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**Investigation of the Interphase Region
in Polymer Matrix - Glass Fiber Reinforced Composites
Using the Interfacial Force Microscope**

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Date

Objective As stated in the original proposal the objectives of the proposed research were two fold. The proposed research was to: 1) provide a critical vehicle to enhance South Dakota researchers' abilities to participate in nationally important energy related research while 2) building and strengthening partnerships between the South Dakota School of Mines and Technology (SDSM&T) and Sandia National Laboratories (SNL), Albuquerque, NM. In collaboration with Dr. J.E. Houston of SNL, the inventor of the Interfacial Force Microscope, expertise was to be developed to utilize the IFM in the investigation of nanomechanics in polymer based systems. The IFM was to be used to obtain quantitative and spatially resolved measurements of nanomechanical properties in polymer matrix glass fiber reinforced composites and other polymeric systems. Because of the unique sensor the IFM utilizes, this work held the promise to reveal the critical relationships between the interphase chemistry, mechanical properties, and the adhesion at the reinforcement interface. It was anticipated that the Department of Energy would benefit from this research from the ability to "engineer" advanced light-weight polymer matrix composites and in the application to aging of polymeric composite systems.

Summary of Accomplishments Over the course of this project a variety of composite systems were investigated which resulted in a number of collaborations with SNL and companies (shown in parentheses). The projects included glass fiber reinforced epoxy composites (SDSM&T-SNL), elastomers (SDSM&T-SNL-Goodyear), metallic fiber reinforced elastomers (SDSM&T-SNL-Goodyear), heterogeneous mock rocket propellant (SDSM&T-SNL), carbon-carbon composites (SDSM&T-Goodrich), and multi-layered composite paint films (SDSM&T-SNL-PPG). Typically the IFM was found to be suitable to obtain spatially resolved (nanometer spatial resolution) elastic modulus.

To accomplish these studies we developed experimental procedures, experimental hardware and software analysis tools. A sample of such developments include:

- 1) assisted in the development and fabrication of IFM sensors,
- 2) developed and refined the methodology to make probes/tips,
- 3) developed EXCEL macros to extract mechanical properties from force profile data,

- 4) developed EXCEL macros to extract mechanical properties from a unique two-step creep testing procedure for soft materials,
- 5) developed chemical kinetic models to interpret spatially resolved chemical data, and
- 6) developed finite element stress-strain models to incorporate spatially resolved elastic modulus data from IFM analysis.

Brief summaries/abstracts of some of the investigations are given below. References to publications and presentations regarding these studies can be found in the Scientific Productivity Section.

Glass Fiber Reinforced Epoxy Composites Fourier transform infrared evanescent wave spectroscopy (FT-IR/EWS) has been utilized to study the interphase chemistry of polymer glass fiber composites. Previous studies have shown that optical constants of polymer systems change during the curing process. It is important to understand the effect of the change of optical constants of the polymer system on the chemical kinetics, when FT-IR/EWS is applied. Herein, we show how the sample optical constants may affect the chemical kinetic results, according to optical waveguide theory and numerical analysis. It is found that change in sample optical constants during the curing process will not significantly affect the chemical kinetic results under the conditions discussed. [3]

The epoxy-amine interphase curing reaction was monitored in-situ using FT-IR/EWS. A high refractive index flint glass fiber was used for a model reinforcement and evanescent wave sensor. The epoxy was EPON 862[®] and the curing agent was ETHACURE 100[®]. The reaction was carried out at constant temperature and with a stoichiometric mixture of epoxy and curing agent. Changes in the primary amine band 5060 cm⁻¹ and epoxide band 4530 cm⁻¹ were monitored with respect to time from which chemical kinetic parameters were obtained. The conversion of epoxy appeared to vary from 82 to 98% within the interphase. This study shows the utility of FT-IR EWS to probe the interphase chemistry for epoxy amine resin fiber reinforced composites. [1,4, 10]

Polymer Surface Analysis Scanning-probe microscopies (SPM) are presently widely used in remarkably diverse applications and, as evidenced by this symposium, these techniques are rapidly expanding into the important areas of polymer surfaces and interfaces. The Atomic Force Microscope (AFM) is presently the most widely used of the scanning-probe techniques. However, the AFM's range of application suffers from an inherent mechanical instability in its deflection force sensor. The instability problem has been overcome by the development of the Interfacial Force Microscope (IFM), which utilizes a force-feedback sensor concept. In the following, we present several examples of polymer applications to illustrate the utility of the IFM sensor concept applied to the study of polymer surfaces. [7]

Elastomers Modulus measurements are among the most useful properties available for monitoring the cure and aging of rubbers. Historically, such measurements were done on macroscopic samples, but over the past 15 years, several penetration techniques have been and are being developed that allow quantitative estimates of modulus to be made with lateral resolutions of 100 μm or better. This review summarizes these developments and the types of unique information that can be generated on rubbery materials. A large part of the review

focuses on the types of results available from a modulus profiling apparatus that has been used to study rubbers for the past 15 years. This instrument allows estimates to be made of the inverse tensile compliance (closely related to Young's tensile modulus) with a lateral resolution of around 50 to 100 μm . Several recently developed alternative methods for achieving similar spatial resolution are also described. Finally, a brief review is given of the recent attempts to measure quantitative modulus values for rubbers with even better resolution using instruments historically focused on metals and other hard materials such as nanoindenters the atomic force microscope and the interfacial force microscope. [6]

Multi-layered Composite Paint Films A mild steel substrate coated with five paint layers was analyzed across each layer using an interfacial force microscope (IFM). The elastic modulus was seen to vary from 0.2 GPa to 1.2 GPa and was a function of the particular layer. The average elastic moduli for each layer were then used in a finite element static stress analysis for comparison to a film of equivalent thickness but having a homogenous elastic modulus of 0.84 GPa. Significant differences in the stress and strain profiles were observed between the two cases. The FEM analysis demonstrated the importance of using actual elastic modulus profiles to predict the failure location in multi-layer automotive paint systems. [2]

Metal Matrix Composites Metal matrix composites (MMCs) combine the properties of metal and ceramic or intermetallic materials. Common examples of metal matrix composites are $\text{Cu-Al}_2\text{O}_3$, $\text{SiC}_w\text{-Al}$, $\text{Al-Al}_2\text{O}_3$, $\text{Al-B}_4\text{C}$, and Ni-NiAl_3 . Mechanical or thermal properties, such as strain-stress behavior, or thermal expansion coefficient can be tailored by changing the content of the reinforcing phase. The most common techniques of measuring mechanical properties of composite materials rely on macroscopic approach. During the past fifteen years, a significant effort has been made to develop various techniques of measuring mechanical properties on a microscopic level. These techniques include atomic force microscope (AFM) and depth sensing indentation techniques, based on Hertzian contact mechanics. However, it is still a challenge to measure reliably and quantitatively the Young's modulus and Poisson's ratio of individual phases as well as properties at the interfaces. This presentation will focus on fundamental aspects of measuring of mechanical properties of metal matrix composites at nano-scale using Interfacial Force Microscopy (IFM). The IFM is a scanning probe microscope, which utilizes a unique self-balancing capacitance force sensor. Force-displacement curves obtained with the IFM are analyzed using Hertzian contact mechanics to extract the Young's moduli of the individual phases and interface region with high spatial resolution. The properties of $\text{Cu-Al}_2\text{O}_3$, Al-SiC_p composites will be discussed in detail. Furthermore, a comparison of experimental data with mechanical properties calculated from first principles will be discussed. [5]

Scientific Productivity The results of this work were in many cases the first results of their kind ever reported. As such they have been disseminated broadly to the scientific community. The following is a compilation of Publications, Presentations, Human Resource Development and Grants that have been a direct result of this work.

Publications

1. H. Liu and R.M. Winter, "Investigation of the Relationship Between the Interphase Nanomechanics and Chemistry in Epoxy-Amine-Glass Fiber Composites," **Composites: Part A Applied Science and Manufacturing**, manuscript in preparation.
2. R.M. Winter and H. Liu, "Measurement of Spatially Resolved Elastic Modulus of a Multi-Layered Paint Film: The Effect of the Modulus Gradient on Finite Element Analysis of Static Loading," **Progress in Organic Coatings**, under revision.
3. H. Liu and R.M. Winter, "Effects of Optical Constants on the Chemical Kinetics from an Optical Glass Fiber Sensor for FT-IR Evanescent Wave Spectroscopy," **Composites: Part A Applied Science and Manufacturing**, under revision.
4. H. Liu, R. Dhavalikar, R.M. Winter, "In-Situ Kinetics of the Epoxy-Amine Interphase Curing Reaction as Revealed by FT-IR Evanescent Wave Spectroscopy," **Composites: Part A Applied Science and Manufacturing**, under revision.
5. B.E. Liebig, A.N. Chantis, J.A. Puszynski, and R.M. Winter, "Interfacial Force Microscopy and Its Application in Metal Matrix Composites," *Symposium P Surface Engineering 2001--Fundamentals and Applications*, Editors: W.J. Meng, A. Kumar, Y-W. Chung, G.L. Doll, Y-T. Cheng, S. Veprek, **Materials Research Society Proceedings**, 697, P8.21.1 – P8.21.6, 2002.
6. K.T. Gillen, E. R. Tirrell, and R.M. Winter, "Modulus Mapping of Rubbers Using Micro- and Nano-Indentation Techniques," accepted **Rubber Chemistry and Technology, Rubber Reviews**, 2001.
7. J.E. Houston and R.M. Winter, "Interfacial Force Microscopy: Applications to Polymer Surfaces," **Polymer Preprints**, 41 (2), pp. 1454-1455, 2000.
8. C. Steffan, H. Liu, H. Cabibil, J. Lozano, H. Celio, J.M. White, J.E. Houston and R.M. Winter, "The Relationship between Nanomechanical and Chemical Properties in Polymer Composites," in the proceedings of Society for Experimental Mechanics IX International Congress and Exposition on Experimental Mechanics, Orlando, FL, pp. 920-923, June 5-8, 2000.
9. R.M. Winter and J.E. Houston, "Interphase Mechanical Properties in Epoxy-Glass Fiber Composites as Measured by Interfacial Microscopy," in **Proceedings of the Society for Experimental Mechanics Spring Conference on Experimental and Applied Mechanics**, pp. 355-358, Houston, TX, June 1-3, 1998.

Presentations

1. S. Adamala, S. Chada, S.B. Yedla, C. Steffan, C.H.M. Jenkins, S.K. Khanna and R.M. Winter, "A Comparison of Depth Sensing Nanoindentation and Interfacial Force Microscopy to obtain Nanomechanical Properties of Polymer Composite Systems," Presented at the AIChE 2003 Annual Meeting, San Francisco, CA, November 15-21, 2003. 2. R.M. Winter and H. Liu, "Measurement of Spatially Resolved Elastic Modulus within a Multi-Layered Paint Film: The Effect of the Modulus Gradient on Finite Element Analysis of Static Loading," Presented at the 2003 ASME International Mechanical Engineering Congress, Washington, DC, November 15-21, 2003.
3. H. Liu and R.M. Winter, "Measurement of the Elastic Modulus Profile Across a Multi-Layered Paint Film and Its Impact on FE Analysis of Static Loading," American Institute of Chemical Engineers 2002 Annual Meeting, November 3-8, 2002, Indianapolis, IN.

4. H. Liu and R.M. Winter, "Investigation of the Relationship between Interphase Nanomechanics and Chemistry in Epoxy-Amine-Glass Fiber Composites," American Institute of Chemical Engineers 2002 Annual Meeting, November 3-8, 2002, Indianapolis, IN.
5. B. E. Liebig, A. N. Chantis, Jan A. Puszynski, and R.M. Winter, "Interfacial Force Microscopy and Its Application in Metal Matrix Composites," presented at the Fall Meeting of the Materials Research Society, November 26-30, 2001, Boston, MA.
6. R.M. Winter, H. Liu, K.T. Gillen and J.E. Houston, "Measurements of Spatially Resolved Elastic Modulus of a Multi-Layered Paint Film and Its Impact of the Modulus Gradient on a Finite Element Analysis of Static Loading," presented at the Fall Meeting of the Materials Research Society, November 26-30, 2001, Boston, MA.
7. C.E. Steffan, H. Liu, and R.M. Winter, "Nanomechanics of Polymer Surfaces," presented at the American Vacuum Society 47th International Symposium, October 2-6, 2000, Boston, MA.
8. R.M. Winter and J.E. Houston, "Nanomechanical Properties of Polymeric Systems Measured by Interfacial Force Microscopy," presented at the 20th International Congress of Theoretical and Applied Mechanics, August 2 – September 2, 2000, Chicago, IL.
9. J.E. Houston and R.M. Winter, "Interfacial Force Microscopy: Application to Polymer Surfaces," presented at the 220th National Meeting of the American Chemical Society, August 2000, Washington, DC.
10. C. Steffan, H. Liu, H. Cabibil, J. Lozano, J.M. White, J.E. Houston and R.M. Winter, "The Relationship between Nanomechanical and Chemical Properties in Polymer Composites," Society for Experimental Mechanics IX International Congress and Exposition on Experimental Mechanics, Orlando, FL, June 5-8, 2000.
11. H. Liu, R. Dhavalikar and R.M. Winter, "In-situ Kinetics of the Epoxy-Amine Interphase Curing Reaction as Revealed by Fourier Transform Infrared Evanescent Wave Spectroscopy," 1999 Annual Meeting of the American Institute of Chemical Engineers, Dallas, TX, November 1999.
12. C. Steffan, H. Liu and R.M. Winter, "Nanomechanical Properties of a Model Epoxy Silane-Glass Composite as Revealed by Interfacial Force Microscopy," 1999 Annual Meeting of the American Institute of Chemical Engineers, Dallas, TX, November 1999.
13. H. Cabibil, J.M. White, J.E. Houston and R.M. Winter, "Interphase Nanomechanical Properties in a Polymer Matrix Composite," 36th Annual Technical Meeting of the Society of Engineering Science, Austin, TX, October 25-27, 1999.
14. H. Cabibil, J.M. White, J.E. Houston and R.M. Winter, "Interphase Nanomechanical Properties in a Model Epoxy-Silane-Glass Composite as Revealed by Interfacial Force Microscopy," 46th International Symposium of the American Vacuum Society, Seattle, WA, October 25-29, 1999.
15. H. Cabibil, J.M. White and R.M. Winter, "Interphase Elastic and Visco-elastic Properties in a Model Epoxy-Silane-Glass Composite as Revealed by Interfacial Force Microscopy," 1st International Conference on Scanning Probe Microscopy of Polymers, Santa Barbara, CA, August 27-29, 1999.
16. R.M. Winter and J.E. Houston, "Interphase Mechanical Properties in Epoxy-Glass Fiber Composites as Measured by Interfacial Microscopy," Society for Experimental Mechanics Spring Conference on Experimental and Applied Mechanics, Houston, TX, June 1-3, 1998.

17. R.M. Winter and J.E. Houston, "Interphase Mechanical Properties in an Epoxy/Glass Fiber Composite as Measured by Interfacial Force Microscopy," Materials Research Society 1998 Spring Meeting, San Francisco, CA, April 13-17, 1998.

Human Resource Development

Two graduate students and six undergraduates were at least partially supported by this project either through salaries or equipment use. The names, degrees, programs and year of graduation for each student are:

Haining Liu, PhD, Materials Engineering and Science (2002)
Craig Steffan, MS, Chemical Engineering (2003)
James Anderson, BS, Chemical Engineering (2001)
Robert Cunningham, BS, Chemical Engineering (2000)
Timothy Goodson, BS, Chemical Engineering (1999)
Jamie Ha, BS, Chemical Engineering (2001)
Jessica Kienow, BS, Chemical Engineering (2002)
Deborah Morgan, BS, Chemistry (2000)

Grants

The results from this project and the expertise developed as a result of the project were used as a foundation for several successful proposals. PI information, grant title, agency, time frame and award amount is provided below.

1. with C. Jenkins (PI), "Investigation of Adhesive Joints for Nano-Engineering and Modeling," DOD EPSCoR – AFOSR, 01/01-12/03, awarded \$257,863.
2. "Camille and Henry Dreyfus Scholar/Fellow Program," the Camille and Henry Dreyfus Foundation, Inc., 11/00-10/02, awarded \$60,000
3. with J.M. White (UT-Austin) and K. Liechti (UT-Austin), "Nanomechanics and Interphase Chemistry of Interfacial Fracture," National Science Foundation, 9/00-8/03, awarded \$442,079.
4. with J. Kellar (PI), D. Heglund, S. Farwell, L. Kjerengtroen, "Acquisition of a Research-Grade FT-IR Spectrometer," National Science Foundation, 6/00-5/03, awarded \$126,290.
5. with S. Khanna (PI), "Development and Manufacturing of Highly Damage Resistant Fiber Glass Reinforced Window Panels for Buildings in Hurricane Prone Areas," National Science Foundation, \$317,772, 8/99-7/02, awarded \$288,958.

Collaborations Several collaborations with scientist at the Sandia National Laboratories was established as a result of this project. In addition, several industrial and university collaborations were also developed as a direct outcome of the SNL collaborations and this project. A list of the collaborators name and location and a description of the project is given below.

Dr. J.E. Houston

Sandia National Laboratories, Albuquerque, NM

Development and novel application of the Interfacial Force Microscope

Dr. K.T. Gillen

Sandia National Laboratories, Albuquerque, NM

Interfacial Force Microscope Analysis of Multi-Layered Thin Film Systems

Interfacial Force Microscope Analysis of Elastomers and Elastomeric Composites

Dr. L.M.G. Minier

Sandia National Laboratories, Albuquerque, NM

Interfacial Force Microscope Analysis of Mock Propellants

Dr. E. Tirrell

Goodyear

Interfacial Force Microscope Analysis of Elastomeric Composites

Dr. S. Khanna

University of Missouri at Columbia

Development and Manufacturing of Highly Damage Resistant Fiber Glass Reinforced Window Panels for Buildings in Hurricane Prone Areas

Dr. K.M. Liechti

University of Texas at Austin

Nanomechanics and Interphase Chemistry of Interfacial Fracture

Dr. J.M. White

University of Texas at Austin

Nanomechanics and Interphase Chemistry of Interfacial Fracture