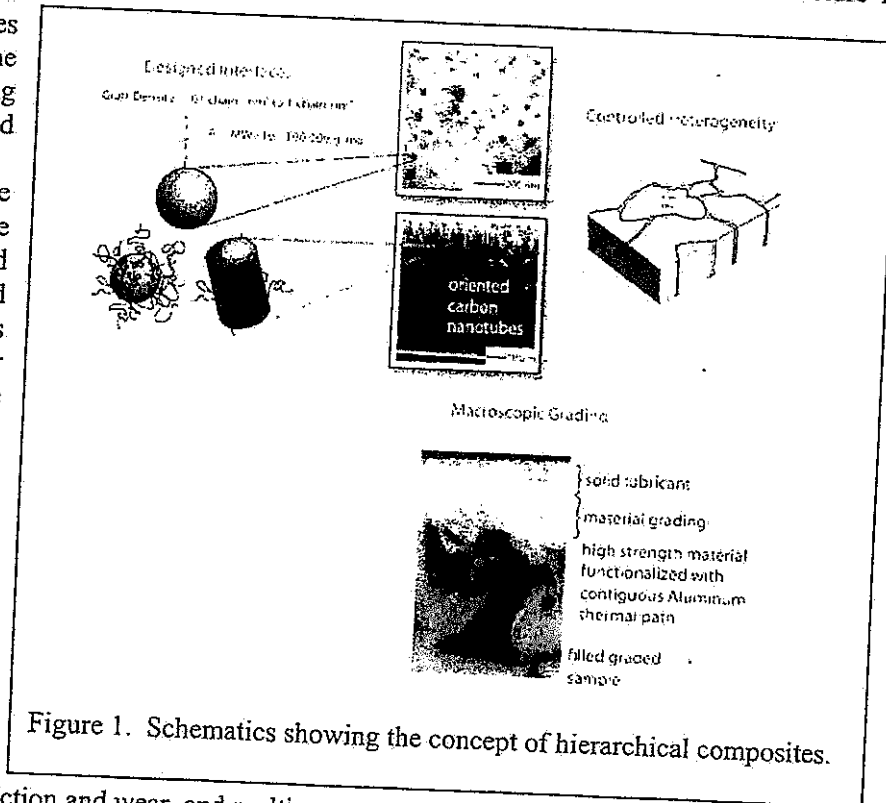


Figure 1. Schematics showing the concept of hierarchical composites.

show both reduced friction and wear, and multi-component nanostructured "chameleon" coatings in which the solid lubricant that functions best in a particular environment is activated by that environment. This work is being conducted by a team of chemists, physicists, tribologists, and materials scientists with extensive background and experience in synthesis, characterization, testing, and simulation of nanoscopic materials. To further enhance the capabilities of this research team and maximize the benefit to the DOD, instrumentation is requested here to allow further nanomechanical testing of these materials. The requested instrumentation is critically needed to assess the materials on the actual length scale of the material components (nanoparticles), and of the nanofiller organization (submicron to micron). The proposed equipment is required to and will provide the unique opportunity to:

- Reach a fundamental understanding of the role of the nanofillers in tailoring polymer morphology and controlling local mechanical response.
- Study the interfacial interactions between nanofillers and polymers and their influence in tribology.
- Ensure the successful space-based operation of next generation tribological materials.

Our goal is to deliver new fundamental understanding of the mechanisms responsible for the remarkable tribological properties and performance of these materials. In turn, we expect to create a wide variety of new multifunctional coating materials and architectures with properties optimized for important DoD space applications. In association with the requested equipment, students will receive training and experience in synthesis, characterization, testing of nanocomposite materials for space tribology applications.

1.1 Research Grand Challenges for Nanocomposite Coatings

Research in nanocomposite tribology, enabled by the acquisition of the Triboindenter will address the following fundamental issues, which were identified as Grand Challenges by this research team within its original MURI proposal and by the tribology community at a 2004 NSF sponsored workshop (Houston, Texas) focusing on the fundamentals of tribology.

a) Predicting the mechanical and tribological behavior of materials from first principles.

It has become clear in the literature and in our own work that the strength of the interaction between nanoscale fillers and the surrounding polymer matrix is critical to controlling the properties of the polymer including morphology, mobility, mechanical, and electrical response. While the modeling work in the effort is approaching the ability to place nanofillers in the matrix and observe sliding, we do not yet know what the degree of interaction is between our fillers and the matrix. The nanoindenter proposed here provides the opportunity to investigate the filler / matrix interaction mechanically, which complements our surface analytical abilities (Figure 2). This is critical to complementing the modeling work, but also in our ability to design future materials.

b) Bridging the gap between nanotribology and macrotribology.

As we develop hierarchical structuring at the submicron and micron scale, it is important that we understand the contributions from each portion of the inhomogeneous material. This can only be achieved through local tribological characterization. The nanotribo-meter identified is an improvement over the current instrument at Florida. In addition, the throughput on these instruments requires that we engage two instruments. The UF instrument will remain focused on combined electrical and tribological characterization, and the RPI instrument will focus on the heterogeneous composites and the role of the size scale of the heterogeneity on the nano / macro correlations.

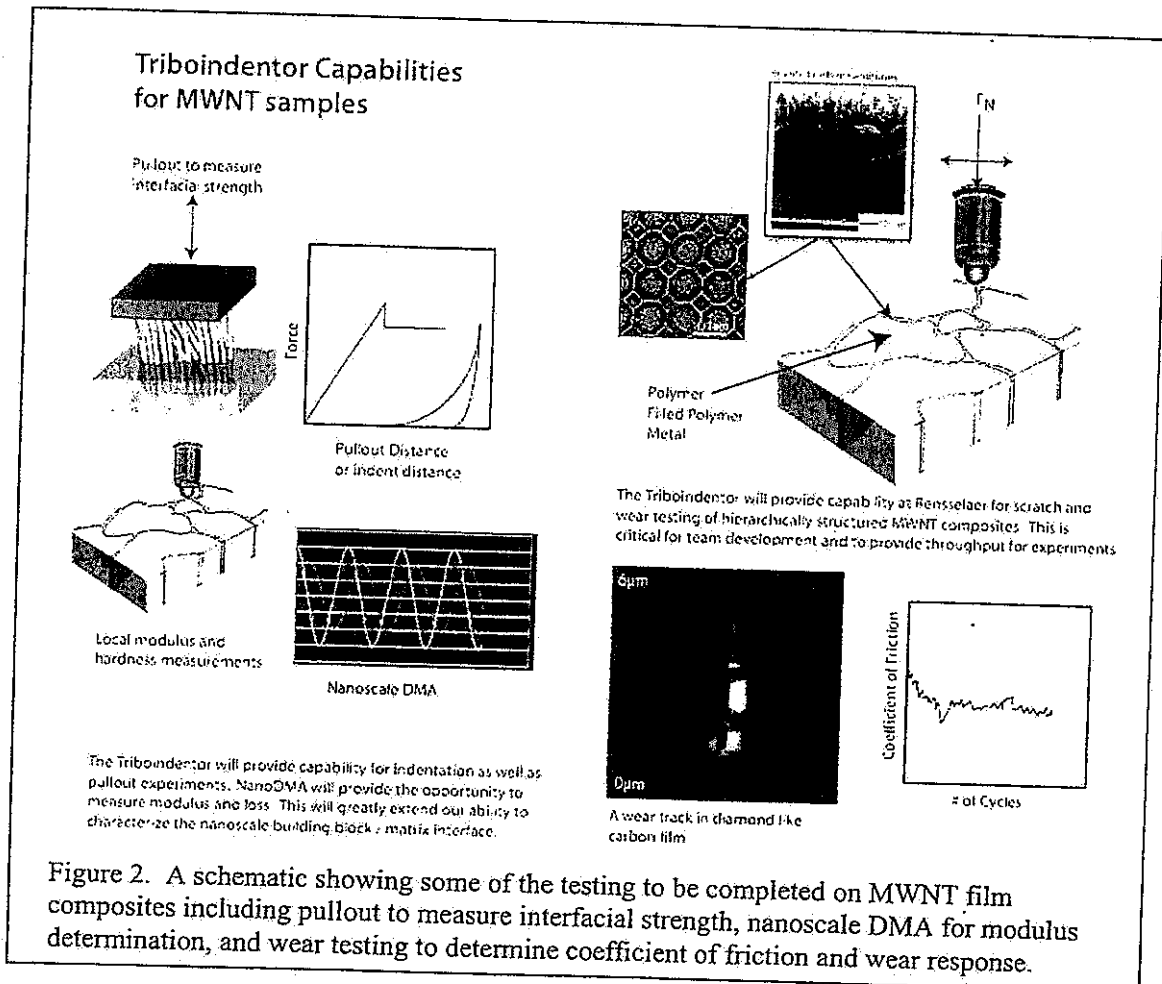
2.0 Experiments with Polymer Nanocomposites

There are two focus areas for polymer nanocomposites within the overall MURI project relevant to this proposal. The first is for applications requiring sliding electrical contacts. Through the use of multi-walled nanotube (MWNT) vertically aligned films with a height of 10 – 500 microns, we have gained a significant understanding of how to control the coefficient of friction (COF) and temperature dependence of the COF. The first relies on the compliance of the film, and the second on the surface chemistry of the MWNT. To increase compliance we have infiltrated the MWNT with polyimide and created materials with half the coefficient of friction and much longer lifetimes than metal contact materials. In addition, to reduce the resistivity, we have created MWNT films with metal coatings. The most promising of these materials, the silver coated MWNT films will be tested in a high frequency electrical switching regime to

further test their applicability. Finally, we have been able to grow MWNT on metal substrates which will further reduce the film resistivity.

There are several fundamental questions to be answered and optimization studies that need to occur in order to allow us to begin designing these composites. The acquisition of the nanotribometer and nanoindenter will provide immediate capability for the following experiments.

1 – Measurement of the strength of the MWNT/infiltrated polymer interface as a function of chemical modification of the MWNT. We have tested this method through another set of funding and have developed a pullout test for MWNT vertically aligned films. The same experiment can be run on the proposed equipment. From these pullout experiments, the strength of the MWNT/polymer interface can be calculated and the effect of plasma treatments, and chemical treatments as well as growth conditions can be determined. This interface plays a critical role in the integrity of the film.



2 – Measurement of the local tribological behavior of the hierarchically structured composites that we will be fabricating this year (Figure 2). These composites contain regions of very high

MWNT density (65%) and regions without MWNT. We fabricate these by growing forests of MWNT and then using appropriate patterning and solvent create two dimensional foams of MWNT. The films are readily infiltrated with polymers such as polyimide and create composites with localized regions of high MWNT density. The behavior of the high density MWNT regions is intriguing and has potential application both for contact switches (in which the current will flow through the regions of high MWNT concentration, but the regions in between will provide the lubrication) and in applications where removal of heat from the tribological surface is important.

Secondly, polymers with good self-lubricity are widely used in bearing applications with the major limitation being their poor wear resistance and short operational life. Nanoparticle filled polymers can provide increased wear resistance (longer life) and decreased friction coefficient. Polytetrafluoroethylene (PTFE) is an excellent candidate for a transfer film lubricant in air and space tribology, because it is insensitive to environmental conditions and has an intrinsically low coefficient of friction. The nanocomposites we have developed have potential applications from inserts in the space-shuttle main engine bearing retainers to solid lubricant guides and bushings in satellites. For example, we have observed wear rates as low as 10^{-7} (mm^3/Nm) with filler concentrations as low as 0.25 wt%. These fillers are tailored at Rensselaer.

In this case, there are similar fundamental questions that need to be understood to enhance our ability to design materials with tailored properties (Figure 3).

Polymer morphology. It is clear that subtle changes in polymer morphology affect the tribology of our nanofilled PTFE. It is also clear that by altering the surface chemistry of the nanofillers, the PTFE morphology is further modified. It is important that we understand not only the role of the morphology on the tribology, but also the role of the surface chemistry in controlling that morphology. We will develop a method similar to that described above for MWNT for a film of nanoparticles and be able to measure the effect of surface modification on particle / polymer interaction. In this case, we may create a film of particles and place a rod of PTFE on the film. The PTFE rod would then be pulled from the particle surface and we will monitor this as a function of nanoparticle surface modification. This combined with the AFM capability at UF and the DSC and XRD capabilities at RPI will provide the foundation for understanding the role of morphology and how to tailor morphology to meet our needs.

Transfer Film Properties. We will also be able to measure the modulus (using indentation and nanoDMA) of the transfer films as well as their adhesion to the substrate (using scratch testing). These films vary widely in thickness and apparent properties as a function of nanoparticle content and surface chemistry. We hypothesize that the transfer film's role is critical to explaining the changes in behavior we observe, but further characterization of these films is necessary to understand their role for these materials.

Dispersion. The role of dispersion in these systems is also not clear. The Triboindenter's hardness mapping and modulus mapping capability will provide the ability to monitor the variability in mechanical properties across the PTFE surface. This coupled with TEM images of the dispersion will help us determine the role of dispersion in the tribological response.

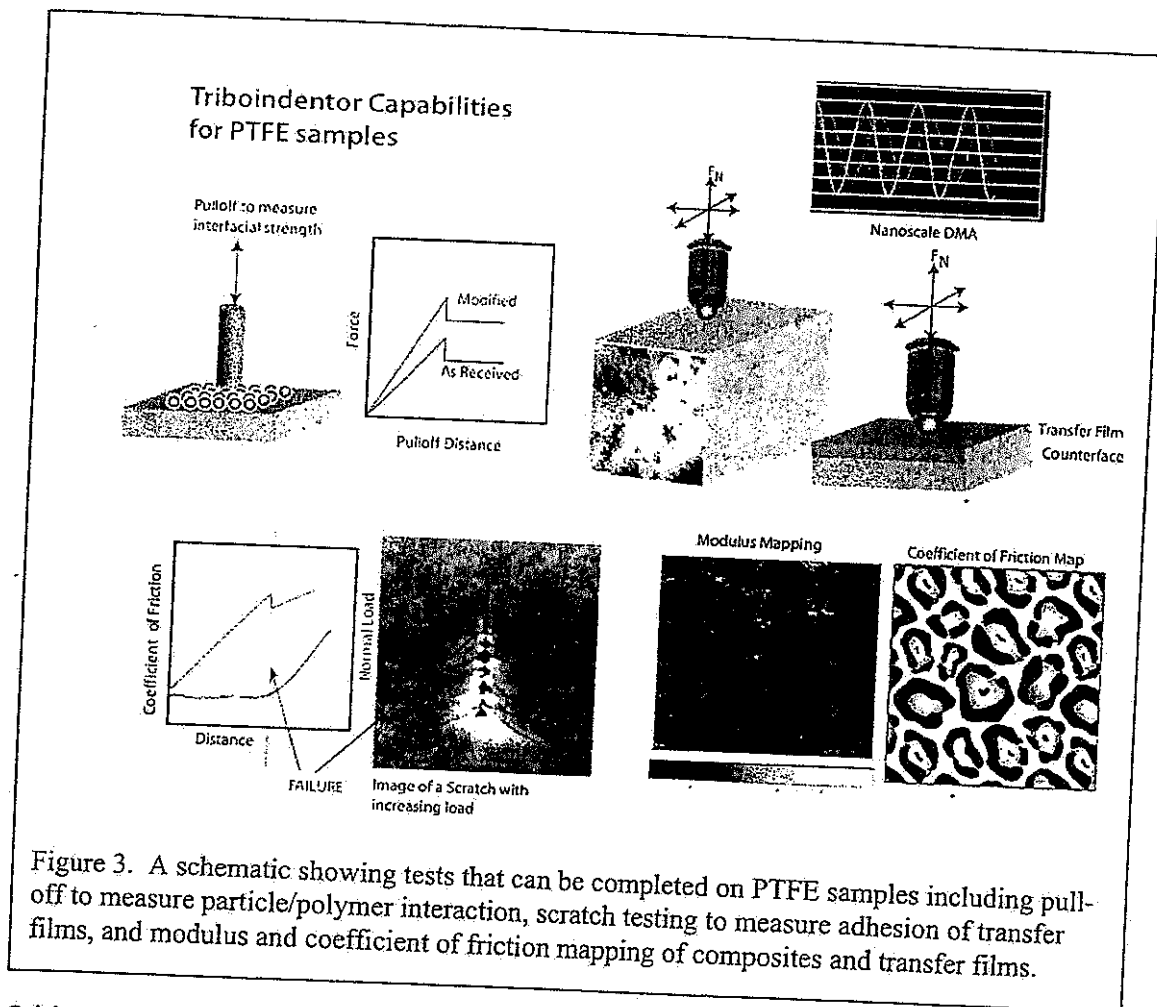


Figure 3. A schematic showing tests that can be completed on PTFE samples including pull-off to measure particle/polymer interaction, scratch testing to measure adhesion of transfer films, and modulus and coefficient of friction mapping of composites and transfer films.

2.1 Instrumentation Request

Nanotribometer

Funds are requested for the purchase of a Hysitron Triboindenter. The Triboindenter is a high throughput instrument designed to support several nanomechanical tests. The system makes use of a three plate capacitive transducer with high sensitivity and stability. It has a load resolution (noise floor) of 100nN and can apply up to 5mN. The displacement resolution (noise floor) is 0.2nm. The stage controlling sample motion has in plane travel of 150mm x 150mm range with 50nm resolution and z direction travel of 50mm with 3nm resolution. In addition, through a unique 3 transducer geometry, the loads both in and out of plane are monitored which is, of course, necessary, for robust tribological characterization. The nanomechanical testing device is coupled to in situ imaging which includes optical imaging and AFM imaging, and scanning probe imaging (SPM) using the nanomechanical tip at low loads. The SPM imaging provides lateral resolution of 15nm ensuring that the measurements are made at the appropriate locations.

The following general nanomechanical tests can be performed:

1 - Nanoindentation to measure local modulus and hardness. The instrument can be programmed to take a thousand measurements across a sample surface or take repeat

measurements at the same point with increasing load (and thus depth). A special feedback loop provides accurate sensing of the sample surface for soft materials.

2 – Scratch testing can be used to measure the scratch behavior, the coefficient of friction, and the load to remove a film from a substrate. Tests can be run at constant load or with increasing load to observe the changes in scratch mechanism with load. To characterize the scratch profile in detail, however, an AFM is required.

3 – Wear testing can be used for static and scanning wear testing. Again the AFM is required for detailed monitoring of the wear surface.

4 – Nanodynamic mechanical analysis (DMA) testing. This provides an opportunity to properly characterize the polymer materials used in our nanocomposites and will provide insight into the effect of sliding rate on the tribological behavior. This can also be used essentially as a small fatigue testing device to determine, for example, if the MWNT / polymer interface stands up to repeated loads. Interface failure would be detected through changes in the modulus.

These tests can all be run from -10°C to 200°C . While not relevant for space environments, it gives us the opportunity to test the behavior as the glass transition temperature of the polymer is reached.

2.2 Details of Collaboration between the Rensselaer Polytechnic Institute and the University of Florida

Rensselaer Polytechnic Institute is a member of the presently funded MURI at the University of Florida entitled "Multifunctional Materials for Air and Space Tribology". The MURI funding has allowed the beginnings of a synergistic multi-scale understanding of tribological events, through the close collaboration of engineers and surface chemists. The proposed instrumentation will allow the further development of this collaboration in which knowledge and experience will be translated between universities and between research disciplines. Such developments will represent valuable opportunities for the training and education of the associated engineering and science students. Evidence of our strong collaboration can be seen through our joint publications that include students from both schools. In addition to the publications listed, we have a joint book chapter and paper in preparation that includes Blanchet, Sawyer, Schadler, and Perry from the MURI. To enhance the collaboration students from both institutions have spent time (a week at a time) at the other institution. Finally, the investigators meet face to face at least 3 times a year at either Rensselaer or Florida and meet twice a month by phone.

"Tribological Investigation of the Effects of Particle Size, Loading and Crystallinity on Poly(Ethylene) Terephthalate Nanocomposites," Praveen Bhimaraj, David Burris, W. Gregory Sawyer, C. Gregory Toney, Richard W. Siegel, Linda S. Schadler, submitted to *Wear* (2006).

"Surface Chemistry and Temperature Dependent Tunable Friction Behavior of Oriented Carbon Nanotube Films," P.L. Dickrell, S.K. Pal, G.R. Bourne, C. Muratore, A.A. Voevodin, L.S. Schadler, P.M. Ajayan, W.G. Sawyer, submitted to *Tribology Letters* (2006).

"Measurements of Coefficient of Friction on a Bed of Aligned Multi-Walled Carbon Nanotubes," Pamela L. Dickrell, W. Gregory Sawyer, Nachiket R. Raravikar, Linda S. Schadler and Pulickel M. Ajayan, *Tribology Letters*, vol. 18, 59-62 (2005).

"Effect of matrix morphology on the wear and friction behavior of alumina nanoparticles/poly(ethylene)terephthalate composites," Praveen Bhimaraj, David Burris, Jason Action, W. Gregory Sawyer, C. Gregory Toney, Richard W. Siegel, Linda S. Schadler, *Wear*, vol. 258 No 9, p.1437-1443 (2005)

3.0 Supporting Information

This MURI team is supported by an outstanding research infrastructure. All of the investigators have state-of-the-art facilities, which is a recognized strength of the experimentalist and theorist involved in this project. In the previous sections we have outlined how this new equipment will enhance the research, contribute to the program thrust and grand challenges, and establish new capabilities.

3.1 Interfacing Equipment to Existing Facilities

The Nanocomposites Laboratory at Rensselaer as well as the Rensselaer Nanotechnology Center does not have a Triboindenter or similar equipment. However, we have a scanning probe facility that can house this instrument. We have technical staff to support this facility, and the proximity to our microscopy and processing facilities in addition to the scanning probe instruments, will provide an opportunity for expanded characterization of tribological materials. In addition, it will lead to other interactions between Schadler, Blanchet and other investigators at RPI. In polling faculty, we have already seen significant interest from 5 other large research groups. The instrument will further assist in the collaborations between the University of Florida Tribology group and Rensselaer's Nanocomposites and Tribology's group.

3.2 Special Circumstances Regarding Acquisition

Due to Rensselaer's commitment to nanotechnology and this MURI program, the Rensselaer Nanotechnology Center and the Office of Research at Rensselaer will contribute 45K to this instrument providing a total cost share of 64K.

3.3 Amounts and Sources of Ongoing or Proposed Support

This DURIP proposal directly supports the efforts of an AFOSR sponsored MURI program, which has an estimated 5 year budget of 2.5 million dollars (both Linda Schadler and Thierry Blanchet are funded as part of this effort). In addition, L. Schadler has NSF NIRT funding to develop multiscale mechanical models of MWNT / polymer nanocomposites. This project has a 4-year budget of about \$450 at Rensselaer. She is also part of an NSF NSEC "Directed Assembly of Nanostructures" and is the Thrust 3 leader for that center. Her direct funding from this center is on the order of \$100K per year. This same NSF center has provided access to a significant portion of the equipment used in the MURI research. Finally, she has about \$300K in industrial funding that is focused on polymer nanocomposites. Thierry Blanchet is a member of another tribology MURI lead by Georgia Institute of Technology and funded by ONR, "Friction and Wear Under Very High Electromagnetic Stress." His funding through this grant is \$500K over 5 years.

3.4 Estimated Useful Life of the Equipment

The proposed nanodindentation system possesses a useful lifetime of at least 10 years, with routine maintenance of the mechanics and occasional software upgrades. This estimate is based upon information from the company and discussion with other users. While the technology is

constantly improving in this field, in this particular case, the equipment already meets the foreseeable needs for measuring the local tribological behavior of hierarchically structured nanocomposites. The early nanoindentors produced by Hysitron, which have the same basic core, have been in operation for 10 years and are still in use.

4.0 Conclusions

The proposed instrumentation is uniquely suited to provide direct insight into the incorporation of polymer nanocomposites into DOD systems and missions. The proposed instrumentation will also facilitate the cross-disciplinary research of a team of scientists and engineers, uniquely aimed at addressing a number of fundamental grand challenges that exist within the respective research community. These studies will directly benefit the Air Force in developing the ability to design materials required for operation in extreme environments in which the Air Force has a demonstrated need. The instrumentation will simultaneously provide the opportunity for developing fundamental insight into the chemical and physical origins of all future tribological systems (ubiquitous throughout DOD).