

NAT'L INST. OF STAND & TECH R.I.C.



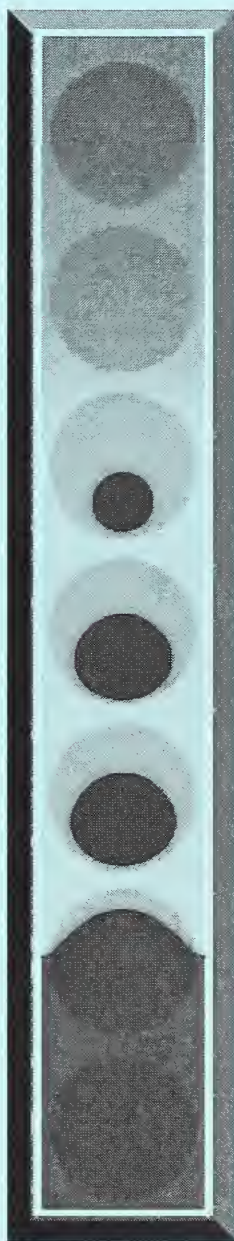
A11105 086027

NIST
PUBLICATIONS

MSEL

Materials Science and Engineering Laboratory

POLYMERS



QC
100
.U56
NO. 5964
1996

NISTIR 5964
U.S. Department of Commerce
Technology Administration
National Institute of Standards
and Technology

Technical Activities 1996

Polymers

Flow simulation of void formation dynamics as occurs in fiber preforms used in liquid composite molding. A Lattice Boltzmann method is used to simulate two-phase flow transverse to an array of porous fiber tows. The fluid being injected (lighter color) flows quickly through open pore space and traps the resident fluid (air) within the porous tows.

MSEL

Materials Science and Engineering Laboratory

POLYMERS

L.E. Smith, Chief
B.M. Fanconi, Deputy

NISTIR 5964
U.S. Department of Commerce
Technology Administration
National Institute of Standards
and Technology

Technical Activities 1996



U.S. DEPARTMENT OF COMMERCE
Michael Kantor, Secretary
TECHNOLOGY ADMINISTRATION
Mary L. Good, Under Secretary for Technology
NATIONAL INSTITUTE OF STANDARDS
AND TECHNOLOGY
Arati Prabhakar, Director

THE UNIVERSITY OF CHICAGO
LIBRARY

1984

TABLE OF CONTENTS

INTRODUCTION	iv
TECHNICAL ACTIVITIES	1
ELECTRONIC PACKAGING AND INTERCONNECTS	
Overview	1
FY-96 Significant Accomplishments	2
Improved Measurement Technique for Hydrothermal Expansion of Polymer Thin Films ..	3
Thermal Properties Measurement	4
Industry Coordination and Workshops in Electronic Packaging	6
Ultra-thin Polymer Films	10
Dielectric Measurements of Thin Films from DC to 1 GHz	12
Residual Stress in Polymer Films Adhered to Silicon Substrates	14
Moisture Effects in Electronic Packaging Polymers	15
Interfacial Energy Between Solids	17
Aging of Light Emitting Polymers	18
POLYMER BLENDS AND PROCESSING PROGRAM	
Overview	21
FY-96 Significant Accomplishments	22
Thermodynamics and Kinetics of Polymer Blends	24
Measurement Techniques and Analysis Procedures for Multi-Phase Systems Under Shear	26
Characterization of Polymers and Polymer Blends Under Shear	27
Temperature Measurements for Polymer Processing	31
Additives and Compatibilizers in Polymer Blends	33
Investigation of Interfacial Interactions for Polymers and Blends	35
Pressure Effects on Polymer Blends and Processing	39
Self-Assembling Micelles, Transient Polymer Networks, Gels, and Interacting	40
Investigations of Statics and Dynamics in Polyelectrolytes	42
POLYMER COMPOSITES PROGRAM	
Overview	45
FY-96 Significant Accomplishments	46
Liquid Composite Molding: Development of Permeability Measurement Techniques and Data	48
Liquid Composite Molding: Development and Verification of Process Simulation Models	49
Liquid Composite Molding: Development and Verification of Permeability Prediction Models	51

Liquid Composite Molding: Bulk Resin Measurements for Process Monitoring and Control	54
Liquid Composite Molding: Interphase Sensitive Sensors for Process Monitoring	57
Environmental Durability Studies: Effect of Fiber Coatings and Interfaces	59
Environmental Durability Studies: Comparison of Test Results for Laminated Composite Samples and Single-Fiber Composite Specimens	61
Environmental Durability Studies: Development of Processing Methods to Fabricate Urethane Samples	64
POLYMER CHARACTERIZATION PROGRAM	
Overview	67
FY-96 Significant Accomplishments	68
Standard Reference Materials	70
Mass Spectrometry of Polymers	71
Characterization of Polymers by Spectroscopic Techniques	73
Characterization of Polymer Morphology by Microscopy Techniques	76
Structural Characterization of Polymers by Small Angle X-Ray Scattering	78
Nonlinear Viscoelasticity of Solid Polymers	79
Physical Aging of Polymers	84
Finite Element Analysis in Polymer Mechanics.I: Dimensional Stability	89
Finite Element Analysis in Polymer Mechanics.II: Fracture	90
Viscoelastic Measurements in Plasticizing Environments	92
Measurement of Craze Initiation and Growth in Polymers	93
DENTAL AND MEDICAL MATERIALS PROGRAM	
Overview	97
FY-96 Significant Accomplishments	98
Dental Polymers Designed with Minimal Polymerization Shrinkage, Residual Vinyl Content and Water Sorption	99
Dental Composites with Improved Interfaces	101
Improved Adhesive Systems for Bonding to Tooth Structure	102
Polymer-modified Porous Ceramics: Interpenetrating Phase Composites for Dental Applications	104
Bioresorbable Polymer-Reinforced Calcium Phosphate Cements	105
Measurement Methods for Process Control of Cell Encapsulation	107
Bioactive Polymeric Dental Materials with Remineralization Potential Based on Amorphous Calcium Phosphate	108
Support for the Biomaterials Integrated Products Industries	110
Durability Assessment of Biomedical Materials/Prostheses	111
THEORY AND MODELING PROGRAM	
Overview	113
FY-96 Significant Accomplishments	114

Theory and Modeling in Polymer Physics	115
Theory and Modeling of the Properties of Polymer Blends, Suspensions and Solutions	115
OTHER PROGRAMS	
Diffusion of Gases in Polymeric Materials	119
Development and Utilization of Test Methods for Qualification of Passport Laminates	119
DIVISION MANAGEMENT	121
RESEARCH STAFF	123
APPENDIX	
NIST Organization Chart	137
MSEL Organization Chart	138
Polymers Division Organization Chart	139

Certain commercial materials and equipment are identified in this report in order to specify adequately the experimental procedures. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology (NIST) nor does it imply necessarily the best available for the purpose.

INTRODUCTION

This report gives a description of the principal technical activities of the Polymers Division during the 1996 fiscal year. It is organized according to the program structure by which we plan our work. The report follows a concise format that was designed to make it easier for readers to understand the total range of our programs. Technologies can seldom be neatly categorized according to their technical content. Correspondingly, our industry customers rarely describe their needs in only one or two technical areas. This organization of the report also provides the reader with the management context in which we view individual projects in order to make our motivation for the work clearer. We hope this will encourage our customers to offer comments and advice on ways we can be more effective in our work.

The Polymers Division is responsible for providing standards, measurement methods, and fundamental concepts of polymer science to assist those U. S. industries that produce or use synthetic polymers in essential parts of their business. We plan our programs primarily to develop improved measurement capability for broad sectors of the industrial community. We rely heavily on advice from industrial and technical communities to set our priorities. This advice stems both from formal workshops, some of which are briefly described in this report, and from extensive informal visits to and from our customers. In all these programs, collaboration with others continues to be the most effective way to develop and transfer technology. In particular, industry collaborators who know both their business and technical needs are vital to planning and execution of the projects.

The Division has focused a majority of its resources on specific industrial sectors. This has allowed us to assess the needs of each industry group and plan a response that is appropriate to our capabilities and role. Each of the program overviews describes the industrial focus of the program even though the program outputs often have wider applicability.

There are many technical accomplishments which are described within this report under each specific program. The following is a selected list of these accomplishments which gives an overview of the output of all the Polymers Division programs.

Significant Accomplishments

ELECTRONIC PACKAGING AND INTERCONNECTION PROGRAM

- Detailed analysis of transient charge response obtained from thermal pulse instrumentation now allows evaluation of the barrier to heat transmission across the interface between a dielectric polymer film and a conducting substrate.

- NMR and NIR spectroscopy have detected liquid-like water as well as molecularly dispersed water in silica-filled epoxy molding compound and a polyimide when equilibrated in liquid water.
- X-ray reflectivity has been used to measure the hygroscopic expansion of thin films of polyimide on silicon for a variety of film thicknesses. The results imply the existence of an interfacial region which absorbs much more water than the bulk.

POLYMER BLENDS AND PROCESSING PROGRAM

- Phase separation kinetics of a model polystyrene-polybutadiene blend during shear was measured by light scattering and phase contrast microscopy in collaboration with Goodyear.
- Steady shear behavior of a solvated model polymer blend sample in the two-phase region was measured using fluorescence microscopy. In order to establish a scaling approach to understand shear mixing, phase compositions as a function of shear rate and temperature were obtained.
- Pressure induced shifts in the miscibility of polyolefin blends were measured via cloud point techniques in collaboration with Exxon.
- Phase separation kinetics in ultrathin blend films were measured to demonstrate suppression of surface induced phase separation and a transition to the behavior of a two dimensional fluid mixture. Results are in agreement with simulations of phase separation in 2-D.
- A patent application was filed for a temperature profile sensor based on confocal optics. The sensor, which fits the standard instrumentation port of processing machines, was used to measure temperature profiles in polyethylene resin during extrusion. The results were consistent with expected effects of shear heating in the barrel of an extrusion machine.
- The distribution of condensed counterions associated with the charged terminal units of polyelectrolyte dendrimer molecules in solution was characterized by small angle neutron scattering.

POLYMER COMPOSITES PROGRAM

- A micromechanical testing method developed for polymer composites was shown to be an effective tool for measuring the interfacial shear properties of dental materials. For example, using the microbond interfacial strength test, a hydrophobic silane coupling agent

was demonstrated to produce more durable adhesion than the dental industry standard formula.

- A traditional Lattice Boltzmann formulation was modified to model flow in heterogeneous media, where the momentum transport is expressed with a combination of the Stokes and Brinkman equations. Lattice Boltzmann techniques enable efficient computation in real materials and the inclusion of important multiphase flow physics.
- A fast cure sensor was developed in cooperation with industry and demonstrated in the fabrication of epoxy, polyurethane, and polyester composite plaques. The technology is being transferred to the Ford Motor Co. laboratory where it will be used on prototype production equipment as part of a NIST/Ford/GE ATP program.
- The Polymers Division and Ohio State University held a three day workshop on Liquid Composite Molding. Since the first workshop on Liquid Molding was held at NIST three years ago, a nascent liquid molding industry has emerged in the United States and a new set of technical challenges revolving around quality control has emerged.

POLYMER CHARACTERIZATION

- A general methodology was developed for comparison of the molecular weight distribution obtained from MALDI mass spectrometry with that obtained from size exclusion chromatography.
- The mixed phase of a metal-sulfonated poly(styrene)/methylated poly(amide) was shown by NMR to contain a near-average level of sulfonated styrenes, rather than a higher level expected from polarity arguments.
- Tension and compression responses of a commercial grade poly(carbonate) were shown to be predictable within 15 % based on properties obtained from torque and normal force data in torsion. This result required the development of a compressible form of Valanis-Landel Strain Energy Function.
- In collaboration with researchers from Kodak, time-temperature and time-aging time data for poly(ethylene terephthalate) and poly(ethylene naphthalate) thin films were obtained by conducting temperature jump experiments in stress relaxation.

DENTAL AND MEDICAL MATERIALS PROGRAM

- Low shrinkage interpenetrating polymer networks were formed by coincident free- radical methacrylate polymerization and cationic double ring-opening polymerization.

- The addition of urethane functional groups to fluorinated methacrylate monomers was shown to provide polymers with significantly improved strength and minimal water uptake.
- The feasibility of developing stress-bearing craniofacial implants from hydroxyapatite and bioresorbable polymers was demonstrated.
- Cooperative Research and Development Agreements were signed with six orthopaedic companies to evaluate the wear properties of orthopaedic joint materials.

THEORY AND MODELING PROGRAM

- A relationship was developed between the entropy of a glass-forming polymer system and its viscosity in which the viscosity is determined by the configurational free energy, rather than by the configurational entropy as expected from earlier theories.
- A new and general analytic description of transport virial coefficients of particles having general shape and arbitrary property mismatch was introduced.

TECHNICAL ACTIVITIES

ELECTRONIC PACKAGING AND INTERCONNECTION

A major element of the U.S. microelectronics business group is the semiconductor and the electronic interconnection industries. Combined, these two industries deliver the power and functionality of semiconductor technology to the hands of the users. They also face changing consumer expectations, product evolutions, design cycles, and international competition with a pace and urgency never before seen in world commerce.

In response to the importance of electronic packaging to the microelectronics industry, this program is focusing on industry's most pressing challenges surrounding the utilization of advanced materials and material processes in **semiconductor packaging, electronic interconnection, and assembly**. Initiated in 1994, the program complements semiconductor fabrication activities supported by the NIST National Semiconductor Metrology Program (<http://www.eeel.nist.gov/810.01/index.html>).

MSEL's program deals with industry's most pressing materials issues which are associated with the product and technology priorities contained within leading industry roadmaps. Roadmapping activities sponsored by major industry associations, namely *The National Technology Roadmap for Semiconductors*, *The National Technology Roadmap for Electronic Interconnects*, and more recently *The National Electronics Manufacturing Initiative*, have led to projects dealing in matters such as electrical, thermal, and mechanical characteristics of thin film materials; solders, solderability and solder joint design (<http://www.ctcms.nist.gov/programs/solder>); interfaces and adhesion; moisture measurement and control; and electromigration. These projects are conducted in conjunction with collaborators from numerous industrial consortia, individual companies, academia, and other government agencies.

The mission of MSEL's program is to develop and deliver to the U.S. electronics and electronic materials industries measurement tools and data for materials and processes used in semiconductor packaging and module interconnection. This program is based upon three primary needs:

- Develop techniques and procedures for making *in-situ*, in-process and in-use measurements on materials and material assemblies having micrometer- and submicrometer-scale dimensions.
- Record and quantify the divergence of material properties from their bulk values as dimensions are reduced and interfaces are approached.
- Develop fundamental understanding of materials needed for future packaging, interconnection and assembly schemes.

More information about this program, and other NIST activities in electronic packaging, interconnection and assembly, is contained in *Electronics Packaging, Interconnection and Assembly at NIST: Guide and Resources*, NISTIR 5817. This publication presents a complete

inventory of NIST's activities in this area and lists information on how to contact project leaders. Copies may be obtained by contacting Michael Schen at (301) 975-6741 or michael.schen@nist.gov.

Significant Accomplishments

- Detailed analysis of transient charge response obtained from thermal pulse instrumentation allows evaluation of the barrier to heat transmission across the interface between a dielectric polymer film and a conducting substrate.
- NMR and NIR spectroscopy have detected liquid-like water as well as molecularly dispersed water in silica-filled epoxy molding compound and a polyimide when equilibrated in liquid water.
- An improved measurement of work of adhesion between solid surfaces using the Johnson-Kendall-Roberts (JKR) technique has been realized by detecting and allowing for the displacement which takes place between the two contacting surfaces.
- X-ray reflectivity has been used to measure the hygroscopic expansion of thin films of polyimide on silicon for a variety of film thicknesses. The results imply the existence of an interfacial region which absorbs much more water than the bulk.

Improved Measurement Technique for Hydrothermal Expansion of Polymer Thin Films

F.I. Mopsik, M.A. Schen, C.K. Chiang, S.C. Roth, and G.T. Davis

Objectives

Determine accuracy and precision of NIST-designed capacitor cell technique for measuring out-of-plane expansion of thin polymer films. Investigate the dimensional stability of electronics packaging materials subjected to temperature and humidity changes. Work with standards-setting bodies to introduce NIST metrology as a new standard test method.

Technical Description

Measurements will be made on a set of well-characterized materials to evaluate the use of a precision capacitance gauge for measuring small dimensional changes in thin films. Studies will be made using this gauge to measure thermal expansion properties of polymer materials used in microelectronics as well as their response to changes in humidity.

External Collaborations

IBM (Endicott), DEC, NRC, NSWC (Crane), Cornell, U. TX (Austin), U. MD, Cornell, Purdue, NASA (JPL), SRC

Planned Outcomes

- Improved standard test method for expansion of thin films.
- reliable data on the expansion behavior of electronic packaging materials with variations in temperature and humidity.

Accomplishments: The NIST-designed capacitance cell for the measurement of thermal expansion of thin polymer films was subjected to tests designed to ascertain accuracy and precision using thin, polished pieces of fused quartz and single crystal silicon cut from a wafer. Prolonged measurements showed that it took too many temperature cycles to achieve elimination of interfacial layers of air between the electrodes and the polished specimens as indicated by gradual drifts in the measured sample thickness. Heating the assembly to moderate temperatures in a vacuum oven shows promise as a measurement protocol to eliminate air layers.

The cell was constructed of Zerodur which has a thermal expansion coefficient of essentially zero. However, in calibration tests, a small temperature-dependent residual capacitance was found which is attributed to a small capacitance involving the Zerodur which has a large variation of permittivity with temperature. Although the residual was reduced by additional shielding, it could not be simply eliminated. A new cell has been designed using quartz electrodes and we are experimenting with metallic films that will be more robust than gold.

An environmental chamber has been purchased and it has been interfaced to a computer. Control has been optimized so that it can run long enough unattended to allow for the slow

equilibrations expected for changes associated with changes in moisture. Also, optimization has been made so that humidity and temperature control will be sufficiently tight to allow for the desired precision in the thickness measurements.

Outputs

Publication

M.A. Schen, F.I. Mopsik, W. Wu, W.E. Wallace, N.C. Beck Tan, G.T. Davis and W. Guthrie, *Advances in the Measurement of Polymer CTE: Micrometer- to Atomic Scale Measurements*, Polymer Preprints **37** 180 (March 1996).

Presentation

G.T. Davis, M.A. Schen, F.I. Mopsik, W.L. Wu, W.E. Wallace, N.C. Beck Tan and W. Guthrie, *Advances in the Measurement of Polymer CTE: Micrometer- to Atomic Scale Measurements*, ACS, New Orleans March 25, 1996.

Thermal Properties Measurement

A. S. DeReggi, P. Bloss

Objectives

Develop laser-pulse-based electrothermal method of measuring (i) the thermal diffusivity of thin dielectric films adhered to substrates, (ii) the thermal resistance of the dielectric-substrate interface of an adhesive layer.

Technical Description

Heat from a laser pulse is used to generate a condenser-microphone-like electrical response from a voltage-biased dielectric specimen that first expands upon gaining thermal energy from the laser pulse and then contracts to its original thickness upon losing this thermal energy to the substrate after diffusive transport across the dielectric. The shape of the electrical response depends on the thermal properties of the dielectric, the thermal barrier properties of the interface, or adhesive layer, and the thermal sinking properties of the substrate.

Curvefitting of the measured response to the theoretical response derived from the heat diffusion equation is used to determine the thermal properties of the dielectric and the characteristics of the thermal contact with the substrate.

External Collaborations

We are collaborating with Prof. Tom Avedesian at Cornell University on his SRC-sponsored project on thermal diffusivity measurements in electronic packaging materials.

Planned Outcomes

- New thin film thermal metrology methods.
- Reliable data of thermal properties of polymeric electronic packaging materials.

Accomplishments

- The mathematical techniques for extracting the parameters of interest from the transient charge response following the thermal pulse have been proven reliable by using simulated data.
- Error analysis and establishment of minimum measurement accuracy has been performed.
- A new sample chamber has been designed and constructed.
- Experimental measurements on polyimide and FEP films glued to a conducting substrate yielded thermal diffusivities of the films which agree with literature values. The thermal barrier deduced for the glue layer of conducting epoxy was also consistent with the thickness and reported conductivity of the epoxy.

Outputs

Publications

Aimé S. DeReggi and Sigfried Bauer, *Adaptation of the thermal pulse method to the measurement of the thermal diffusivity of dielectric films on conducting substrates*, 1995 Annual Report of Conf. on Electr. Insul. and Diel. Phenom., pp. 536-539. IEEE Pub. No. 95CH35842.

Peter Bloss, Aimé S. DeReggi, and Hartmut Schafer, *Adaptation of the thermal pulse method to the determination of thermal parameters of thin layers*, Proc. 9th Int. Symp. on Elect., pp. 684-689 (1996). IEEE Public. No. 96 CH35808.

Peter Bloss, Aimé S. DeReggi, and Hartmut Schafer, *Application of the regularization technique to the deconvolution of thermal pulse data*, Proc. 9th Int. Symp. on Elect., pp. 171-176. IEEE Public. No. 96 CH35808.

Peter Bloss, Aimé S. DeReggi, and Hartmut Schafer, *Thermal properties and electric field profile in metallized dielectric film adhesively bonded to substrate*, 1996 Annual Report of Conf. on Electr. Insul. and Diel. Phenom., pp. 721-725. IEEE Pub. No. 96CH35985.

Presentations

A.S. DeReggi and S. Bauer, *Adaptation of the Thermal Pulse Method to the Measurement of the Thermal Diffusivity of Dielectric Films on Conducting Substrates*, Conf. Elec. Insul. and Dielec. Phenom., Virginia Beach, VA October 23, 1995.

A.S. DeReggi, *Thermal Pulse Investigation of the Generation, Transport and Trapping of Space Charge in Microelectronics Buried Oxide Structures*, Conf. Elec. Insul. and Dielec. Phenom., Virginia Beach, VA October 23, 1995.

Industry Coordination and Workshops in Electronic Packaging

Michael Schen

Objectives

Enhance NIST's role and effectiveness in metrology for electronics packaging, interconnection and assembly by coordinating and cooperating with U.S. industry and other government agencies in technology planning, infrastructure research and development, implementation of industry established technology roadmap research priorities, and technology benchmarking.

Technical Description

The NIST materials program in electronics packaging, interconnection and assembly has the role of helping the U.S. microelectronics and electronic materials industries identify, develop and use improved materials technology for the design, manufacture and reliability assessment of new electronics products and processes. As part of this, NIST takes an active role in working closely with companies, associations, consortia, universities and other government agencies in a number of different fashions; all aimed at enhancing the linkage between industry's measurements and standards needs and NIST's research. The methods being used to accomplish this and build NIST's contribution to this business arena include the following activities:

- participate in national technology planning activities,
- incorporate industry established technology roadmap priorities into NIST's research efforts,
- conduct research in measurement science to support the Nation's electronic materials and microelectronics infrastructure,
- apply NIST competencies to industry driven development exercises,
- cooperate in the evaluation of technical and manufacturing capabilities of industry,
- disseminate information related to its program and its capabilities to U.S. planners and practitioners, and
- conduct industry-led workshops to enhance the exchange of information between the diverse businesses and organizations supporting the microelectronics industry and government bodies.

External Collaborations

In FY 1996, significant coordination and workshop collaborations took place with the following organizations:

- Private Firms IBM Endicott
 - Intel
 - Motorola
 - National Semiconductor
- Government Defense Advanced Research Projects Agency
 - Department of Commerce, Technology Administration
 - Department of Energy
 - National Aeronautics and Space Administration
 - National Science Foundation
 - Naval Research Laboratory
 - Office of Science and Technology Policy
 - United States Air Force, Rome Laboratory
- Associations Institute for Interconnecting and Packaging Electronic Circuits
 - Optoelectronics Industry Development Association
 - Semiconductor Industry Association
- Consortia Semiconductor Research Corporation (SRC)
 - SEMATECH
 - Interconnection Technology Research Institute (ITRI)
 - National Center for Manufacturing Sciences (NCMS)
 - National Electronics Manufacturing Initiative (NEMI)

Accomplishments

In FY 1996, NIST and the President's National Science and Technology Council's (NSTC) Electronic Materials Working Group (EMWG) also released a report, *Beyond the Technology Roadmaps: An Assessment of Electronic Materials Research and Development*, NISTIR 5777. This report assesses the R&D needs of U.S. industry in electronic materials. The report covers industry's short and long term materials issues in microelectronics, photonics, RF & microwave technologies, mass storage, module interconnects, materials characterization, and research opportunities. NIST participates along with other government agencies that have activities in electronic materials in the EMWG to enhance the efficient utilization of government resources and coordinate among agencies. The EMWG was established to support the activities of both the Materials Technologies and the Electronics Subcommittees of the NSTC's Civilian Industrial Technology Committee. It has the objective of pursuing methods to team industry groups and government agencies to create a national strategy in high leverage and/or critical materials and material processing technologies to significantly enhance U.S. competitiveness in electronics and supporting industries, and to provide a forum, knowledge base and recommendations for coordination among government agencies.

In the areas of infrastructure research and development and implementation of technology roadmap research priorities, NIST is cooperating with the Semiconductor Research Corporation (SRC) and SEMATECH in a number of ways to better link NIST's activities to industry's needs and SRC and SEMATECH activities. In the case of the SRC, NIST is a

participating member of the SRC Packaging Science's Technical Advisory Board and has become a mentor for a number of their individual research projects in packaging. Technical collaborations between SRC award recipients and NIST have also taken place. NIST has also built new links to SEMATECH's Assembly and Packaging efforts through its involvement in SEMATECH workshops and programs.

NIST continues to work closely with the Institute for Interconnecting and Packaging Electronic Circuits (IPC), which represents the printed wiring board and assembly industries, in the roadmapping of their technology needs for the early part of the next century as well as their standards activities. NIST is a member of the IPC Roadmap Steering Committee and contributed substantially to their 1996 report, *Technology Benchmarking: Worldwide Competitive Analysis of Electronic Interconnections*. NIST is also a member of the IPC's Test Methods Subcommittee (7-11) and made major contributions to newly issued IPC test methods. At the IPC's 1996 Capital Hill Day event, NIST Director Arati Prabhaker was the invited banquet speaker and spoke about Government and NIST's continued support for this business segment.

Workshops are an extremely important tool for NIST to not only understand industry's greatest needs but to also foster technical exchange between researchers and technologists within public and private sectors. In addition to sponsoring workshops, members of NIST's packaging team also participate in a large number of other industry and government sponsored workshops throughout the year. Since the inception of our program in electronic packaging materials, NIST has conducted the following industry workshops:

- *6th International Workshop on Moisture in Microelectronics*, sponsored by NIST and the U.S. Air Force Rome Laboratory, October 15-17, 1996, Gaithersburg, MD.
- *Materials Metrology and Data for Commercial Electrical and Optical Packaging and Interconnection Technologies*, sponsored by NIST, Institute for Interconnecting and Packaging Electronic Circuits, Optoelectronics Industry Development Association, Semiconductor Research Corporation, May 5-6, 1994, Gaithersburg, MD.
- *Workshop on Moisture Measurement and Control for Microelectronics*, sponsored by NIST and the U.S. Air Force Rome Laboratory, April 5-7, 1993, Gaithersburg, MD.
- *Measurement of the Properties of Materials in Microelectronic Packaging*, sponsored by NIST, Semiconductor Research Corporation, Microelectronics and Computer Technology Corporation, Microelectronics Center of North Carolina, U.S. Army Harry Diamond Laboratory, U.S. Air Force Wright Research and Development Center, and U.S. Naval Weapons Support Center, May 1-3, 1990, Gaithersburg, MD.

Impacts

Over 300 copies of NISTIR 5520, *Metrology and Data for Microelectronic Packaging and Interconnection*, have been distributed among companies, consortia, associations, universities and other government agencies. This report remains the only public document that builds

upon technology roadmaps for the microelectronics industry to identify fundamental challenges in materials science and engineering for electronics packaging.

To date, NIST has distributed nearly 3000 copies of its report *Electronics Packaging, Interconnection and Assembly at NIST: Guide and Resources* to U.S. companies, universities, associations, and consortia. At the 1996 Semicon West Expo, this report, commonly referred to as the 'yellow book,' was the most sought after item at the NIST exhibition booth. In addition, as a consequence of the publication, NIST has hosted a number of visitors wishing to tap into the organization's competencies. It is our view this and future similar reports will be essential towards insuring NIST's technical contributions reach the right people at the right time.

The Electronic Materials Working Group report, *Beyond the Technology Roadmaps: An Assessment of Electronic Materials Research and Development*, NISTIR 5777, has also seen wide distribution since its publication this year. To date over 1000 copies have been requested. The report, the first of its kind to comprehensively assess materials R&D issues across today's electronic and optical technologies, is being used by planners and practitioners from industry, government and academia.

NIST took a leadership role this year in reviewing and enhancing a number of new IPC test methods originating from the Deposited Dielectrics Task Group. Enhancement of the seven new test methods by NIST was recognized by the IPC and the Chairman of the IPC Test Methods Subcommittee as "a valuable contribution" by NIST and recommended that NIST's recommended changes be incorporated into the final standards.

Outputs

Publications

Michael A. Schen, ed., NISTIR 5817, *Electronics Packaging, Interconnection and Assembly at NIST: Guide and Resources*, April 1996.

Michael Schen, Thomas J. Russell, Robert F. Leheny, Henry Simon, Verne Hess, Gerald Borsuk, eds., NISTIR 5777, *Beyond the Technology Roadmaps: An Assessment of Electronic Materials Research and Development*, MatTech Electronic Materials Working Group report, March 1996.

Michael A. Schen, ed., *Government and Industry Relations*, in "Technology Benchmarking: Worldwide Competitive Analysis of Electronic Interconnections," IPC June 1996.

M.A. Schen, G.T. Davis, F.I. Mopsik, W.L. Wu, W.E. Wallace, J.R. Manning, C.A. Handwerker, D.T. Read, *Electronics Packaging Materials Research at NIST*, Mat. Res. Soc. Symp. Proc., 390, 19-31, 1995.

M.A. Schen, R. Scace, T. Leedy, *NIST Strategies, Activities and Collaborations in Electronics Packaging, Interconnection and Assembly*, Proceedings of the Eleventh Biennial University, Government, Industry Microelectronics Symp., IEEE Catalog #95CH35779, Austin, TX, 1995

M.A. Schen, G.T. Davis, F.I. Mopsik, W.L. Wu, W.E. Wallace, J.R. Manning, C.A. Handwerker, D.T. Read, *Electronics Packaging Materials Research at NIST*, in Electronic Packaging Materials Science VIII, R.C. Sundahl, K.A. Jackson, K-N. Tu, P. Børgesen, ed., Proceedings of the Materials Research Society (Materials Research Society, Pittsburgh, PA) 390, pgs. 19-32, 1995.

Presentations

M.A. Schen, *NIST's Activities in Packaging and Interconnection*, SEMATECH/ITRI Workshop, Moisture in Microelectronics, Austin, TX, March 1996.

M.A. Schen, *Competitive Analysis of World Products*, IPC Printed Circuits Expo, San Jose, CA, March 1996.

M.A. Schen, *Technical Advances in Materials for Electronics Packaging and Interconnection: A Report on NIST Research*, ISHM Capital Chapter, Columbia, MD, November 1995.

M.A. Schen, *Electronic Packaging Measurement Capabilities at NIST*, Chesapeake Electronics Show, Greenbelt, MD, November 1995.

M.A. Schen, *Implications of the National Semiconductor Roadmap for Module Interconnection and Assembly*, IPC Roadmap Steering Committee, Tempe, AZ, 1995.

M.A. Schen, *NIST Strategies, Activities and Collaborations in Electronics Packaging, Interconnection and Assembly*, Eleventh Biennial University, Government, Industry Microelectronics Symposium, Austin, TX, 1995.

Ultra-thin Polymer Films

W. Wu, W.E. Wallace, E.K. Lin, G.T. Davis

Objectives

Determine the role of interfaces on the properties of polymers by measuring the properties of ultra-thin polymer films adhered to well characterized substrates. Measure the thickness at which properties of thin films depart from those of the bulk material. Compare results with statistical mechanics calculations using a self-consistent mean-field procedure.

Technical Description

The physical properties of polymer thin films are measured using a variety of techniques including specular and off-specular x-ray and neutron reflectivity, energy-dispersive x-ray reflectivity, total external reflectance x-ray fluorescence, MeV ion scattering, atomic force microscopy, and ellipsometry. For single-component films, the physical properties measured include the coefficient of thermal expansion, glass transition temperature, and density. For liquid crystal materials, the density profiles were determined and correlated with an isotropic liquid crystal transition zone near the interface. For multicomponent films, interdiffusion dynamics and interfacial segregation are measured. Surface roughness is examined through a combination of off-specular reflectivity and atomic force microscopy. Typical materials considered include polystyrene, poly(methyl methacrylate), polyvinyl pyridine, polyimides, and epoxies. By varying the thickness of the film, the type of polymer and its molecular weight, the sample temperature and environment, and the film substrate surface, fundamental physical insight is gained into the behavior of polymer molecules at impenetrable interfaces. The experimental results are compared with self-consistent mean field calculations to build a theoretical framework for future predictions of polymer film properties. In the course of this work, new techniques have been developed to aid in measuring the subtle properties of polymer thin films. These include a new theory to interpret off-specular reflectivity data and a new method of x-ray reflectivity to determine thin film density.

External Collaborations

Gelest, Inc., University of Pennsylvania, U. Tennessee, U. Delaware, Army Research Laboratory, Sandia National Laboratory

Accomplishments

- Developed a new theory to quantify surface roughness from off-specular reflectivity data.
- Developed a method that improves the accuracy in the measurement of thin film density by at least a factor of five.
- Demonstrated that the polymer thin film coefficient of thermal expansion depends sensitively on the substrate surface for film thicknesses up to three times the polymer radius of gyration.
- Discovered that the polymer interdiffusion dynamics are significantly retarded for interfaces within several polymer radii of gyration of an impenetrable interface.

Outputs

Publications

W.L. Wu, W.E. Wallace, J.H. van Zanten, B.J. Bauer, D.W. Liu, and A. Wong, *Diffusion of Linear Polystyrene into Crosslinked Polystyrene*, Polymer (in press).

W.E. Wallace, W.L. Wu, and R.A. Carpio, *Chemical-Mechanical Polishing of SiO₂ Thin Films Studied by X-Ray Reflectivity*, *Thin Solid Films* **280** (1996) 37.

J.H. van Zanten, W.E. Wallace, and W.L. Wu, *Substrate Interaction Induced Transitions in Ultrathin Polymer Films*, *Physical Review E* **53** (1996) R2053.

W.E. Wallace and W.L. Wu, *Determining Thin Film Density by Energy-dispersive X-ray Reflectivity: Application to a Spin-on-Glass Dielectric*, *Materials Research Society Proceedings* **406** (in press).

W.L. Wu, *Application of Off-Specular X-ray Reflectivity to Surface Characterization*, *SPIE Proceedings*, Denver, (1996) in press.

Presentations

W.E. Wallace, *Analysis of Silica Thin Film Derived from Pyrolysis of Polysilsesquioxanes*, MRS, San Francisco, CA April 10, 1996.

W.E. Wallace, *A Novel Method for Determining Thin Film Density by Energy Dispersive X-Ray Reflectivity*, MRS, Boston, MA November 29, 1995.

W.E. Wallace, *Gas Absorption During Ion Irradiation of a Polymer Target*, MRS, Boston, MA November 28, 1995.

W.L. Wu, *Molecular Structure of Bimodal Epoxy Networks*, Workshop on Development and Characterization of Inhomogenieties during Network Formation, Czech Republic Academy of Science, Prague, Czech Republic, September 16, 1996.

W.L. Wu, *Molecular Structure of Bimodal Epoxy Networks*, Gordon Research Conference on Thermosetting Resins, Plymouth State College, Plymouth, NH, July 9, 1996.

W.L. Wu, *Application of Off-Specular X-Ray Reflectivity for Surface Characterization*, SPIE-International Society of Optical Engineering, Denver, CO August 8, 1996.

W.L. Wu, N.C. Beck Tan, B.J. Bauer, J. Plestil and K. Dusek, *Structure in Bimodal Epoxy Networks*, APS, St. Louis, MO March 20, 1996.

W.L. Wu, *Diffusion of Linear Chains into Crosslinked Networks*, Intersociety Polymer Conference, Baltimore, MD October 8, 1995.

Dielectric Measurements of Thin Films from DC to 1 GHz

F. I. Mopsik, C.K. Chiang, S.C. Roth, and G.T. Davis

Objective

Inductance-Capacitance-Resistance bridges (LCR meters) are designed for accurate measurements over a discrete range of frequency, often with constraints on the sample configuration. The objective of this project is to establish measurement protocols and sample configurations for the accurate determination of dielectric constant and loss at frequencies from DC to 1 GHz of thin polymeric films important to the electronic packaging industry, many of which can be obtained only as these thin films.

Technical Description

Measurements will be made with known standards and films to establish the LCR meter limits. Measurements will include the use of other methods, such as the Time Domain Spectrometer to evaluate and extend the measurement range in a known way. Sample configurations and data reduction methods will be determined to optimize the film parameters.

Planned Outcomes

We expect to develop a sample configuration and measurement protocol for the accurate measurement of dielectric constant and loss of thin films for frequencies approaching 1 GHz. The method is expected to provide consistent results for both producers and users of polymeric resins used in electronic packaging. Current standards apply to lower frequencies and thicker materials.

Accomplishments

The LCR meters that operate to 30 MHz were shown to be much more reproducible, uncertainties of less than 1%, if a coaxial admittance is directly connected to their terminals. No 4-wire configuration could achieve this level of precision. Calibration procedures showed, however, that the bridges still had significant systematic errors approaching 5%. If 100 ohm or 50 ohm resistance standards were used, it was found that measurements on a broad range of standard, high frequency capacitors from 10 to 1000 pF could be recomputed so that the errors, referred to the terminals of the bridge, could be made to much less than 1%, including loss uncertainty.

For polymer samples made from low loss polypropylene, this accuracy still held if they were mounted directly at the bridge terminals. This was true even up to near 1 GHz using a Coaxial LCR meter. For temperature control, however, the samples will have to be mounted at the end of precision coaxial air-filled lines. For this case, good results were found if the admittance was measured at the bridge terminals using the proper calibration procedures. The sample is then evaluated at the other end of the line using values determined directly on the line by direct propagation using transmission line theory.

The main remaining issues are the estimation of residual jig capacitances, the variation of the propagation constant of the air line with temperature and the best estimation of the samples geometric capacitance for a predetermined electrode configuration.

Outputs

Publication

F.I. Mopsik, *Dielectric Relaxation Phenomena in Composite Systems*, MRS Proceedings Fall 1995.

Presentation

F.I. Mopsik, *Dielectric Relaxation Phenomena in Composite Systems*, MRS, Boston, MA November 29, 1996.

Residual Stress in Polymer Films Adhered to Silicon Substrates

A. S. DeReggi, C. K. Chiang

Objectives

Evaluate wafer bow technique for deducing the residual stress in polymer-coated silicon wafers resulting from differential contraction after cure. Investigate all factors affecting measurement and modeling of such stress.

Technical Description

Average wafer curvature is determined, using a commercial instrument and accompanying software, from measurements of the reflection angle of a near-normal-incidence laser beam, at 50 points sampled while the incident beam is scanned linearly along a diameter of a wafer. A temperature-regulated wafer holder allows varying the temperature in a user-determined program in the range from ambient to 500 °C, allowing the monitoring of wafer bow while a polymer precursor solution spin-coated on the wafer is heated to a curing temperature and is then cooled back to room temperature. An enclosure allows controlling the atmospheric environment of the wafer-supported polymer film. Sources of errors are identified and measurement protocols are being developed.

Accomplishments

- Showed that bow of polyimide-coated silicon wafer depends strongly on the relative humidity of its atmospheric environment.
- Proposed fast-responding humidity sensor based on measurement of capacitance of air gap between uncoated bowed wafer surface and a planar counter-electrode.
- Showed that stress measurement must take account of relative humidity.

Moisture Effects in Electronic Packaging Polymers

M.A. Schen, D.L. VanderHart, B. Dickens, G.T. Davis

Objectives

Develop measurement approaches that allow the determination of the physical nature and distribution of water within filled polymer systems and apply these approaches to the evaluation of industrial materials and processes used in the manufacture of semiconductor packages, electronic interconnects or assembled systems.

Technical Description

Two individual investigations have been underway in FY 1996 related to measuring the effects of moisture in polymeric dielectrics and filled polymer resins used in electronic packaging applications. One of the key reliability and performance issues associated with the manufacture and use of electronic systems that utilize either plastic semiconductor packages or multilayer polymer interconnects is the effects of moisture on the mechanical reliability of the polymer encapsulant, in the case of plastic packages, or on the electrical performance of the interlayer dielectric, in the case of multilayer interconnects. Consequently, metrology aimed at documenting the effect of moisture on the reliability performance characteristics of industrially important materials is vital as more widespread utilization of plastics in packaging occurs.

In the first activity, NIST uses solid state proton NMR to: a) characterize the state of water in plastic encapsulant materials (mold compound); b) identify the presence of and the amount of void volume in these materials; and c) ascertain whether these voids contribute to package delamination and/or cracking, commonly referred to as 'popcorning' during solder reflow.

In the second activity, NIST employs near infrared, NIR, spectroscopy to yield information on the physical state of absorbed moisture in polyimide films. The frequency of the NIR absorbance of a water molecule depends on the hydrogen bonding of the molecule. Furthermore, since the absorbance is weak, samples much thicker than those required for the mid IR range can be examined (typically 25 μm to 1 cm).

External Collaborations

National Semiconductor, DARPA's Plastic Packaging Consortium (this includes National Semiconductor, Amoco Electronic Materials Plaskon Division, Integrated Packaging Assembly Corp., Sheldahl Corp., Olin Corp., Dexter Electronic Materials, Sandia National Laboratories, Delco Electronics, Leading Technology Corp.)

Planned Outcomes

Provide industry with convenient metrology tools to examine moisture ingress into mold compounds on a molecular scale beyond simple weight uptake.

Provide experimental data which will validate or invalidate the appropriateness of commonly used conditioning treatments, for example steam ageing, for the accelerated testing of moisture sensitivity of mold compounds. NIST will work with standards bodies, such as IPC and JEDEC, and individual companies to refine current practices and standards.

Accomplishments

In the solid state NMR studies, a 'typical' cresol-novolac compounding material, supplied via a collaboration with National Semiconductor, has been examined. It was demonstrated that NMR is capable of distinguishing water distributed in the polymer matrix from water that is self associated within regions believed to be voids within the mold compound.

Results from these studies led to the following conclusions:

- a) Of the total water picked up by the mold compound, about three fourths becomes associated with the matrix and one fourth associates as liquid water within voids after sample equilibration in liquid water. By measuring the amount of water in voids, the void content has been assessed to be about 0.2 % of the overall volume.
- b) Voids do not contain liquid water after equilibration at 89 % relative humidity (RH) and 29 °C, but rather, fill with water at RH levels somewhere between 89 % and 100 %. This late-filling behavior for the voids is anticipated on the basis of thermodynamic arguments.
- c) It is unlikely that voids act as reservoirs for liquid water, even when electronic assembly is carried out in warm, humid climates.
- d) Voids, as formed, do not appear to provide a low-resistance, interconnected path to surfaces.
- e) Rapid heating of mold compound to simulate solder reflow conditions does not appear to change the rate at which water within the voids empty upon exposure to vacuum. Hence, rapid heating of encapsulant previously exposed to high humidity conditions does not generate persistent, new, low-resistance paths for water to escape.
- f) Simulation of solder reflow for mold compound previously exposed to high humidity conditions leaves a 400-micron thick specimen thoroughly dry. Consequently, moisture will migrate during reflow to encapsulant surfaces and interfaces where it can either escape or accumulate.

The NIR spectra of water were examined as function of concentration in a variety of polar and non-polar organic solvents. It was established that a good correlation exists between the quantity of water present and the area under the NIR absorption peak from 5400 to 4000 cm^{-1} , even though the shape of the peak changes significantly. Comparing the spectra of water absorbed by polyimide films equilibrated at a variety of relative humidities with those obtained from various solvents reveals that the water absorbed by polyimides is molecularly dispersed, as opposed to being in water clusters, even when equilibrated in liquid water. When filled with unsilanized silica and equilibrated at high humidities, polyimide films do show evidence for accumulation of liquid-like water. The NIR spectra of neat samples (unfilled) of a cresol-

novolac epoxy encapsulation resin when soaked in water for two days did not differ from the same resin equilibrated with room air (nominally 25 °C and 50 % RH).

Outputs

Publication

David L. VanderHart, *Partitioning of Water Between Voids and the Polymer Matrix in a Molding Compound by Proton NMR*, Proceedings of 6th International Workshop on Moisture in Microelectronics, sponsored by NIST and the U.S. Air Force Rome Laboratory, Gaithersburg, MD, Oct. 15-17, 1996.

Presentations

M.A. Schen, *Moisture and Stress Measurements at NIST*, Technology Reinvestment Program Plastic Packaging Consortium, Sheldahl, Longmont, CO September 10, 1996.

N.C. Beck Tan, W.E. Wallace, W.L. Wu and G.T. Davis, *Interface Effects on Moisture Absorption in Thin Polyimide Films on a Silicon Substrate*, MRS, Boston, MA November 29, 1995.

Interfacial Energy between Solids

W. Wu, Pearl Chin and G.T. Davis

Objective

Improve the Johnson-Kendall-Roberts (JKR) technique for measuring the interfacial energy between solids by allowing for nonlinear elastic effects and finite size effects in the data analysis.

Technical Description

The interfacial energy between polymers and solid substrates is an important parameter controlling the structure and physical properties of polymers near the interface. The JKR technique has been demonstrated as a viable method for determining interfacial energies. To improve the accuracy of the measurement, the displacement as well as the contact area are measured simultaneously, this is in contrast to all the JKR work published so far where the only parameter measured is the contact area. In addition, a methodology has been established to identify and to discriminate regions where the nonlinear elastic effect and the finite size effect render the results inapplicable to the current JKR theory. Efforts have also been started to modify the JKR theory to accommodate these effects. To improve the precision of this measurement, work is now in progress to automate the data acquisition and analysis.

External Collaboration

Pearl Chin recently obtained her Ph D from the University of Delaware under the guidance of Prof. Roy McCullough in the Department of Chemical Engineering and performed her experimental work on the JKR technique at NIST under the guidance of Dr. Wen-li Wu.

Accomplishments

- An instrument has been constructed which enables the simultaneous measurement of contact area and displacement.
- A methodology has been developed to identify the data domain over which the JKR theory in its current form is applicable.

Outputs

Publications

P. Chin, *Characterization of Polymer-Solid Adhesion*, PhD Thesis, University of Delaware, (1996).

P. Chin, R.L. McCullough and W. Wu, *An Improved Procedure for Determining The Work of Adhesion Between Polymer-Solid Contact*, J. Of Adhesion Science (submitted)

Aging of Light Emitting Polymers

G.T. Davis, E. Etedgui, and C.K. Chiang

Objective

Determine the important parameters and underlying mechanisms responsible for the time-dependent decay of light intensity from electroluminescent polymer devices.

Technical Description

The examination of polymer devices using optical, scanning electron and atomic force microscopies reveals how device morphology evolves during operation as well as during storage. Absorption and fluorescence spectra of polymer devices give a global (not spatially resolved) indication of the optical properties of the electroluminescent polymer. These may indicate useful changes in the light emission properties of the polymer as a result of surface treatments. Imaging the polymer devices during operation using a CCD camera reveals the spatial distribution as well as time dependent evolution of the electroluminescence intensity. Electrical impedance spectroscopy measures changes in the electrical characteristics of polymer devices non-destructively during operation as well as during storage.

External Collaborations

We are collaborating with Prof. Frank Karasz and his group at the University of Massachusetts who are supplying polymer samples and light emitting devices.

Accomplishments

- Investigations have concentrated on two electroluminescent polymers, poly(*p*-phenylenevinylene) and a copolymer of derivatized phenylene vinylene and dioxyoctane.
- Optical and scanning electron microscopies revealed that the metal cathode overlying the polymer layer breaks down by forming holes which grow until they become adjacent to one another and merge. Eventually, the electrical continuity of the cathode is compromised and the device ceases to function.
- Optical and scanning electron microscopies also revealed that the polymer film itself may not be stable since its morphology gradually evolves in a manner reminiscent of dewetting during storage in ambient atmosphere. The resulting loss of polymer film integrity leads to catastrophic device failure after a few seconds of operation.
- Cathode formation by the deposition of metal on the polymer film affects the absorption and fluorescence properties of the device depending on the metal. A gold layer 40 Å thick attenuates the fluorescence intensity by 50 % and results in the formation of a new broad absorption band centered at approximately 630 nm. Removing the gold restores the device to its original state. Aluminum deposition, on the other hand, does not appear to affect either the fluorescence intensity or the absorption spectrum of the device.
- Areas of inhomogeneity in the polymer film appear when imaging the electroluminescence intensity distribution across the device using a CCD camera. These areas correspond to some regions of non-uniform film thickness as found using optical and atomic force microscopies, suggesting a dependence of device failure on polymer film uniformity.
- Impedance spectroscopy reveals changes in the interface between the electrode and the polymer following device degradation.

Outputs

Publication

E. Ettetdgui, G.T. Davis, B. Hu and F.E. Karasz, *Degradation of Polymer Based Light Emitting Diodes during Operation*, Synthetic Metals (in press).

Presentation

E. Ettetdgui, G.T. Davis, B. Hu and F.E. Karasz, *Degradation of Polymer Based Light Emitting Diodes during Operation*, International Conference on Science and Technology of Synthetic Metals, Salt Lake City, UT August 2, 1996.

POLYMER BLENDS AND PROCESSING PROGRAM

Applications of polymer blends continue to enjoy growth in terms of market share, consumption, and employment within the plastics industry. This growth challenges the flexibility of materials suppliers to meet customer needs with new materials and reduced product development cycles. The futility of trial and error approaches to address these challenges led industry to solicit measurement tools and methods of analysis which enhance their efforts to understand and control resin compatibility, phase morphology, and material properties. These demands have been further sharpened by the advent of new methods which provide better control in polymer synthesis and therefore more precise definition of blend components.

The Polymer Blends and Processing Program began with clear scientific goals to establish expertise in static and kinetic aspects of phase behavior in polymer blends, effects of shear flow on mixing and separating, and reactive processing to promote compatibility. The focus on these areas furthers program objectives by accelerating development of new measurement tools, including specialized light and neutron scattering methods, and by applying those tools to expand the knowledge base for thermodynamics and kinetics of polymer blends. Work extends to the effects of a copolymer additive in a blend system, the relative behavior of blends in bulk compared to in thin films at interfaces, and the effects of complex thermal and mechanical histories on the phase separation. Fundamental advances in theory and modeling continue to guide and interpret the measurements.

Current research in the program has four areas of emphasis: measurement technology for on-line characterization of temperature, phase behavior, and shear deformation; shear effects on phase diagrams and phase morphology; activity of additives, compatibilizers, and fillers; and control of interfacial effects in blends and during processing. In each of these areas the program works with industry to develop measurement methods using tools of fluorescence, light scattering, neutron scattering and reflectivity, x-ray scattering, birefringence, microscopy (AFM, TEM, phase contrast), and rheology. CRADA partners and other active industrial collaborators include: Aristech Chemical, Armstrong World Industries, Dendritech, Dow Chemical, Dow Corning, DuPont, Dynisco, Exxon, Kodak, GE, Goodyear, Mobil, Raychem, Rohm and Haas, and 3M.

In order to promote communication and technology transfer with an even broader range of industrial partners the Polymer Blends and Processing Center has been established. The focus of the center is efficient adoption of measurement technologies developed at NIST and assessment of new research directions for the polymer blends and processing program. The Center is an outgrowth of the successful completion of two industrial consortia, the Polymer Blends Consortium and the Measurements for Polymer Processing Consortium and is intended to facilitate even greater participation by industrial scientists.

Significant Accomplishments

- Phase separation kinetics of a model polystyrene-polybutadiene blend during shear was measured by light scattering and phase contrast microscopy in collaboration with Goodyear.
- Measurements demonstrated homogenization of phase separated polymer blends by mixing under steady shear flow. Analysis and interpretation of the data was based on macroscopic theories of Taylor and Tomotika together with the renormalization and scaling calculations of Onuki and Kawasaki.
- Steady shear behavior of a solvated model polymer blend sample in the two-phase region was measured using fluorescence microscopy. In order to establish a scaling approach to understand shear mixing, phase compositions as a function of shear rate and temperature were obtained.
- The relationship between compatibilizer type and resultant morphology was established by synthesizing compatibilizers of random and graft copolymers having athermal or strong interactions and studying melt blends of immiscible polymers with and without these compatibilizers.
- The shift of phase boundary arising from the addition of diblock and triblock copolymers, and small molecule additives, to polymer blends was measured and are in qualitative agreement with recent theory of such additive induced phase boundary shifts.
- Demonstrated excellent agreement between optical birefringence and small angle neutron scattering measurements of pressure induced phase transition of diblock copolymer.
- Pressure induced shifts in miscibility of polyolefin blends were measured via cloud point technique in collaboration with Exxon.
- Phase separation and kinetics in ultrathin blend films were measured to demonstrate suppression of surface induced phase separation and a transition to the behavior of two dimensional fluid mixtures. Results are in agreement with numerical simulations of phase separation in 2-D.
- Demonstrated the effectiveness of diblock copolymers as compatibilizers in thin films of polymer blends by observation of suppressed surface pattern formation.
- A patent application was filed for a temperature profile sensor based on confocal optics and which fits the standard instrumentation port of processing machines. The

sensor was demonstrated by measuring temperature profiles in polyethylene resin during extrusion. The results were consistent with expected effects of shear heating in the barrel of an extrusion machine.

- A new class of fluorescent dyes was identified which can be used as sensor probes at the higher temperatures employed during polymer processing.
- Established solvent conditions that promote micelle formation in ionic graft copolymers. The micelles were characterized using dynamic light scattering, small angle neutron scattering, and TEM.
- Small angle neutron scattering and solvent contrast matching were used to characterize the preferential absorption of small organic molecules into the interior of the micelles as a function of micellar geometry.
- The distribution of condensed counterions associated with the charged terminal units of polyelectrolyte dendrimer molecules in solution was characterized by small angle neutron scattering.
- Demonstrated that the so-called “extraordinary regime” dynamic light scattering and “anomalous” static scattering, usually observed in salt free aqueous polyelectrolyte solutions, is an ionic effect by measurements in non-aqueous polar solvents which are also good solvents for the neutral chain backbone.
- Small angle neutron scattering was combined with static light scattering to cover three decades of q space and scattering intensity to characterize the static scattering from polyelectrolyte solutions. Observation of a peak at high scattering wavevector and upturn at low scattering vector demonstrate that fluctuations occur on multiple length scales in polyelectrolyte solutions.
- Annual meetings of the Polymer Blends Consortium and Measurements for Polymer Processing Consortium were held. An anthology of research accomplishments from the past decade of polymer blends and processing work at NIST was prepared and distributed to members. The two consortia were merged to establish the new Polymer Blends and Processing Center.

Thermodynamics and Kinetics of Polymer Blends

J. Douglas, C. Han, B. Bauer, D. Liu, D. Johnsonbaugh, L. Sung, S. Kim, C. Gettinger, C. Jackson

Objective

The objective is to establish measurement techniques and analysis procedures to characterize phase separation in polymer blends. This project provides support for all other projects which may focus on specific factors, including effects of shear, additives, compatibilizers, pressure, and chemical reactions.

Technical Description

- Study influence of finite-size constraints on phase separation of polymer blend thin films by optical microscopy and develop theoretical framework for interpreting these measurements.
- Investigate influence of block copolymer additives on the kinetics of blend phase separation in the bulk and in blend films having a range of thicknesses.
- Study late-stage phase separation in reactive phase separating blends and develop models of inhibited coalescence and the novel morphologies observed in these systems.
- Measure coexistence curve and scattering data (light and neutron) of blends diluted by additives to determine the extent of critical exponent renormalization.

External Collaborations

- University of Chicago - Collaboration to examine the shift of the phase boundary of blends with additives.
- Pennsylvania State University - Collaboration to study the influence of finite film thickness on blend phase stability by numerical simulation.
- Yamagata University - Collaboration to study the influence of finite film thickness and surface interactions on phase separation models by lattice enumeration methods.

Accomplishments

- Investigated influence of block copolymer additives on the kinetics of blend phase separation in the bulk and in blend films having a range of thicknesses.
- Phase separation and kinetics in ultrathin blend films were measured to demonstrate suppression of surface induced phase separation and a transition to the behavior of a two dimensional fluid mixtures. Results are in agreement with numerical simulations of phase separation in 2-D.
- Determined kinetics of phase separation in bulk blends with and without symmetric block copolymer additives. Demonstrated slowing down of phase separation kinetics of blend films with additives and inhibition of late stage hydrodynamic coarsening.

- Measured shift of phase boundary arising from the addition of diblock and triblock copolymers to polymer blends and compared results to recent theory of such additive induced shifts on the phase boundary.
- Measured shift of critical exponents of blends by block copolymer and small molecule additives.
- Investigated role of chemical reaction on late stage blend phase separation. Observed inhibited blend coalescence in these reactive systems.

Outputs

Publications

L. Sung, A. Karim, J.F. Douglas, and C.C. Han, *Dimensional Crossover in the Phase Separation Kinetics of Thin Polymer Blend Films*, Physical Review Letters 76,4368(1996).

A. Karim, J.F. Douglas, L. Sung, and B. Ermi, *Influence of Dimensionality on the Phase Separation Kinetics of Blend Films*, American Physical Society News, in press.

L.L. Sung, and C.C. Han, *Light-Scattering Studies on Phase Separation in a Polymer Blend with Addition of Diblock Copolymer*, Journal of Polymer Science, Physics Edition, 37, 2405 (1995).

A. Karim, J.F. Douglas, S.K. Satija, A.P. Wong, and C.C. Han, *Phase Separation in Chemically Reactive Polymer Blend Films*, Macromolecules, submitted.

J. Dudowicz, K.F. Freed, and J.F. Douglas, *Modification of the Phase Stability of Polymer Blends by Diblock Copolymer Additives*, Macromolecules, 28, 2276 (1995).

L.L. Sung, A. Karim, J. Douglas, and C.C. Han, *Phase Separation in Thin Polymer Blend Films With and Without Block Copolymer Additives*, ACS-PSME, 74, 106 (1996).

Presentations

A. Karim, *Phase Separation in Thin Reactive Polymer Blend Films*, ACS-APS Intersociety Polymer Conference, Baltimore, Maryland, October, 1995.

L.-P. Sung, *Dimensional Crossover in the Phase Separation Kinetics of Thin Polymer Blend Films*, American Chemical Society, New Orleans, April, 1996.

A. Karim, *Inhibited Coalescence in Reactive Blend Films*, American Chemical Society, Orlando, August, 1996.

Measurement Techniques and Analysis Procedures for Multi-Phase Systems Under Shear

A. Nakatani, D. Johnsonbaugh, A. Bur, K. Migler, S. Roth, E. Amis, S. Kim, S. Li, C. Han

Objective

The objective is to develop instrumentation, measurement methods, and analysis procedures for multi-phase polymer systems under shear and to transfer these methods to on-line extruder processing applications.

Technical Description

- Transfer light scattering and optical microscopy instrumentation and measurement techniques previously developed for a laboratory cone-and-plate shear apparatus to a slit die of a bench top twin screw extruder for on-line morphological characterization.
- Contrast controlled shear flow results to measurements made under processing conditions in a slit-die extruder by light scattering, optical microscopy, and fluorescence anisotropy.

External Collaborations

Dow Corning Corporation - CRADA developed to examine polydimethyl siloxane blends blended with highly branched resins by SANS.

Exxon Research and Engineering Company - CRADA developed to examine the high pressure and shear rate dependence of the phase behavior of metallocene catalyzed polyolefin blends by SANS and optical birefringence techniques.

Raychem Corporation - Polymer Blends Consortium member utilizing SANS to examine liquid crystalline droplets in a polymer matrix.

Planned Outcomes

- Provide instrumentation and techniques for laboratory and on-line characterization of morphological structures for processing design of polymer blends.

Accomplishments

- Steady shear behavior of model polymer blend sample measured by light scattering and phase contrast optical microscopy.
- Phase separation kinetics of a model polymer blend during shear measured by light scattering as a function of shear rate and quench depth.

- Developed fluorescence anisotropy sensor containing polarization optics for real-time processing measurements.

Outputs

Publication

S. Kim, J.-W. Yu, and C. C. Han, *Shear Light Scattering Photometer with Optical Microscope for the Study of Polymer Blends*, *Reviews of Scientific Instruments*, **67**, 1, (1996).

Presentations

S. Kim, *Shear Induced Phase Behavior of Polymer Blends Studied by Light Scattering and Microscopic Observation*, Intersociety Polymer Conference, Baltimore, Maryland, October 1995.

A. I. Nakatani, *Applications of Neutron Radiation to Probe Invisible Structures in Polymer Materials*, Dow Corning Corporation and Dow Chemical Company, Midland, Michigan, March 1996.

C. C. Han, *Small Angle Neutron Scattering Study of Polymer Blends*, CEA, Saclay, France, May 1996.

C. C. Han, *Small Angle Neutron Scattering Study of Polymer Blends*, KFA, Julich, Germany, June 1996.

Characterization of Polymers and Polymer Blends Under Shear

C. Han, A. Nakatani, K. Migler, B. Bauer, J. Douglas, D. Liu, S. Kim, C. Jackson, L. Sung, E. Amis

Objective

The objective is to characterize polymer blends under shear flow to isolate physical parameters which control morphology and composition of co-existent phases.

Technical Description

- Characterize phase separation kinetics and morphology of polymer blends under the influence of shear by small angle neutron scattering, light scattering, optical and fluorescence microscopy techniques.
- Apply measurement techniques to characterize behavior of model polymer systems of commercial interest, including block copolymer melts, liquid crystalline polymers, metallocene catalyzed polyolefin blends, and polymer-oligomer blends.

External Collaborations

Sandia National Laboratories and the University of Cincinnati - Polymer Blends Consortium member utilizing SANS to study polydimethyl siloxane blends.

Goodyear Tire and Rubber Company - Polymer Blends Consortium member utilizing shear light scattering and SANS to characterize the phase behavior of elastomeric blends.

Michigan Technological University - Examine the shear dependence of the order/disorder transition in block copolymers by SANS.

Planned Outcome

- Provide collaborators and members of Polymer Blends and Processing Center with a sufficiently broad data base to enable testing of models for predicting the shear rate dependent behavior of polymer blends.

Accomplishments

- Spinodal curves of model compatibilized blend system under quiescent conditions were measured by SANS as a function of block copolymer concentration.
- Coexistence curves of model compatibilized blend system were measured by temperature jump light scattering under quiescent conditions as a function of block copolymer concentration.
- Phase separation kinetics of model compatibilized blend system were measured as a function of block copolymer concentration and quench depth.
- Quiescent behavior of compatibilized blend system were compared to unmodified model blend behavior. Results are the basis for comparison with shear results.
- Measurements of mixing and homogenization of phase separated polymer blends under steady shear flow were demonstrated, and the analysis and interpretation by macroscopic theories of Taylor and Tomotika together with the renormalization and scaling calculations of Onuki and Kawasaki.
- Steady shear behavior of a solvated model polymer blend sample in the two-phase region was measured using fluorescence microscopy. In order to establish a scaling approach to understand shear mixing, phase compositions as a function of shear rate and temperature were obtained.
- Steady shear behavior of model polymer blends with and without additives was measured by SANS as a function of shear rate and temperature. The model systems had either one of the two homopolymers and one of the two blocks of the diblock copolymer labelled or only one block of the copolymer labelled.

- SANS of a diblock copolymer melt was measured as a function of shear rate and temperature. Both steady shear and transient measurements were performed for comparison with previous data on a triblock copolymer melt.
- SANS of a thermotropic liquid crystalline polyether was performed to measure the radius of gyration as a function of shear rate, temperature, and spacer length. Measurements on quiescent samples were also performed for comparison.
- Phase separation kinetics during shear of the model modified polymer blend was measured by light scattering as a function of quench depth, shear rate, and additive concentration.

Outputs

Publications

L. Sung, and C. C. Han, *Light Scattering Studies on Phase Separation in a Binary Blend with Addition of Diblock Copolymer*, Journal of Polymer Science: Polymer Physics Edition, **33**, 2405, (1995).

A. I. Nakatani, F. A. Morrison, J. F. Douglas, J. W. Mays, C. L. Jackson, M. Muthukumar, and C. C. Han, *The Influence of Shear on the Ordering Temperature of a Triblock Copolymer Melt*, Journal of Chemical Physics, **104**, 1589, (1996).

A. I. Nakatani, F. A. Morrison, C. L. Jackson, J. F. Douglas, J. W. Mays, M. Muthukumar, and C. C. Han, *Shear Induced Changes in the Order-Disorder Transition Temperature and the Morphology of a Triblock Copolymer*, Journal of Macromolecular Science - Physics, **B35**, 489, (1996).

E. K. Hobbie, A. I. Nakatani, H. Yajima, J. F. Douglas, and C. C. Han, *Shear Suppression of Critical Fluctuations in a Diluted Polymer Blend*, Physical Review E, Rapid Communications, **53**, R4322, (1996).

C. L. Jackson, L. Sung, and C. C. Han, *Morphology and Phase Separation Kinetics of a Compatibilized Blend*, ANTEC Proceedings, **1**, 1559, (1996).

R. N. Thudium, and C. C. Han, *Microstructure Effect on the Phase Behavior of Blends of Deuterated Polybutadiene and Protonated Polyisoprene*, Macromolecules, **29**, 2143, (1996).

C. C. Han, *Phase Separation of Polymer Blends Under Shear Field*, Macromolecular Symposia, **101**, 157, (1996).

A. I. Nakatani and C. C. Han, *Shear Dependence of the Equilibrium and Kinetic Behavior of Multicomponent Systems*, in *Structures and Properties of Multi-Phase Polymeric Materials*, T. Araki Q. Tran-Cong and M. Shibayama, Eds., Marcel Dekker, New York, NY, in press.

E. K. Hobbie, S. Kim and C. C. Han, *String-like Patterns in Critical Polymer Mixtures Under Steady Shear Flow*, *Physical Review E*, in press.

C. C. Lin, S. V. Jonnalagadda, N. P. Balsara, C. C. Han, and R. Krishnamoorti, *Neutron Scattering from Multicomponent Flory-Huggins Blends*, *Macromolecules*, in press.

Presentations

L. Sung, *The Effect of Block Copolymer as an Interfacial Modifier in Polymer Blends*, Intersociety Polymer Conference, Baltimore, Maryland, October 1995.

C. C. Han, *Phase Separation and Shear Mixing of Polymer Blends*, Intersociety Polymer Conference, Baltimore, Maryland, October 1995.

C. C. Han, *Phase Separation and Shear Mixing of Polymer Blends*, Physical Chemistry Colloquium, Department of Chemistry, University of Wisconsin, Madison, Wisconsin, November 1995.

C. C. Han, *Neutron Scattering from Polymers*, Symposium on "Research with Neutrons", The Bavarian-American Friendship Week, Munich, Germany, November 1995.

A. I. Nakatani, *Effect of Block Copolymer on the Mixing Behavior of a Polymer Blend*, International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, December 1995.

C. C. Han, *Phase Separation and Shear Mixing of Polymer Blends*, International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, December 1995.

C. C. Han, *Statics, Kinetics, and Pattern Formation of Multiphase Blends*, American Physical Society Meeting, St. Louis, Missouri, March 1996.

C. C. Han, *Statics, Kinetics, and Pattern Formation of Polymer Blends Under Shear Flow*, Karlsruhe Technical University, Department of Physics, Germany, April 1996.

C. C. Han, *Statics, Kinetics, and Pattern Formation of Polymer Blends Under Shear Flow*, Max Plank Institute for Polymer Research, Mainz, Germany, April 1996.

C. C. Han, *Shear Mixing and the Critical Temperature Shift of a Binary Polymer Mixture Under Shear*, Koln University, Department of Physics, Germany, April 1996.

- C. C. Han, *Shear Mixing and Pattern Formation of Polymer Blends Under Shear*, University of Freiburg, Department of Physics, Germany, May 1996.
- C. C. Han, *Fractal Growth and Spinodal Decomposition in a Hydrogen-Bonded Polymer Blends*, University of Konstanz, Department of Physics, Germany May 1996.
- C. C. Han, *Transesterification and Phase Separation of Polymer Blends in Bulk and in Thin Film*, University of Marburg, June 1996.
- L. Sung, *Effect of Copolymer Additives on the Phase Behavior of Polymer Blends*, Materials Research Group, NASA Lewis Research Center, Cleveland, Ohio, June 1996.
- C. C. Han, *Phase Behavior of Polymer Mixtures Under Simple Shear*, Gordon Research Conference on Polymer Physics, Newport, Rhode Island, July 1996.
- C. C. Han, *Shear Mixing and Phase Diagram Shift of Polymer Blends*, IUPAC International Symposium on Macromolecular Condensed State, Beijing, China, August 1996.
- C. C. Han, *Shear Mixing and Phase Diagram Shift of Polymer Blends and Effects of Block Copolymers on the Phase Separation in a Binary Polymer Blend*, Chungchun Institute of Applied Chemistry, Academia Sinica, China, August 1996.
- C. L. Jackson, *Morphology and Phase Separation Kinetics of a Compatibilized Blend*, Society of Plastic Engineers ANTEC Meeting, Indianapolis, Indiana, May 1996.
- C. L. Jackson, *Morphology Evolution and Phase Separation Kinetics in a Polymer Blend with Diblock Copolymer Additive*, Gordon Research Conference on Polymer Physics, Poster Session, Newport, Rhode Island, July 1996.

Temperature Measurements for Polymer Processing

A. Bur, K. Migler, D. Johnsonbaugh, S. Roth, E. Amis

Objective

The objective is to develop sensors for measurement of temperature and temperature profiles in polymers under processing conditions. Applications of these sensors will be demonstrated for shear heating effects in polymer blends in simple and complex shear flows, temperature of wire insulation during extrusion, and temperature of films during stretching.

Technical Description

- The method uses fluorescent dyes which exhibit changes in their spectrum with temperature.
- Sensors for absolute measurements and ones for temperature profile measurements will be designed to fit standard instrumentation ports on processing machines.
- The temperature profile sensor uses confocal optics to isolate the point of measurement.

External Collaborations

The project involves collaborations with DuPont, Mobil Chemical, and DELPHI Packard Electric.

Accomplishments

- Development of a sensor for measuring temperature profiles which contains confocal optics and which fits the standard instrumentation port of processing machines.
- Measurement of temperature profiles during extrusion of polyethylene through an exit slit die.
- Measurement of shear heating in the barrel of an extrusion machine.
- The discovery of a new class of fluorescent dyes which can be used at high temperatures employed during polymer processing.
- A patent application for this sensor and methodology has been submitted to the Patent Office.

Impact

The technology developed in this project has been used by the 3M Co. in R&D studies of processing technology and is the subject of ongoing collaborations with 3M, DuPont Co., DELPHI Packard Electric and Mobil Chemical Co. The studies with DuPont are being carried out in order to demonstrate measurements of temperature profiles during extrusion and to assess the effects of shear heating. With DELPHI Packard Electric, temperature measurements are being extended to polymer resin during wire insulation extrusion. Mobil Chemical is collaborating with us to apply the methods to temperature measurements of thin polymer films during the stretching process. These companies have all sought the NIST technology because existing temperature measuring methods are inadequate for their processing applications.

Outputs

Publication

A. J. Bur and C. L. Thomas, *Volume Viscoelastic Relaxation in a Glass Forming Polymer During Injection Molding*, Soc. Plastics Eng. Ann. Tech. Mtg., May, 1996.

Presentations

A. J. Bur and C. L. Thomas, *Volume Viscoelastic Relaxation in a Glass Forming Polymer During Injection Molding*, Soc. Plastics Eng. Ann. Tech. Mtg., May, 1996.

A. J. Bur, *Optical Monitoring of Polymer Processing: Model Developments*, Gordon Conf. on Non-Destructive Evaluation, August, 1996.

Additives and Compatibilizers in Polymer Blends

B. Bauer, A. Nakatani, A. Karim, K. Migler, D. Liu, J. Douglas, E. Amis, C. Gettinger, C. Han, C. Jackson

Objectives

The objectives are to develop measurement techniques for characterizing: effects of block copolymer addition and strong interactions on miscibility of polymer blends.

Technical Description

- Develop model polymer systems for measurement of the compatibilization effects of block copolymers and strongly interacting blends.
- Characterize the phase diagram and phase separation kinetics of a model polymer blend system without the addition of block copolymers.
- Measure by small angle neutron scattering and light scattering the changes in a model polymer blend system by addition of model block copolymers.
- Measure the strength of hydrogen bonding interactions in model polymers and produce phase diagrams.
- Produce melt mixed immiscible polymer blends with and without various block and random copolymer additives and study the effect of the additives on the dispersions.
- Use our extruder with light scattering/microscopy capability to determine mixing behavior of blends capable of reactive extrusion.
- Determine the effects of film thickness and block copolymer addition on the phase behavior on polymer blends by atomic force microscopy and reflectivity.
- Measure the segment density distribution of dendrimers and associated counterions in solution.

- Prepare dendrimer/linear polymer blends and interpenetrating polymer networks and characterize them by SANS, SAXS, AFM, TEM and reflectivity.

External Collaborations

Michigan Macromolecular Institute - CRADA developed to examine the location of the terminal generation of a dendrimer.

Samples of blends with compatibilizers were produced and distributed to consortium member, 3M Corporation, for transmission electron microscopy.

Accomplishments

- Spinodal curves of model compatibilized blend system were measured by small angle neutron scattering as a function of block copolymer concentration.
- Determined by temperature jump light scattering coexistence curves of model compatibilized blend system as a function of block copolymer concentration.
- Phase separation kinetics of model compatibilized blend system were measured as a function of block copolymer concentration and quench depth.
- Phase diagrams have been constructed for blends that exhibit hydrogen bonding interactions.
- The interaction parameters for blends of polyethylene oxide and poly(methyl methacrylate) and/or polymethacrylic acid have been measured.
- Compatibilizers of random and graft copolymers having athermal or strong interactions have been synthesized. Melt blends of immiscible polymers with and without these compatibilizers have been made, and the relationship between compatibilizer type and resultant morphology has been established.
- Established the effects of film thickness on the phase boundaries and the kinetics of phase separation.
- The internal segment density distribution of dendrimers in solution has been measured. The size and distribution of the counterions in dendrimer solutions was also measured.
- Conditions for forming miscible dendrimer blends have been established.

Outputs

Publications

C. L. Jackson, L. Sung, and C. C. Han, *Morphology and Phase Separation Kinetics of a Compatibilized Blend*, ANTEC Proceedings, **1**, 1559, (1996).

L. P. Sung, and C. C. Han, *Light Scattering Studies on the Phase Separation in a Binary Blend with Addition of Diblock Copolymer*, Journal of Polymer Science: Polymer Physics Edition, **33**, 2405, (1995).

G. Merkle, B. J. Bauer, and C. C. Han, *Relaxation After a Temperature Jump Within the One-Phase Region of a Polymer Mixture*, J. Chem Phys, **104**, 9647, (1996).

E. K. Hobbie, G. Merkle, B. J. Bauer, and C. C. Han, *Spinodal Decomposition in Hydrogen-Bonded Polymer Blends*, Modern Phys. Lett. B., in press.

Presentations

A. I. Nakatani, *Effect of Block Copolymer on the Mixing Behavior of a Polymer Blend*, International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, December 1995.

B. J. Bauer, *Compatibilizers Made from Block Copolymers That Have Strong Specific Interactions*, ACS National Meeting, March 1996.

L. P. Sung, *Phase Separation in Thin Film Polymer Blends With and Without Block Copolymer Additives*, ACS National Meeting, March 1996.

B. J. Bauer, *Small Angle Neutron and X-ray Scattering Studies of Polyamidoamine Dendrimers* MRS National Meeting, April, 1996.

Investigation of Interfacial Interactions for Polymers and Blends

A. Karim, J. Douglas, B. Ermi, D. Liu, E. Amis, C. Han

Objective

The objective of this project is to characterize factors controlling the interface between polymer phases in thin film coatings and phase separated bulk polymer blends. Investigations of thin films on substrates are to be generalized to polymer interactions with fillers in bulk and suspensions in solution.

Technical Description

- Characterize equilibrium interfacial profiles in thin films blend coatings as a function of temperature close to the two phase boundary using neutron and x-ray reflection.

- Quantify kinetics of phase separation in ultrathin film blends through surface pattern formation using optical microscopy and atomic force microscopy.
- Compare results of phase separation in thin blend films with theoretical predictions.
- Contrast kinetics of phase separation and morphology development in regular versus reactive blends using atomic force microscopy and neutron reflection.
- Use neutron reflection to determine the segregation of block copolymer to interfaces in homopolymer blends.
- Characterize the influence of adding diblock copolymer to blend films exhibiting surface pattern formation and examine its role in suppressing the kinetics of phase separation.
- Measure the efficacy of diblock compatibilizers as a function of composition and molecular weight.
- Investigate modification of surface properties by end-grafted polymers and filler-type materials using x-ray reflectivity and atomic force microscopy.

External Collaborations

3M Corporation - Collaborative project to examine interfacial development in reactive polymer systems using neutron reflection.

Raychem Corporation - Study *in-situ* blend film phase separation using atomic force microscopy.

Goodyear Tire and Rubber Company - Study phase separation kinetics in ultrathin elastomeric blend films.

Penn State University and University of Maryland - Examine shift of phase boundary in confined thin blend films.

University of Texas - Characterize interface development through transesterification reactions in polymer bilayer films.

University of Connecticut - Synthesis and characterization of properties of grafted polymer layers.

Accomplishments

- Determined the evolution of equilibrium concentration profiles in thin film blends as a function of temperature in the vicinity and far from the two phase boundary using

neutron reflectivity. Shifts in critical temperatures for confined blend films were estimated using SANS.

- Measured the kinetics of phase separation in ultrathin (quasi-two dimensional) blend films and compared with those in thicker and bulk films. Results agree well with existing numerical simulations of phase separation in 2-D.
- Observed a strong suppression of phase separation induced surface pattern formation in thin blend films with addition of small amounts of diblock copolymer, demonstrating the effectiveness of diblock copolymers as compatibilizers in thin blend films.
- Monitored the slowing down of kinetics of phase separation with diblock addition. The magnitude of this effect cannot be simply explained by a stabilization of the bulk phase boundary with addition of block copolymer.
- Measured the development of novel morphology during late stage phase separation in reactive blend films indicating a suppression of coalescence behavior due to the formation of copolymer material through chemical reactions.
- Investigated the interfacial evolution in strongly interacting polymer bilayers and observed a strong temperature dependence to the interface healing process.
- Successful preparation and characterization of grafted polymer layers under varying solvent conditions and also of spin coated dendrimer thin films.

Outputs

Publications

L. Sung, A. Karim, J. Douglas, and C.C. Han, *Dimensional Crossover in the Phase Separation Kinetics of Thin Polymer Blend Films*, Phys. Rev. Lett., **76**, 4368 (1996).

Y. Feng, R. Weiss, A. Karim, C. Han, J. Ankner, H. Kaiser, and D. Peiffer, *Compatibilization of Polymer Blends by Complexation: 2. Kinetics of Interfacial Mixing*, Macromolecules, **29**, 3919 (1996).

P. Brant, A. Karim, J. Douglas, and F. Bates, *Surface Composition of Amorphous and Crystallizable Polyethylene Blends as Measured by Static SIMS*, Macromolecules, **29**, 5628 (1996).

L. Norton, E. Kramer, F. Bates, M. Gehlsen, R. Jones, A. Karim, G. Felcher, and R. Kleb, *Neutron Reflectometry Study of Surface Segregation in an Isotopic Poly(ethylene-propylene) Blend: Deviation from Mean-Field Theory*, Macromolecules, **28**, 8621 (1995).

A. Karim, V. Tsukruk, J. Douglas, S. Satija, L. Fetters, D. Reneker, and M. Foster, *Self-Organization and Structure of Polymer Brush Layers in a Poor Solvent*, J. Phys. II France **5**, 1441 (1995).

A. Karim, J. Douglas, L. Sung, and B. Ermi, *Demixing of Polymer Blends in Ultrathin Films*, APS News, in press.

C. Guttman, E. Di Marzio, and J. Douglas, *Influence of Polymer Architecture and Polymer-Surface Interaction on the Elution Chromatography of Macromolecules through a Microporous Media*, Macromolecules, **29**, 5723 (1996).

M. Trache, W. McMullen, and J. Douglas, *Segmental Concentration Profiles of End-Tethered Polymers with Excluded-Volume and Surface Interactions*, J. Chem. Phys., **105**, 4798 (1996).

Y. Feng, R. Weiss, A. Karim, C. Han, J. Ankner, and D. Peiffer, *Kinetics of Mixing at Polymer-Polymer Interface Capable of Forming Intermolecular Complexes*, ACS New Orleans Polymer Preprints, Spring 1996.

L. Sung, A. Karim, J. Douglas and C. Han, *Phase Separation in Thin Polymer Blends With and Without Block Copolymer Additives*, ACS-PMSE, **74**, 106 (1996).

A. Karim, J. Douglas and C. Han, *Frustrated Coalescence in Reactive Blends*, ACS-PMSE, Orlando, Fall 1996.

A. Wong, A. Karim and C. Han, *Neutron Reflection Studies of Phase Separation and Transesterification in Thin Film Polymer Blends*, Physics B, **221**, 301 (1996).

A. Karim, J. Douglas, F. Horkay, L. Fetters and S. Satija, *Comparative Swelling of Gels and Polymer Brush Layers*, Physica B, **221**, 331 (1996).

Presentations

A. Karim, *Phase Separation in Thin Films of Reactive Polymer Blends*, Intersociety Polymer Conference, Baltimore, Maryland, October 1995.

A. Karim, *Polymer Brush Profiles in Critical Binary Solvent Mixtures*, Intersociety Polymer Conference, Baltimore, Maryland, October 1995.

A. Karim, *Frustrated Coalescence in Reactive Polymer Blend Films*, International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, December 1995.

L. Sung, *Dimensional Crossover in Phase Separation Kinetics in Thin Polymer Blend Films*, American Chemical Society, Spring Meeting, New Orleans, April 1996.

A. Karim, *Kinetics of Mixing at Polymer-Polymer Interface Capable of Forming Intermolecular Complexes*, American Chemical Society, Spring Meeting, New Orleans, April 1996.

A. Karim, *Self-Organization and Structure of End-grafted Polymer Brush layers*, Polymer Physics Gordon Conference, Newport, July 1996.

A. Karim, *Inhibited Coalescence in Reactive Blend Films*, American Chemical Society, Fall Meeting, Orlando, August 1996.

A. Karim, *Atomic Force Microscopy studies of Phase Separation in Polymer Thin Films*, American Chemical Society, Fall Meeting, Orlando, August 1996.

L. Sung, *Influence of Dimensionality on Phase Behavior of Polymer Blend Films*, Reactor Division, NIST, September 1996.

J. Douglas, *Surface Pattern Formation Processes in Thin Polymer Layers*, Dept. of Chemical Engineering, Princeton, April 1996.

J. Douglas, *Surface Pattern Formation Processes in Thin Polymer Layers*, Dept. of Physics, Cornell University, Ithaca, April 1996.

Pressure Effects on Polymer Blends and Processing

K. Migler, C. Han, E. Amis

Objective

The objective is to measure the effect of pressure, an important processing variable, on polymer blends, diblock copolymers and supercritical solutions. The focus is on determination of pressure induced changes in miscibility, interaction parameters and radius of gyration.

Technical Description

- Conduct cloud point and small angle light scattering studies at high pressure to measure the changes in miscibility of binary polymer blends.
- Use small angle neutron scattering to measure pressure induced changes in molecular size, binary interaction parameter and spinodal line of polymer blends.
- Use birefringence measurements to determine pressure induced shifts in anisotropic materials such as diblock copolymers and liquid crystal polymers.

External Collaborations

Exxon Research and Engineering Company - CRADA developed to examine the high pressure and shear rate dependence of the phase behavior of metallocene catalyzed polyolefin blends by small angle neutron scattering and optical techniques.

University of Delaware - Examination of polymeric supercritical solutions utilizing small angle neutron scattering.

University of Tennessee - Examine of pressure induced changes in phase diagram of lyotropic liquid crystals.

Accomplishments

- A technique for measurement of birefringence at high pressure was developed.
- Pressure induced phase transition of diblock copolymer was measured via two complementary techniques: optical birefringence and small angle neutron scattering with the two methods showing excellent agreement.
- Measured large pressure induced shifts in miscibility of polyolefin blends via cloud point techniques.

Outputs

Presentation

K.B. Migler, *Pressure Induced Order-Disorder Transition in Diblock Copolymers*, American Physical Society Meeting, St. Louis, Missouri, March 1996.

Self-Assembling Micelles, Transient Polymer Networks, Gels, and Interacting Systems

C. Gettinger, C. Han, C. Jackson, E. Amis, B. Ermi

Objective

The objective is to characterize polymers interacting by way of strong specific interactions such as ionic interactions or hydrophobic interactions to form ionic micelles, transient networks, and gels.

Technical Description

- Light scattering, neutron scattering, rheological studies, and TEM are used to characterize solubility, size, structure, and interactions of model polymers with specific interacting groups incorporated as ionic grafted copolymers and combs, telechelics, hyper-branched stars, and hydrophobically modified copolymers.

- Synthesize and characterize model graft copolymers made up of neutral backbones and ionic grafts.
- Small angle neutron scattering, dynamic light scattering, TEM, and computer modeling are used to characterize the solubility, size, shape, and specific interactions of self-assembled micelles as a function of grafting density, concentration, solvent composition, ionic strength, and charge density.

External Collaborations

M. Pitsiklis, J. Mays Department of Chemistry, University of Alabama, Birmingham.

H. Chanzy, Centre de Recherches sur les Macromolécules Végétales, Grenoble, France.

Accomplishments

- Selective solvents have been identified for PS/PMAA- Na^+ and PS/P4VPBz $^+$ Br $^-$ graft copolymers and micellization has been observed and characterized in six samples using dynamic light scattering, small angle neutron scattering and TEM.
- Structures observed in these systems include multi-molecular spherical micelles with core-shell morphology as well as intra-molecular cylindrical micelles.
- With changes in solvent composition, structural changes were observed in micelles of PS/PMAA graft copolymer micelles including reverse micellization. Ionic strength was observed to affect micelle dimensions and chain extension.
- Using SANS and solvent contrast matching, the preferential absorption of small organic molecules into the interior of the micelles has been investigated as a function of micellar geometry.

Outputs

Publication

C.L. Gettinger, C.C. Han, M. Pitsikalis, and J. Mays, *Micelles Formed by a Model Ionic Graft Copolymer*, Polymer Preprints 37(1) 406 1996.

Presentations

E. Amis, *Associating Polymers and Transient Gels*, Case Western Reserve University, Polymer Science Department, Cleveland, October 1995.

C. L. Jackson, *Micelles Formed by a Model Ionic Graft Copolymer*, American Physical Society, St. Louis, MO, March 1996.

C. Gettinger, *SANS of Micellization of Model Ionic Graft Copolymers in Selective Solvents*, American Physical Society, St. Louis, MO, March 1996.

E. Amis , *Associations of Model Polymers with Strong Specific Interactions*, APS National Meeting, Joint Session of Divisions of Chemical Physics and High Polymer Physics, St. Louis, MO, March 1996.

C. Gettinger, *Micelles Formed by a Model Ionic Graft Copolymer*, American Chemical Society, New Orleans, LA, March 1996.

E. Amis, *Associations of Model Polymers with Strong Specific Interactions*, Frontiers in Rubber Science Colloquium, ACS Rubber Division Meeting, Montreal, May 1996.

C. Gettinger, *Micelles Formed by a Model Ionic Graft Copolymer*, GE Plastics, Selkirk, NY, June 1996.

C. Gettinger, *Micellization of Model Ionic Graft Copolymers*, 3M Corporate Research, St. Paul, MN, September 1996.

Investigations of Statics and Dynamics in Polyelectrolytes

D. Valachovic, B. Ermi, **E. Amis**

Objectives

The objective is to provide experimental methods and quantitative data for molecular interpretation of the structure and dynamics of polyelectrolyte solutions.

Technical Description

Measurements with static and dynamic light scattering, small angle neutron and x-ray scattering, and spin echo are used to characterize model systems which provide control of chain conformation, charge density, backbone solvation, and hydrophobic interactions.

External Collaborations

This project is being carried out under in cooperation with the University of Southern California Department of Chemistry.

Accomplishments

- First demonstration of so-called “extraordinary regime” of polyelectrolyte behavior in non-aqueous solutions by dynamic light scattering.
- Dynamic light scattering from salt free solutions prepared in good solvents for chain backbones show slow mode scattering. This effectively eliminates the argument for microphase separation as the explanation for this persistent effect.
- A companion study using small angle neutron scattering verifies the conclusions from the dynamic light scattering and furthermore shows that the peak at finite scattering

wavevector is not dependent on backbone solvation in its scaling law with concentration.

- Small angle neutron scattering was combined with light scattering to cover over three decades of both q space and scattering intensity and characterize the static scattering from polyelectrolyte solution as a function of concentration. The appearance of a peak at high scattering wavevector and an upturn at low scattering vector were demonstrated conclusively for the first time. These experiments show that current models for polyelectrolyte solutions, which include only a single length scale, are inadequate.
- The condensed counterion distribution surrounding polyelectrolyte dendrimer molecules was characterized by small angle neutron scattering.

Outputs

Publication

B. D. Ermi and E. J. Amis, *Model Solutions for Studies of Salt-Free Polyelectrolytes*, *Macromolecules*, 29, 2701, (1996).

Presentations

E. Amis, *Model Polyelectrolytes in Model Solvents*, International Symposium on Polyelectrolytes, Potsdam, Germany, September 1995.

E. Amis, *Structure and Dynamics of Polyelectrolyte Solutions*, Polytechnic University, Chemistry and Chemical Engineering Department Colloquium, NY, November 1995.

E. Amis, *Structure and Dynamics in Polyelectrolyte Solutions*, Michigan Molecular Institute, Midland, MI, March 1996.

E. Amis, *Model Polyelectrolytes in Low-Salt Solutions*, International Symposium on Laser Light Scattering, Hong Kong, July 1996.

E. Amis, *Structure and Dynamics in Polyelectrolyte Solutions*, South China Institute of Chemical Technology, Department of Materials Science, Guangzhou, China, August 1996.

E. Amis, *Model Polyelectrolytes in Low-Salt Solutions*, IUPAC International Symposium on Macromolecules, Seoul, August 1996.

E. Amis, *Structure and Dynamics in Polyelectrolyte Solutions*, Pennsylvania State University, Department of Materials Science, State College, PA, September 1996.

...the ... of ...

...the ... of ...

...the ... of ...

Output

...the ... of ...

...the ... of ...

...the ... of ...

...the ... of ...

...the ... of ...

...the ... of ...

...the ... of ...

...the ... of ...

POLYMER COMPOSITES PROGRAM

The Polymer Composites Program seeks to facilitate the introduction of light-weight, corrosion-resistant composite materials into commercial applications by expanding the essential science base and generating test methods, reference data, and standard materials. The outstanding properties of composites mean they can be used to make products that are superior and competitive in international markets. Industries as diverse as transportation, construction, marine, off-shore oil, medical devices, and sporting goods have recognized the benefits and are beginning to make significant use of these materials. For this to continue, however, two significant barriers must be addressed: the lack of rapid, reliable, cost-effective fabrication methods, and the poor understanding of and predictive capability for long term performance. These barriers were identified in a series of industry workshops, exchange visits, and consultations. In response to these challenges, the composites program initiated two tasks: one on processing science and the other on interfacial microstructure. The degradation of the interface over time is primarily responsible for the loss of mechanical properties. The automotive industry strongly influences the composites program since many of the processing and durability issues span many automotive applications, and solutions developed at NIST are expected to rapidly propagate throughout the industry. Additionally, the group interacts with companies interested in off-shore oil platforms, infrastructure, aerospace, and a variety of other applications.

The goal of the Processing Science Task is to develop the technology required to monitor, model, and control the events that occur during composite fabrication. The program focuses on liquid composite molding (LCM) since this fabrication method is of great interest to all industry sectors and is the consensus choice of the automotive industry as the method with the most promise for making structural automotive parts. The approach in this task involves three steps. First, measurement tools are developed and used to characterize the material properties that control processing, for example, permeability. Second, sophisticated process simulation models are formulated to analyze the effects of processing parameters rapidly and inexpensively so they can be optimized. Finally, process monitoring sensors are developed and used to provide feedback for verification and improvement of the simulation models and to help develop the technology for on-line process control. The current activities in this Task involve five projects, including a major industry-university-government program sponsored by the Defense Advanced Research Projects Agency.

The work in the Microstructure Task focuses on developing test methods for assessing the resin/fiber interfacial adhesion, and the subsequent degradation of adhesion resulting from fluid attack, particularly moisture. The long term goals are to first develop effective test methods, then to use those tests to identify the chemical and physical mechanisms of degradation, and finally to formulate reliable predictive models. The program focuses on glass fiber materials since they are the primary candidates for automotive applications. In addition, the work is beginning to look at graphite reinforced composites since these systems are important for marine and infrastructure applications. Microscale tests such as the single fiber fragmentation test are currently being analyzed to determine if they can provide realistic estimates of the performance of the resin/fiber

interface in composite systems. A variety of interfacial physical and chemical structures are generated during preparation of microscale test specimens by varying the coating chemistry on the fiber, the resin processing speed, and the moisture content of the material. Full scale composite specimens are also produced and tested with identical fiber coatings and processing conditions for comparison with the microscale tests and to provide, in conjunction with the microscale tests, realistic structure-performance relationships. There are currently four specific projects in this Task, including a collaboration with the Automotive Composites Consortium to determine the effects of processing conditions on the interface of polyurethane matrix composites.

FY-96 Significant Accomplishments

- A micromechanical testing method developed for polymer composites was shown to be an effective tool for measuring the interfacial shear properties of dental materials. For example, using the microbond interfacial strength test, a hydrophobic silane coupling agent was demonstrated to produce more durable adhesion than the dental industry standard formula.
- A traditional Lattice Boltzmann formulation was modified to model flow in heterogeneous media, where the momentum transport is expressed with a combination of the Stokes and Brinkman equations. Lattice Boltzmann techniques enable efficient computation in real materials and the inclusion of important multiphase flow physics.
- A sensor capable of detecting rapid polymerization reactions was developed in cooperation with industry and demonstrated in the fabrication of epoxy, polyurethane, and polyester composite plaques. Ford is transferring the technology to their laboratory where it will be implemented on prototype production equipment as part of a NIST/Ford/GE ATP program.
- The role of resin viscoelasticity in determining the strength and durability of the interphase of single-fiber-composite test specimens was demonstrated for a model glass-epoxy system. Previous micromechanical testing has largely ignored resin rheology, and that is now thought responsible for much of the scatter and unreliability of typical test methods.
- An international collaboration through the Versailles Advanced Materials and Standards Program (VAMAS) was initiated to develop standard techniques for the preparation and testing of single-fiber-composite test specimens. To date, 17 laboratories representing 6 different countries have agreed to participate in the program.
- An industry/NIST workshop considered different types of sensors in the context of composite manufacturing challenges and plausible process control scenarios. Only inexpensive, nonintrusive sensor systems hold the interest of manufacturers and systems developers, but very sophisticated control schemes that can make use of minimal sensor information are in demand.

- A new set of technical challenges revolving around quality control were identified in a workshop co-sponsored by the Polymers Division and Ohio State University on Liquid Composite Molding. The focus on quality control results from the emergence of a nascent liquid molding industry since the first workshop on Liquid Molding was held at NIST three years ago.

Liquid Composite Molding: Development of Permeability Measurement Techniques and Data

R.S. Parnas

Objective

The objective is to establish a data base of permeability values for use in the design tools used by the composites industry for process and mold design.

Technical Description

Permeability measurements conducted over several years at NIST have been documented, collected, and placed into a Clipper based database. External sources of reliable data have been identified and attempts to document the adequacy of their measurements for inclusion in the database continue. Permeability measurements are continuing with an emphasis on the permeability of fabrics deformed around curves as would be found in molds of complex shape.

External Collaborations

NIST: Standard Reference Data Division

Industrial: Textile Research Institute

Academic: University of Montreal, University of Nottingham

Planned Outcomes

Version 1 of the database is planned for release in early 1997 and it is expected that molders will use it to help design their processes and parts. Version 2 is planned for release in 1998 with an expanded dataset and enhanced graphics display.

Accomplishments

Over 100 experiments conducted at NIST with a variety of glass reinforcements have been entered into the database. The database was demonstrated at the Second Workshop on Liquid Molding, and a number of requests for the database were made at that time. Collaborations with two other sources of data have been successfully started, as measured by approximately 20 additional data sets that have been imported into the database.

Impacts

Over the past several years engineers from companies including Ford, Boeing, and Northrup/Grumman, as well as several engineering students, have learned how to make accurate permeability measurements through participation in the NIST permeability measurement project.

Outputs

Publications

R.S. Parnas, *Chapter 8. Perform Permeability*, in RTM for Aerospace Applications, Chapman & Hall, 1997.

H.L. Friedman, R.A. Johnson, B. Miller, D.R. Salem and R.S. Parnas, *In-Plane Movement of Liquids Through Curved Fabric Structures*, Proc. ASME Symp. on Processing, Design and Performance of Composite Materials, Nov.1995.

Liquid Composite Molding: Development and Verification of Process Simulation Models

F. R. Phelan Jr.

Objectives

The objectives are to develop and apply models that can simulate the events which occur during the LCM process by including the effects of preform deformation and heat transfer. The model will be developed specifically to simulate injection compression molding for the automotive industry and their suppliers.

Technical Description

Process optimization has been done with time-consuming and expensive trial and error methods on full scale equipment. Simulation models can greatly reduce the cost and increase the speed of this task. The simulation models developed in this project are based on a finite element / control volume numerical solution procedure to the governing transport equations. For example, the momentum transport equation is expressed by Darcy's law. In previous work, a Darcy's law simulation, called CRIMSON, for modeling the mold filling phase of LCM was developed. CRIMSON enables modeling of resin injection for either constant flow rate or constant pressure injection conditions, in geometries ranging from 2-D to fully 3-D.

In the next phase of this project, CRIMSON is extended to a second generation LCM process, called Injection/Compression Liquid Composite Molding (I/CLCM). This process has been selected by the automotive companies as the most promising method for fabrication of large structural parts. I/CLCM differs from conventional "injection-only" LCM in that subsequent to preform placement, the tool is only partially closed. An initial charge of resin is then injected, followed by full mold closure. The final closing action of the mold compresses the preform to the desired net shape and volume fraction while distributing the initial shot of resin throughout the part. There are two main I/CLCM process variants. In "closed mold" I/CLCM, shown in *Figure 1a*, the tool is

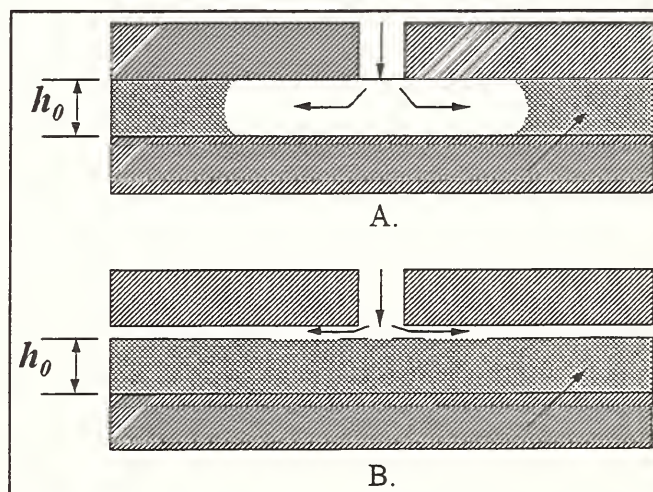


Figure 1 -- Schematic of the two main I/CLCM process variants. A. The closed mold process. B. The open mold process.

closed enough to partially compress the preform, and thus, hold the preform in place during the injection phase of the process. In the “ideal” open mold process shown in *Figure 1b*, a gap exists between the preform and the upper tool surface. The strategy in this case is to try and fill the gap region with fluid first, and then use the compression step to drive the fluid into the preform in the thickness direction. This scenario is termed “ideal” because during an actual open mold injection, there is some penetration of resin into the preform during the injection phase, so that during the compression step there is also some in-plane flow.

External Collaborations

Industrial: Structural Dynamics Research Corp., Automotive Composites Consortium, Northrup/Grumman

Academic: University of Illinois

Planned Outcome

- Provide The Budd Co. and other interested organizations with NIST simulation tools for design and optimization.

Accomplishments

In previous work, CRIMSON was modified to model the case of closed mold I/CLCM. This year, work has begun in cooperation with the University of Illinois at Urbana-Champaign to develop a numerical simulation of the general open mold I/C process. This work is not yet complete, however, a comparison of “ideal” open mold I/C and closed mold I/C is illustrative of the differences between the two processes. *Table 1* compares the maximum pressure obtained when filling of a 30.48 x 30.48 x 1 cm flat plaque using the two processes. Since the ideal case is a simple 1-D flow, these calculations were done analytically while the closed mold calculations were performed using the computer simulation. The processing parameters were the same for both cases. The result shows that quite a substantial reduction in the maximum pressure is obtained for the ideal case as compared to the closed mold flow. This difference can be attributed mainly to the very short penetration distance needed in the ideal case, as compared to the long flow path required in the in-plane flow closed mold process.

Method	Maximum Pressure (MPa)
Closed Mold	300
Ideal Open Mold	0.1

Table 1 -- Comparison of maximum pressure for closed mold injection/compression, and “ideal” open mold I/C in the injection of a 30.48 x 30.48 x 1 cm plaque. The compression rate is -0.1 (cm/s) in both cases.

The development of I/CLCM stems from the need to mold high fiber volume fraction components in applications with fast cycle times. In pure-injection LCM, such process constraints can result in

excessively high injection pressures that induce undesirable fluid-structure interactions involving preform, foam core, or tool deformation.

In an effort to link the CRIMSON software with the user community, Structural Dynamics Research Corp. (SDRC) has developed a graphical user interface enabling the interfacing of the NIST flow modeling software CRIMSON with their I-DEAS Master Series mechanical design software. The interface allows the user from within I-DEAS to design a part, specify preform and fluid properties such as permeability and viscosity, enter boundary conditions, and then run the CRIMSON program. Results are automatically read back into I-DEAS when the simulation is finished.

Impact

The simulation software has been transferred to the ACC, Budd, and Northrup/Grumman, and is regularly used as a design tool.

Outputs

Publications

Phelan Jr., F.R., *Analysis of Injection/Compression Liquid Composite Molding Process Variants*, Proceedings of the ASME96 Symposium on Multi-Disciplinary Issues in Manufacturing of Composites, Non-metals and Metals, (1996), in press.

Phelan Jr., F.R., *Simulation of Injection/Compression Liquid Composite Molding*, Proceedings of the First Joint Topical Conference on Processing Structure and Properties of Polymeric Materials, to appear, (1996).

Presentations

Phelan Jr., F.R., *Numerical simulation of injection/compression liquid composite molding*, presented at the 11th Annual ASM/ESD Advanced Composites Conference and Exposition (ACCE95), ASM International, (November 1995).

Phelan Jr., F.R., *Simulation of injection/compression liquid composite molding*, presented at The Second Workshop on Liquid Composite Molding, Ramada University Hotel, The Ohio State University, Columbus, OH, (June 14,1996).

Liquid Composite Molding: Development and Verification of Permeability Prediction Models

F.R. Phelan Jr. and Michael A. A. Spaid

Objective

The objective is to develop theoretical tools to aid industrial designers for predicting the permeability tensor of the fiber reinforcement materials used in Liquid Composite Molding (LCM) from a knowledge of their microstructures.

Technical Description

During the past year, a novel approach for computing the flow behavior in real reinforcement materials was developed. Rather than solving the fluid flow problem with standard numerical techniques such as finite elements or finite differences, a lattice Boltzmann (LB) method has been adopted. The primary advantage of the LB method is in its ability to model robustly the two-phase nature (resin/air) of the flow processes.

LB methods involve the solution of the discrete Boltzmann equation for the particle distribution function $f(\mathbf{x}, \mathbf{v}_\alpha, t)$, given by

$$f_\alpha(\mathbf{x} + \mathbf{v}_\alpha, t + 1) = f_\alpha(\mathbf{x}, t) + \delta_{c,\alpha}(\mathbf{x}, t) \quad (1)$$

where \mathbf{v}_α is the discrete representation of the velocity space, and $\delta_{c,\alpha}$ is the collision operator which couples the velocity states. For suitably symmetric lattices, it is possible to prove that the Navier-Stokes equations are recovered from the LB formulation. Traditional fluid flow quantities such as velocity and density may be recovered by taking moments of the particle distribution function as follows

$$\begin{aligned} \rho(\mathbf{x}, t) &= \sum_{\alpha=1}^b f_\alpha(\mathbf{x}, t) \\ \mathbf{u}(\mathbf{x}, t) &= \frac{1}{\rho(\mathbf{x}, t)} \sum_{\alpha=1}^b \mathbf{v}_\alpha f_\alpha(\mathbf{x}, t) \end{aligned} \quad (2)$$

Most LB formulations employ a linear form of the collision operator $\delta_{c,\alpha}$, under the assumption that the particle distribution may be expanded about its equilibrium value:

$$\delta_{c,\alpha} = -\frac{f_\alpha(\mathbf{x}, t) - f_\alpha^{eq}(\mathbf{x}, t)}{\tau} \quad (3)$$

In (3), f_α^{eq} is the equilibrium distribution function, and τ is a parameter which controls the rate of relaxation to equilibrium. For a 2-D hexagonal lattice, the velocity space is comprised of six vectors of equal magnitude v_0 which point along the lattice links, and the zero vector to incorporate rest particles. The particle equilibrium distribution function for the hexagonal LB model is given by

$$f_{\alpha}^{eq} = \rho \left(\frac{1-d_0}{6} + \frac{1}{3v_0^2} \mathbf{v}_{\alpha} \cdot \mathbf{u} + \frac{2}{3v_0^4} (\mathbf{v}_{\alpha} \cdot \mathbf{u})^2 - \frac{1}{6v_0^2} u^2 \right), \quad \alpha=1\dots6$$

$$f_{\alpha}^{eq} = \rho \left(d_0 - \frac{1}{v_0^2} u^2 \right), \quad \alpha=7 \quad (4)$$

where d_0 is the fraction of rest particles.

Accomplishments

In this study, a traditional LB formulation was modified to enable the modeling of flow in heterogeneous media, where the momentum transport is expressed with a combination of the Stokes and Brinkman equations.

To validate the LB formulation of the Stokes and Brinkman equations, simulations were performed for flow over porous cylinders with elliptical cross section. The effective permeability predicted by the simulations was then compared to a semi-analytical lubrication model previously developed in this project, and known to agree with rigorous finite element results. Excellent agreement between the LB calculations and the semi-analytical model were obtained for both cylinders and ellipses with relatively small lattice sizes.

The LB model developed is a viable alternative to directly solving the Stokes-Brinkman equations using standard numerical techniques. One of the advantages of the LB method is the ability to model the dynamics of the flow, which is of particular interest in an inherently unsteady flow problem such as the infiltration of RTM preforms. In addition, modifications of the LB model to include important physics such as wicking forces are relatively simple to implement. Future work will focus on the implementation of a multiple phase LB code in order to study the mechanisms of void formation as a function of the relative importance of viscous and surface tension forces, as measured by the dimensionless capillary number.

Outputs

Publications

Spaid, M.A.A., and F.R. Phelan Jr., *Lattice Boltzmann Methods for Modeling Microscale Flow in Fibrous Porous Media*, Proceedings of the Third International Conference on Composites Engineering (ICCE/3), pp. 785-786, (1996).

Spaid, M.A. and F.R. Phelan, Jr., *Lattice Boltzmann methods for modeling microscale flow in heterogeneous porous media*, Physics of Fluids, (submitted).

Liquid Composite Molding: Bulk Resin Measurements for Process Monitoring and Control

J. P. Dunkers, R. S. Parnas, K. M. Flynn, R. E. Neff, D. L. Woerdeman, and D. D. Surlas

Objective

The objective is to develop optical fiber sensors, spectroscopic measurement methods, and control structures for monitoring and controlling chemical and physical processes during composites manufacturing.

Technical Description

The need to reduce the variation in composite quality has been recognized for many years. Variation in cure between parts and within a part is a major contributor to composite non-uniformity. The cure monitoring work focuses on fluorescence and near infrared spectroscopies, using an optical fiber drawn from a NIST standard glass as the sensing element. The information from the cure sensor is transferred to a process control computer that makes adjustments to the mold temperature to bring the cure into agreement with the desired cure trajectory, thus reducing part non-uniformity. For slowly curing materials, a model-assisted feedback controller uses the cure data provided by the sensor and a kinetic model of the resin to bring the actual cure trajectory into agreement with the desired cure profile. For rapidly curing materials, receding horizon control strategies are under development.

External Collaborations

Industrial: Automotive Composites Consortium, Ford, ICI Polyurethanes, Northrup/Grumman (DARPA)

Academic: University of Missouri, Florida State University

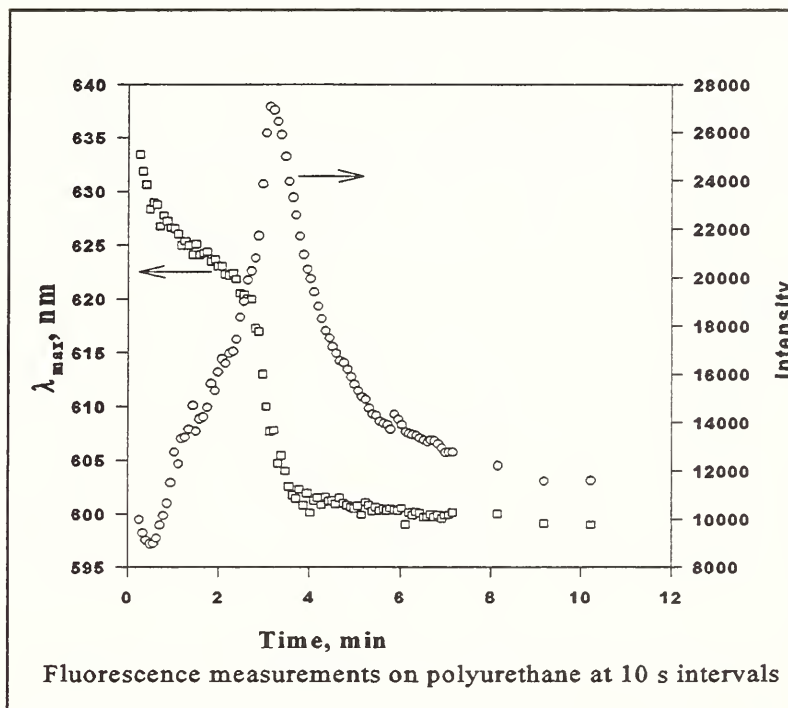
Accomplishments

Fluorescence Sensor:

Advances were made this past year in data analysis, interpretation, and instrumentation. A number of molding experiments were done with varying processing parameters and resin systems to evaluate the accuracy and range of operation of this monitoring technique. The sensor was found to work well in epoxy, polyurethane (see figure), and polyester systems.

Furthermore, the fluorescence measurements distinguished resin quality degradation in epoxy/amine systems. From statistical treatment of the data, it was found that errors in the measurements were largest early in the reaction and more pronounced at higher temperatures.

Time resolution was concluded to be the major source of error at early times, with the measurements approaching the instrument error, $\pm 2\text{nm}$, in the later stages of cure.



Development of a high speed fluorescence system continued during the past year to solve the problems associated with poor time resolution. A charged coupled device (CCD) camera detector and on-line spectral analysis were implemented, providing real-time data for rapidly curing systems. An example of the system capability is illustrated by the cure data obtained in a glass reinforced polyurethane composite. Data were obtained every 10 seconds, and the gel point is clearly indicated by the intensity peak at approximately 3 minutes. This speed and gel point detection is a requirement of the automotive industry for cure sensing. The sensor was made rugged and portable through the use of fiber optic components and a portable Ar^+ laser. The sensor system is implemented in an industrial liquid molding facility, where the ability of the sensor to predict the final molded part quality will be assessed.

Near Infrared Sensor:

The fiber optic sensor is coupled with a Fourier transform infrared spectrometer to monitor the cure of the resin in the middle of a resin transfer molded part using evanescent wave spectroscopy. Near infrared spectroscopy provides a direct measure of chemical information and the ability to follow multiple reactions simultaneously. A mini-bundle fiber optic sensor was constructed of three, $130\ \mu\text{m}$ diameter fibers with a refractive index of 1.62. A mini-bundle configuration was chosen to optimize the signal to noise ratio by increasing energy throughput.

The spectrometer, optics, and detector are constructed in a 0° configuration where light is launched into one end of the fiber mini-bundle and detected at the other end.

A number of molding and sample cell cure experiments were successfully performed using an epoxy/amine resin system up to 150 °C. From these spectra, information about the oxirane and amine consumption or the hydroxyl group evolution can be analyzed in real time to provide cure data to the controller. The isothermal sample cell spectra are used to generate a kinetic model for the control algorithm. Using rapid scanning software, spectra of a reacting polyurethane resin system were also obtained, demonstrating that the near IR system can also be used with rapidly curing systems.

Control:

A model-assisted feedback cure control algorithm, previously developed in this project, was tested with cure simulations and experiments. Simulations helped optimize the controller parameters and experiments demonstrated the controller effectiveness with epoxy/amine resins in glass reinforced composites. The control algorithm was also analyzed for robustness to measurement noise. Both simulations and experiments demonstrated that the presence of noise did not alter the optimum control parameters, and that acceptable control was maintained up to approximately 5 % measurement noise.

The previously developed algorithm was useful for controlling the cure to relatively simple pathways, and was generalized to permit arbitrarily complex cure pathways as functional setpoints. Analytical approximations to nonisothermal cure models were developed to permit the algorithm to invert measured cure data to find history dependent temperature setpoints.

Impact

Sensor and control technology implemented at Grumman for the manufacture of the greenbody of a ceramic matrix composite part of a jet engine. Sensor technology implemented at Ford shortens the time to assess part quality from 1 day to 1 minute.

Outputs

Publications

R.A. Neff, D.L. Woerdeman and R.S. Parnas, *Use of a Charged Coupled Device (CCD) Camera for Evanescent Wave Optical Fiber Cure Monitoring of Liquid Composite Molding Resins*, Polymer Composites (submitted).

D. L. Woerdeman, J. K. Spoerre, K. M. Flynn and R. S. Parnas, *Cure Monitoring of the Liquid Composite Molding Process Using Fiber Optic Sensors*, Polymer Composites (in press).

J. P. Dunkers, K. M. Flynn and R. S. Parnas, *A Mid-Infrared Attenuated Total Internal Reflection Cure Sensor for the Control of the Resin Transfer Molding of a Pre-Ceramic Polymer*, Composites: Part A, December 1996.

J. P. Dunkers, K. M. Flynn, R. S. Parnas and D. D. Surlas, *The Effect of Noise and Control Parameters on the Efficiency of a Model Assisted Feedback Control Algorithm for Liquid Composite Molding*, Proceedings of the 1st Joint Topical Conference on Processing, Structure, and Properties of Polymeric Materials, in press.

D. L. Woerdeman, K. M. Flynn, J. P. Dunkers and R. S. Parnas, *The Use of Evanescent Wave Fluorescence Spectroscopy for Control of the Liquid Molding Process*, J. of Rein. Plas. & Comp., 15(9), 922 (1996).

Presentations

J. P. Dunkers, K. Flynn and R. S. Parnas, *An IR-ATR Cure Sensor for the Control of the Resin Transfer Molding of a Pre-Ceramic Polymer*, Gordon Research Conference on Composites, Ventura, CA, January 11, 1996.

R. Neff, *Evanescent Wave Optical Fiber Sensors for Monitoring and Control of the Liquid Molding Process*, Advanced Composites Conference and Exposition, Dearborn, MI, November 15, 1995.

R. S. Parnas, *Attenuated Total Reflection Infra-Red Cure Monitoring of the Liquid Molding Process for Ceramic Matrix Composites*, AIChE Meeting, Miami, FL, November 16, 1995.

R. S. Parnas, *Evanescent Wave Fluorescence Cure Monitoring for Use with Process Control of the Liquid Molding Process*, AIChE Meeting, Miami, FL, November 16, 1995.

R. S. Parnas, *Evanescent Wave Optical Fiber Cure Monitoring and Model Assisted Control of the Liquid Molding Process*, American Society of Nondestructive Testing Spring Conference, Norfolk, VA, March 19, 1996.

R. S. Parnas, *Sensors and Control*, Second Workshop on Liquid Composite Molding, Columbus, OH, June 14, 1996.

R. S. Parnas, *A Fiber Sensor for Simultaneous Fluorescence and Near Infrared Measurements During Composite Processing*, 1996 Fifth World Congress of Chemical Engineering, San Diego, CA, July 17, 1996.

D. L. Woerdeman and R. S. Parnas, *In-Mold Sensors to Monitor the Liquid Molding Process and Post Process Performance*, Society of Engineering Science, New Orleans, LA, October 31, 1995.

Liquid Composite Molding: Interphase Sensitive Sensors for Process Monitoring

R.S. Parnas

Objective

The objective is to develop sensors with sensitivity to the 100 Å region near the fiber surface, a critical region of composite materials that determines many of the bulk mechanical properties.

Technical Description

One possible route to such a sensor lies through localizing fluorescent dyes at the surface. The process of localizing fluorescent dyes at the surface entails synthesizing the appropriate dye with a chemical tail containing a surface reactive group, typically a silane coupling group. After completing the synthesis, surface grafting is conducted onto a substrate such as a flat glass slide or an optical fiber. The fluorescence of the surface bound material is measured in the presence of various solvents and resins to assess the ability of the surface bound fluorophore to respond to the environment. Critical technical issues that must be resolved after the surface chemistry is understood concern the structure of the surface layer, and the calibration of the surface bound fluorophore.

A second possible route to an interphase sensitive sensor lies through fiber ultrasonics, and work has begun to build on a previous project based on ultrasonic shear wave reflection. A substrate with known mechanical properties and a low attenuation for the propagation of ultrasonic shear waves is used, and a polymer is placed on its surface. A shear wave is generated in the substrate and reflects from the substrate-polymer interface. The amplitude and phase of the reflected wave depend on the mismatch in mechanical properties. By measuring the reflected wave and combining the results with the properties of the substrate, the viscoelastic behavior of the polymer in the region close to the interface can be calculated. Even thin polymer films can be characterized with this technique.

External Collaborations

Academic: Howard University, The Johns Hopkins University

Accomplishments

A second batch of Robello siloxane (fluorescent dye linked to silane coupling agent) was synthesized. Most importantly, the difficulty of reproducibly synthesizing the dye was elucidated by the different behavior exhibited by the second batch of dye. The solubility of the second batch was much higher than the first batch in organic solvents such as xylene, and the fluorescence behavior of the grafted layers was much worse. Once it was determined that the second batch of material was actually purer than the first batch, experiments were carried out to redevelop the grafting procedure. Controlled hydrolysis experiments demonstrated the necessity of water in the surface reaction to produce a fluorescing surface layer, and this result is consistent with the solubility behavior of the materials. Alternative synthesis routes involving the production of Robello alcohols are being explored in an attempt to better control the structure of the surface bound layer.

Previous ultrasonics studies used a manual technique for determining phase shift. It was time consuming, used just a few selected points in the signal, and produced a resolution that was only

marginal. A new technique has now been developed that digitizes the signal for the first two reflections and transfers the data to a computer for analysis. The data acquisition and analysis processes are fully automated and use the complete signal for maximum accuracy. To determine the stability of the result, several hundred measurements were made over a two day period with a bare substrate. The data show very little variation in the transit time, two standard deviations were less than 100 picoseconds. The practical limit to the scatter is governed by the temperature control, and this value is very close to that limit.

Environmental Durability Studies: Effect of Fiber Coatings and Interfaces

Gale A. Holmes and Donald L. Hunston

Objective

The objective is to determine the effects of fiber surface treatments and coatings on the durability of composites. The research is focused primarily on determining the effect of moisture attack on the fiber and fiber-matrix interface in glass fiber/epoxy systems.

Technical Description

Model composites containing a single bare E-glass fiber, with various silane coating treatments, embedded in an epoxy resin were prepared. Four types of silane coatings were employed, n-octadecyl trichlorosilane (n-OTCS), n-octadecyl triethoxysilane (n-OTES), γ -aminopropyl triethoxysilane (γ -APTMS), and γ -glycidyoxypropyl trimethoxysilane (γ -GOPTMS). In addition, a 35%/65% mole percent mixture of n-OTCS and γ -APTMS, respectively, was prepared. To determine the effect these coatings have on the interfacial shear strength and durability of the fiber and fiber-matrix interface when exposed to moisture, the single fiber fragmentation test (SFFT) has been used. Additionally, the coatings on the fibers are characterized by dynamic contact angle measurements for quality control and to determine the hydrophobicity for later correlation with the durability results.

Previous research in this project indicated that simplifying assumptions concerning the resin properties used in the analysis of SFFT data may have a significant impact on the interfacial shear strength and durability results. The micro mechanics models developed for the SFFT use simple linear elastic or elastic-plastic models for the resin mechanics, whereas it is well known that the resins are viscoelastic. Improved micromechanics models of the SFFT are being developed and tested with the data obtained from the samples with various coatings. To support the analysis effort, improved instrumentation and experimental techniques have been implemented to insure that the necessary data are acquired for the improved models.

External Collaborations

Industry: Owens Corning, OSI

Academic: University of Utah, Michigan State University

International: Versailles Advanced Materials and Standards Program (VAMAS)

Planned Outcome

- Develop a standard test method for measuring the interfacial shear strength in composites.

Accomplishments

Previous work used a coating procedure that was vulnerable to pH variation, and consequently caused experimental inconsistencies. Therefore, a new procedure, using 95 % ethanol, was devised to simplify the precipitating solution and control the pH. To eliminate the production of HCl, n-octadecyl triethoxysilane (n-OTES) was used instead of n-OTCS. In an effort to avoid excessive protonation of the amine group on γ -APTMS and minimize the hydrolysis of the epoxide group on γ -GOPTMS all solutions were precipitated under basic conditions. Characterization of the coated fiber surfaces by dynamic contact angle measurements showed that a fiber surface coated by the new procedure was slightly more hydrophobic than when prepared by the old procedure.

Careful attention to the experimental procedures used in the SFFT have revealed the following: (1) detectable viscoelastic relaxation often occurs with each strain increment, (2) the resin matrix is nonlinear elastic over the strain region of interest, (3) fiber fracture often occurs primarily in the nonlinear region of the matrix stress strain curve, and (4) absorption of moisture in the resin matrix reduces the yield stress of the matrix and significantly alters the stress strain curve of the matrix. These observations suggest that the linear elastic micro mechanics models do not accurately reflect the impact of the matrix on the shear-stress transfer process during the SFFT. In addition, significant changes in the matrix properties, *e.g.*, plasticization of the matrix due to moisture absorption, can result in significant changes in the shear-stress transmissibility of the fiber-matrix interface. Changes in the transmissibility of the fiber matrix interface are also caused by degradation of that interface. Therefore, it is important to ascertain the importance of changes in the matrix viscoelastic properties on the durability analysis and shear-stress transfer process. If these changes are important, the durability of the fiber-matrix interface can only be accurately ascertained by developing a method to decouple transmissibility changes due to changes in the matrix properties from transmissibility changes due to degradation of the fiber matrix interface.

To accomplish these tasks the fragmentation apparatus has been modified to include a load cell and a data acquisition program was written to take load measurements and fragment data during the SFFT. To obtain a better understanding of the fragmentation process, accurate measurements of the fragment lengths are being made after each strain increment. As a result, fragmentation maps are readily generated and the fragmentation results are being compared with updated micro mechanics models. To compare these results with the predictions of stress analysis, the basic viscoelastic properties of the resin are being determined by conducting stress relaxation experiments at a variety of strains using pure epoxy resin. The characterization data will be used for stress analyses conducted at NIST and will also be made available to others in the field through the VAMAS program.

In a further effort to examine fiber-matrix test methods, an international research effort has been organized with the assistance of Prof. Larry Drzal at Michigan State University. The initial focus

will be on the single fiber fragmentation test (SFFT). Previous round robins on the SFFT have been discouraging in that the data show a large scatter. Close examination of the results, however, suggests that the variations within each laboratory were significantly less, and where laboratories had close collaboration, the agreement between them was better. Consequently, it was suggested that much of the scatter may be attributable to differences in sample preparation technique and testing procedure among the various groups involved. The proposed program will examine this hypothesis. To date, 17 laboratories representing 6 different countries have agreed to participate in the program. It will be conducted under the auspices of the Composites Working Group of VAMAS, the Versailles Advanced Materials and Standards Program.

Outputs

Publications

K. S. Macturk, C. R. Schultheisz, D. L. Hunston and C. L. Schutte, *The Effect of Coupling Agent on Composite Durability*, p. 403 in Proc. Adhesion Soc. (Adhesion Society, Blacksburg, 1996).

D. L. Hunston, K. S. Macturk, C. R. Schultheisz, G. Holmes, W. G. McDonough and C. L. Schutte, *The Role of Silane Surface Treatments in Strength and Durability of Fiber-Matrix Bonding in Composites*, Vol. 2, pp-427-432 in Proc. EurAd'96, European Adhesion Conference (The Institute of Materials, London, 1996).

Environmental Durability Studies: Comparison of Test Results for Laminated Composite Samples and Single-Fiber Composite Specimens

C.R. Schultheisz and D.L. Hunston

Objective

The objective is to determine if micromechanical measurements on model systems can predict the long-term durability of composite materials.

Technical Description

The single-fiber fragmentation test (SFFT) has been shown to provide a qualitative ranking of resin/fiber interface strengths. This test also provides information about the degradation of the interface when samples are subjected to long term exposure to heat, water, and other environmental effects. To determine the accuracy of SFFT tests for predicting composite material behavior, the results have been compared with mechanical measurements on composites.

An E-glass/epoxy model system was chosen as the initial focus in the overall task, because glass-fiber composites involve lower raw- material costs and a potentially larger-volume market as structural composites when compared to carbon-fiber composites. The program involves testing single-fiber samples in a dry state and after varying times of immersion in 25 °C and 75 °C distilled water, and evaluating the degradation of the fiber and fiber/matrix interface. In addition,

tests on macroscopic samples in the dry state and at two levels of moisture uptake at 25 °C and 75 °C were performed for comparison. Four types of mechanical tests have been used: tension tests to reflect the degradation of the fiber strength, while compression tests and interlaminar fracture tests in Mode I and Mode II reflect the degradation of the interfacial strength and changes in the matrix material.

External Collaborations

Industrial: Automotive Composites Consortium, Owens-Corning, Dow Chemical, Morrison Molded Fiber Glass, Textile Research Institute.

Academic: University of West Virginia, Northwestern University

Accomplishments

Fabrication, immersion (in 25 °C and 75 °C distilled water for up to 5000 hours), and testing of the single-fiber fragmentation samples and the macroscopic composites have been completed. Although there is considerable scatter in the data, degradation of both the glass fibers and the fiber/matrix interface is apparent. Tension and Mode I fracture tests on the resin alone have also been completed. The tests on the macroscopic samples show good correlation with the results from tests on the micro-composites up to a point. The tensile test results do reflect the changes in the fiber strength determined using the single-fiber test quite well. However, the compression samples were found to be too thick, leading to failure by crushing in the grips; the transverse failure mode may also reflect changes in the interfacial strength, but the test is not designed to measure that property. The results from the interlaminar fracture tests are also somewhat ambiguous because of the large increase in fracture toughness in the matrix material alone associated with moisture uptake: the interlaminar fracture results reflect a competition between decreasing interfacial strength and increasing matrix toughness.

A model for the degradation of the glass fibers has been developed. The model includes the effects of stress corrosion (attack by moisture of stressed fibers) and zero-stress aging (attack by moisture of unstressed fibers). From the rate of degradation (initially rapid, then slowing) it appears that zero-stress aging is the dominant effect. This point is important, as it implies that the presence of water at the surface of the glass fiber is sufficient to cause significant degradation, even without the influence of additional tensile stresses (which were quite large in the single-fiber fragmentation samples, caused by swelling of the matrix). It appears that the zero-stress aging behavior can be described by an activation energy, in which case elevated temperature can be used as a means of accelerated testing of the strength of the fibers. If the interfacial degradation and matrix changes could also be described with activation energies, elevated temperatures would be a means of accelerating the changes in these properties as well, with different activation energies associated with different rates of change with temperature.

Additional experiments have been performed in collaboration with the Automotive Composites Consortium to investigate the effects of water and other fluids (notably windshield washer and brake fluids) on candidate E-glass/polyisocyanurate materials of interest to the automotive

industry; the work at NIST has focused on the micro-mechanical tests for comparison with tests on macroscopic composites performed at Oak Ridge National Laboratory.

Finally, an additional collaboration to study the use of composites in infrastructure applications (such as bridges and roads) has begun with Northwestern University's Basic Industrial Research Laboratory, the University of Kentucky, Morrison Molded Fiber Glass and a number of State Departments of Transportation. The corrosion resistance and light weight of composite materials offer many advantages for civil engineering uses. An initial literature survey on this topic is nearly complete, and experiments have been performed to investigate the durability of pultruded composite materials that can be used to retrofit existing structures or for new construction.

Outputs

Publications

C. Schultheisz, C. Schutte, W. McDonough, K. Macturk, M. McAuliffe and S. Kondagunta, *The Durability of Glass-Fiber/Epoxy Composites Evaluated from Single-Fiber Fragmentation Tests and Full-Scale Composites Immersed in Water*, Proceedings of the Society for Experimental Mechanics, VIII International Congress on Experimental Mechanics, pp. 106-107, June 10-13, 1996, Nashville, Tennessee.

C. Schultheisz, W. McDonough, S. Kondagunta, C. Schutte, K. Macturk, M. McAuliffe and D. Hunston, *Effect of Moisture on E-glass/Epoxy Interfacial and Fiber Strengths*, American Society for Testing and Materials, 13th Symposium on Composite Materials: Testing and Design, ASTM STP 1242, Orlando, Florida, May 20, 1996.

K. Liao, R. Altkorn, S. Milkovich, J. Gomez, C. Schultheisz, L. Brinson and J. Fildes, *Long-Term Durability of Composites in Secondary Infrastructure Applications*, 28th International SAMPE Technical Conference, November 4-11, 1996, Seattle, Washington.

Presentations

C.R. Schultheisz, W.G. McDonough and G.A. Holmes, *The Effects of Automotive Fluids on the Degradation of Glass/Isocyanurate Composites*, American Institute of Chemical Engineers 1995 Annual Meeting, Miami Beach, Florida, November 16, 1995.

W.G. McDonough, C.R. Schultheisz and G.A. Holmes, *Durability Issues in Glass/Polysocyanurate Composites when Exposed to Automotive Fluids*, Materials Research Society 1995 Fall Meeting, Boston, Massachusetts, December 1, 1995.

C. Schultheisz, *Durability of Composites*, The Materials Science Club of New York, Hoboken, New Jersey, April 4, 1996. Also, Exxon Research and Engineering Company, Annandale, New Jersey, April 5, 1996.

C. Schultheisz and G.A. Holmes, *Durability of E-glass/Epoxy Composites Immersed in Water*, Regional Technical Conference, Society of Plastics Engineers, October 28-29, 1996.

C. Schultheisz, *Durability of Composites*, University of Delaware, November 8, 1996.

Environmental Durability Studies: Development of Processing Methods to Fabricate Urethane Samples

W.G. McDonough and R.S. Parnas

Objective

The objective is to develop new processing procedures that will enable the preparation of urethane test specimens that can be used in the microstructure program and which are equivalent to materials made in industry by structural reaction injection molding (SRIM).

Technical Description

Single fiber specimens for the SFFT are typically prepared by pouring premixed resin into an open rubber mold, and then curing the resin in an autoclave. That method cannot work with rapidly curing resins of interest to the auto industry. Consequently, an injection molding procedure is being developed that will closely mimic the processing speed, temperature, and pressure observed in the SRIM process used with the resins of interest. The dogbone samples thus prepared will be tested by SFFT to determine if the interface strength is degraded under rapid processing conditions.

External Collaborations

Industrial: Automotive Composites Consortium (ACC), The Dow Chemical Co., and Bayer Corporation

Accomplishments

A mold from the Liquid Composite Molding Projects was modified by adding an insert that contains several dog bone shaped cavities. When the resin is injected, the cavities produce multiple fragmentation samples. A specially designed injection system was made to simulate the SRIM process. The isocyanate resin is put into one chamber and the polyol mixture is put into another chamber, and during processing, the liquids are combined together in a static mixer and injected into the mold. Preliminary trials with the Dow system were very encouraging, but a shift in requirements at the ACC has necessitated the shift to the Bayer system.

Flow visualization experiments have been carried out with nonreacting fluids to simulate the hydrodynamic loads experienced by the single fiber in each mold cavity. The fibers survived high speed injections, indicating that dogbone samples can be prepared in a rapid injection and cure process.

Impact

- Showed the ACC how to make void free polyurethane composites in an SRIM process by controlled application of backpressure to the mold during and after injection.

Outputs

Publication

G. Holmes, W. McDonough and C. Schultheisz, *Comparison of Polyisocyanurate Networks Using Swelling Tests*, Proc. of 11th Annual Advanced Composites Conference and Exhibition 11/95.

Presentations

W. G. McDonough, *Durability of composites: processing and testing issues in model single fiber composites*, Tokyo Institute of Technology, Tokyo, Japan, September 2, 1996.

W. G. McDonough, *Evaluating a polyurethane/glass fiber composite for interfacial strength studies*, National Fisheries University of Pusan, Pusan, South Korea, September 12, 1996.

...the ... of ...

Output

...the ... of ...

...the ... of ...

...the ... of ...

...the ... of ...

POLYMER CHARACTERIZATION

The Polymer Characterization Program provides measurement methods, data, and standard reference materials needed by U.S. industry, research laboratories, and other federal agencies to characterize polymers for processibility, properties, and performance. Molecular weight and molecular weight distribution are the molecular characteristics of polymers that most affect their processing, properties and performance. Properties and performance, particularly mechanical attributes, may also vary widely depending on the solid state structure formed during processing. Furthermore, unlike other materials, polymers exhibit mechanical properties that are both time and rate dependent, even at sub-ambient temperatures. As a result, the focus of the program is on techniques that measure molecular weight and its distribution, the solid state structure of polymers, and time and rate dependent (viscoelastic) mechanical properties.

Primary methods employed for molecular weight characterization are dilute solution light scattering and osmometry. Chromatographic techniques, which require calibration by standards of known molecular mass, provide information on molecular weight distribution. Recent activities exploit advances in mass spectrometry using mass assisted laser desorption ionization (MALDI) to develop the method as a primary tool for the determination of the molecular weights of synthetic polymers. Solid state structure of polymers is elucidated using spectroscopic methods such as solid state nuclear magnetic resonance (NMR) and infrared spectroscopy. Other techniques such as small and wide angle x-ray scattering, and dilatometry are also used in this endeavor.

Adequate characterization of the time, rate and strain dependencies of mechanical properties of polymer requires a large number of tests. For this reason, methods are developed that reduce the number of tests necessary to describe the nonlinear thermo-viscoelastic properties of polymers. The approach applies the theoretical frameworks of continuum mechanics (solid and fluid rheology) and micro- to meso-scale physical models to interrelate the mechanical responses under different loading conditions. Model predictions are tested using the torsional dilatometer, conventional rotational rheometry tools and servo-hydraulic mechanical test devices. The combination of experimental and modeling provides the basis for both improved models and the development of new experimental methods for measuring material properties.

The polymer industry and standards organizations assist in the identification of current needs for standard reference materials. Based on these needs, research on characterization methods and measurements are conducted leading to the certification of standard reference materials. Molecular standards are used primarily for calibration of gel permeation chromatographs, the principal method employed by industry for assessing molecular weight and molecular weight distributions. Melt flow standards are used in the calibration of instruments used to determine processing conditions for thermoplastics.

Significant Accomplishments

- Recertified SRM 706, a polystyrene molecular weight standard used in the calibration of size exclusion chromatographs.
- Completed a procurement requisition for a Matrix Assisted Laser Desorption Ionization mass spectrometer (MALDI MS) scheduled for delivery in February, 1997.
- Developed a general methodology for comparison of the molecular weight distribution, MWD, obtained from MALDI MS with that obtained from size exclusion chromatography.
- Determined by NMR that the mixed phase of a metal-sulfonated poly(styrene)/methylated poly(amide) had a near-average level of sulfonated styrenes, rather than a preferential higher level anticipated from polarity arguments.
- Determined by transmission electron microscopy the polydispersity of the micelles composed of graft copolymers of polystyrene (PS) and poly(methacrylic acid) (PMMA) as well as the number of aggregates per micelle.
- Designed and constructed an attachment to the small angle x-ray facility for crazing samples under constant deformation to study microstructural changes in polymers due to pre-craze damage accumulation.
- Established that the tension and compression responses of a commercial grade poly(carbonate) can be described within 15 % based on properties obtained from torque and normal force data in torsion. The result required development of a compressible form of Valanis-Landel Strain Energy Function.
- Collaborated with researchers from GE in the development of time-temperature and time-aging time shift data base for amorphous poly(carbonate) in torsion and in the linear viscoelastic range.
- Collaborated with researchers from Kodak to obtain time-temperature and time-aging time data for poly(ethylene terephthalate) and poly(ethylene naphthalate) thin films by conducting temperature jump experiments in stress relaxation.
- Conducted preliminary calculations of warpage in polymer sheet structures using a finite element code that incorporated non-exponential temperature dependence and physical aging shift factors.
- Verified model of failure in adhesive joints based on local deformation at the crack tip through comparisons of experimental observations of local shear strains in adhesive joints

and model predictions.

- Designed and constructed apparatuses for performing mechanical tests under conditions of sudden changes in concentrations of plasticizers.

Standard Reference Materials

Charles Guttman, William Blair, Bruno Fanconi, John Maurey

Objective

Provide the U.S. polymer industry with standards for calibration of instruments used in the control of the synthesis and processing of polymers. Principal polymer standards are certified for molecular weight and melt flow rate; the former are used to calibrate gel permeation chromatographs and the latter to calibrate melt flow indexers.

Technical Description

New Polyethylene Molecular Weight Standards

Polyethylene is the dominant commercial polymer in the United States and worldwide. High temperature (150°C) size exclusion chromatography (SEC), although a relative method requiring calibration, is the most commonly used method to establish the molecular weight of these polymers. Yet, few SEC calibration standards are available on the market for the calibration of high temperature SEC. Molecular weight fractions with M_w/M_n of less than 1.2 are the most useful materials for calibrating SEC. The only commercial supplier of sharp fractions of polyethylene offers repackaged NIST polyethylene standard reference materials. These SRMs will soon be out of stock.

The lack of commercial standards arises out of the difficulties obtaining sharp relative molecular mass fractions of these materials and in measuring absolute relative molecular masses by light scattering or osmometry at temperatures as high as 150°C.

The original fractionation of a whole polyethylene that provided the fractions previously certified also yielded other fractions including ones with molecular weights around 5,000, 70,000 and 160,000 g/mol in sufficient quantity to produce three additional narrow fraction polyethylene SRMs.

These new materials along with current SRM 1482 and 1483 would provide a set of polyethylene fractions having molecular weights of

5,000
14,000 SRM 1482
32,000 SRM 1483
75,000
160,000

g/mol. This will provide the polymer industry with an adequate set of molecular weight calibrants for polyethylene. This work is supported by the Standard Reference Materials Program at NIST.

Recertification of Standard Reference Materials

In addition to producing new SRMs measurements are conducted leading to recertification of SRMs that are out of stock, exceeded normal shelf life, or repackaged for market reasons. If an SRM is out of stock then a complete certification must be carried out on a new batch of material, preferably one with molecular weight characteristics similar to those of the material being replaced. Light scattering and osmometry are the customary techniques used in complete recertifications. In cases where shelf life or repackaging are issues the approach is to use indirect measurements of molecular weight such as SEC or viscometry and compare results with those obtained during the original certification.

Accomplishments

New Polyethylene Molecular Weight Standards

All three polyethylene fractions have been purified by recrystallization. Preliminary SEC analyses were conducted to check homogeneity. Instrumentation required for the certification, refractometer and light scattering apparatus, were modified for high temperature operations. Sufficient amounts of the solvent, *alpha*-chloronaphthalene have also been purified.

Polystyrene SRM 706

When the packaged inventory of SRM 706 was depleted the Standard Reference Materials Program, SRMP, proceeded to bottle the remaining polystyrene pellets from the original material. Size exclusion chromatography was used to check bottle-to-bottle variability and a recertification by light scattering was carried out.

Polyethylene SRM 1482, a narrow molecular weight fraction

Due to a dwindling supply of 1482, SRMP repackaged the existing stock, reducing the amount of material from 1 g to 0.4 g. Size exclusion chromatography measurements were made to ascertain bottle-to-bottle variability of the newly packaged material and intrinsic viscosity measurements were made to insure that the material had not changed since the original certification.

Planned Outcome

The three polyethylene standards, together with existing standards will improve calibration of size exclusion chromatographs by providing the polymer industry with molecular mass standards covering the range (5000 to 160,000) g/mol.

Mass Spectrometry of Polymers

Charles Guttman

Objectives

Improve calibration standards for size exclusion chromatographs (SEC) to make these instruments, widely used by the polymer industry, more reliable for characterizing the molecular weight and distribution of polymers. Develop mass spectrometry as a primary tool for the determination of the molecular weights of synthetic polymers that will become the next generation calibration materials for SEC.

Technical Description

Recent advances in Matrix Assisted Laser Desorption Ionization (MALDI) Time of Flight (TOF) Mass Spectrometry (MS) extend the range of detectability of whole undegraded polymer molecules with molecular masses up to 300,000 g/mol. An evaluation of MALDI TOF MS was made to determine its usefulness in determining the absolute molecular mass of synthetic polymers which would become molecular weight Standard Reference Materials (SRM) for calibration of size exclusion chromatographs. Initially, the repeatability of the spectra obtained on current molecular mass SRM's will be tested as a function of sample preparation methods, as well as instrument operation parameters and data analysis.

Accomplishments

After an extensive survey and evaluation of available instrumentation a procurement requisition for a MALDI TOF MS was completed leading to the successful procurement of an instrument scheduled for delivery in February, 1997.

A collaboration with Rohm and Haas provided an opportunity to gain experience on a MALDI instrument and study SRM 1487, a poly(methyl methacrylate), PMMA, SRM having a narrow molecular weight distribution centered near 6300 g/mol. The mass spectrum revealed features attributable to α - methyl styrene, the initiator used in the anionic polymerization of this material. It was found that each PMMA polymer molecule contained zero to seven α -methyl styrene units. The molecular weight distribution, MWD of polymer chains containing a fixed number of α -methyl styrene units was obtained. The MWD, M_w and the average number of α -methyl styrene units at a given molecular mass determined from MALDI TOF MS compared well with those obtained from more traditional methods such as ultracentrifugation and Size Exclusion Chromatography (SEC).

Recently, some researchers reported limited success in comparing the MWD of synthetic polymers obtained from SEC with the MWD obtained from time of flight mass spectrometry (TOF-MS). As part of the effort to apply MALDI-MS to the determination of the absolute molecular weights and molecular weight distributions of synthetic polymers, a general methodology was developed for comparison of the MWD obtained from MALDI TOF MS data of number of molecules of a particular mass with the MWD obtained from SEC data of concentration of molecules of a particular retention time.

Although the determination of the absolute molecular weights and molecular weight distributions of synthetic polymer SRM's by MALDI TOF MS appears promising, it must be verified that the detected molecular weight distribution is identical to that of the polymer.

External Collaboration

A collaboration with Dr. Paul Danis, a research chemist at Rohm and Haas, resulted on a joint publication on the MALDI TOF MS of NIST SRM 1487, a poly(methyl methacrylate).

Planned Outcomes

The methods developed in this project will simplify and improve the use of size exclusion chromatography to measure the molecular weight distribution (MWD) of polymers. Common industrial practice is to measure MWD by size exclusion chromatography (SEC) that requires calibration by a set of polymers of known molecular weight. Since standards are unavailable for most polymers crude approximations are used which introduce uncertainties in the measurement results. The methods developed will yield standards of known MWD adequate for SEC calibration. The availability of such standards for a wide range of commercial polymers will provide the polymer industry and research community with reliable calibrants for SEC to optimize the synthesis, processing and performance properties of polymers.

Outputs

Publications

Charles M. Guttman, *The Relationship between the Signals from Size Exclusion Chromatography and Time of Flight Mass Spectrometry to a Polymer Molecular Weight Distribution*, Polymer Preprints, vol. 37 #1, March 1996.

Charles M. Guttman, William R. Blair, Paul O. Danis, *Mass Spectroscopy and SEC of SRM 1487, a Low Molecular Weight Poly(methyl methacrylate) Standard*, Journal Polymer Science, Part B: Polymer Physics, submitted.

Presentations

Charles M. Guttman, *The Relationship between the Signals from Size Exclusion Chromatography and Time of Flight Mass Spectrometry to a Polymer Molecular Weight Distribution*, ACS Spring, 1996 Meeting, New Orleans, LA.

Charles M. Guttman, William R. Blair, Paul O. Danis, *Mass Spectroscopy and SEC of SRM 1487, a Low Molecular Weight Poly(methyl methacrylate) Standard*, Polymer Physics Gordon Conference, Kingsport, RI, July, 1996.

Characterization of Polymers by Spectroscopic Techniques

David VanderHart

Objectives

The objectives are to develop and use Nuclear Magnetic Resonance (NMR) techniques for characterization of molecular and microstructural level features that control properties of polymers.

Technical Description

Conceptually, the NMR work is aimed both at uncovering new insights into polymer structure and at the continuing development of NMR techniques for characterizing polymers. The following

techniques have been drawn upon in our studies.

Proton spin diffusion is characteristic of an extended network of dipolar-coupled protons and is typical of organic solids; it is evidenced by the flow of proton polarization following the imposition of a polarization gradient. This flow is in a direction that restores spin equilibrium. Thus, properly designed proton spin diffusion experiments yield information about spatial relationships and domain size in organic polymers.

Multiple pulse proton techniques offer a way to quench spin diffusion and simultaneously, especially in the presence of magic angle sample spinning (MAS), achieve some chemical shift resolution for protons in solids.

Paramagnetically induced proton relaxation is the enhancement of proton relaxation rates which results from proximity to unpaired electrons. These electrons themselves relax, thereby causing large fluctuations in the local magnetic fields at the protons; and this, along with spin diffusion, is the mechanism for perturbing the proton relaxation.

¹³C spectra, obtained using MAS, offer the best chemical resolution for organic solids. Also, one can often distinguish signals arising from the same chemical species in different states of order, e.g. crystal or non-crystal. Efforts continue to develop strategies for improving resolution in order to provide greater ability to distinguish not only chemically different species but also chemically similar species in physically different sites.

Applications of these techniques to polymers include the following.

- Develop a better understanding of the morphology which evolves when a semicrystalline polymer is mixed with an ionomer. The ionomer possesses a few 'decorations' which strongly interact with the semicrystalline polymer; in the absence of these few strong interactions, there would be no compatibility. The morphology and its stability reflect the interplay between the favorable energetics of crystallization and the tenacity of the strong intermolecular interactions. Furthermore, the work includes studies of the effects of the extent of chemical substitution and the influence of polar diluents, such as water, on the blend morphology.
- Develop a better understanding of chemical changes and their uniformity in high-temperature chars when additives are used to promote char formation. The search for less toxic flame retardant polymers is currently intense worldwide. This research seeks to get at the mechanism of enhanced char formation.

External Collaborations

Yi Feng of AT&T Bell Laboratories, Murray Hill, NJ

Professor Robert Weiss of Univ. of Connecticut, Storrs, CT

R.H. Atalla of the USDA, Forest Products Laboratory, Madison WI

Professor Norritsu Terashima of Nagoya, Japan

Accomplishments

For the ionomer blend (metal-sulfonated poly(styrene)/methylated poly(amide)), experiments were carried out to determine the relative importance of temperature versus water in aging. Experiments showed that water was much more effective than a 20°C temperature rise. The morphological changes during aging are also interesting: for a blend consisting of 18 % by mass Zn⁺⁺-containing ionomer (12 % of the rings decorated), the overall dimension for compositional heterogeneity is (20 to 25) nm and this does not change with aging. However, with aging, the size of the polyamide crystals increases and the ionomer becomes increasingly demixed from the non-crystalline poly(amide). Thus, the smaller-scale morphology is demixing while the larger-scale morphology is stable.

In addition, the use of Cu⁺⁺ as a paramagnetic metal ion in the ionomer caused the proton relaxation to be dominated by the fluctuating electrons. As a result of analyzing the heterogeneity of proton relaxation, two conclusions were reached: a) In the pure ionomer where 12 % of the aromatic rings are randomly sulfonated, the range of variation of local Cu ion concentrations, averaged over a distance scale of 14 nm, was less than a factor of 1.35 for 95 % of such domains. b) In a blend of 75 % ionomer (with 2.3 % of the rings decorated) and 25 % poly(amide), phase separation takes place where all or most of the poly(amide) mixes with 12-16 % of the ionomer in one phase; the remainder of the ionomer goes to the other phase. It was expected that the portion of the ionomer in the mixed phase would possess above-average decoration levels. Surprisingly, the data suggested that the ionomer in the mixed phase had a near-average level of decoration.

The work on polymer chars is at a preliminary stage and is being carried out with Dr. Jeff Gilman of the Fire Science Division at NIST. The ¹³C spectra, elemental analysis and electron spin resonance (ESR) spectra were obtained on chars of poly(vinylacetate) containing silica gel and potassium carbonate additives that promote the level of charring. The ESR results show that there is a substantial number of free radicals in the chars which have the potential of reducing ¹³C signals. Although ¹³C spectra are obtained on the chars it is likely the less than one-half of the total ¹³C are measured. The question is whether the spectra, while not quantitative, are representative of the whole. To address this, proton 'spin counting' experiments are performed to see if the proton signal intensity is consistent with elemental analysis. The results to date indicate that a larger fraction of the protons are observed than the ¹³Cs. Furthermore, the relaxation of the protons is inhomogeneous on a T₁^H timescale of a few hundred ms. Hence, there is considerable inhomogeneity of composition in the chars and that raises more serious questions about the representative character of the ¹³C spectra. Another consideration which can be invoked to explain inhomogeneously reacted region of chars is the difference between physically encapsulated and unencapsulated regions. This aspect is also under investigation.

With respect to the issue of spectral resolution in ¹³C spectra with magic angle spinning, linewidth and transverse-relaxation (T₂^C) data have been accumulated on crystalline polyethylene, a polymer whose carbons have strong dipolar couplings with protons. These data were taken at different spinning speeds, proton rf-decoupling field strengths, static fields and different choices of the proton rf frequency in the vicinity of the proton resonance. The resolution achieved for the ¹³Cs in polyethylene is a function of all of these parameters. Of particular interest is the observed

dependence on the static field which points to the important role that the proton chemical shift anisotropy plays at higher static fields. The second important finding is the rather long lifetimes of the proton spin states for those protons attached to the ^{13}C nuclei. A recognition of this longer lifetime will allow certain modulation schemes to be effective in enhancing resolution.

Outputs

Publications

N. Terashima, R.H. Atalla and D.L. VanderHart, *Solid State NMR of Specifically ^{13}C Enriched Lignin in Wheat Straw*, submitted to *Phytochemistry*.

D. L. VanderHart and G.B. McFadden, *Some Perspectives on The Interpretation of Nmr Spin Diffusion Data in Terms of Polymer Morphologies*, *Solid State NMR* (in press)

Presentations

D. L. VanderHart, Y. Feng, C.C. Han and R. Weiss, *Morphological Investigation of Sulfonated Poly(styrene) Ionomers and their Blends with a Poly(amide) Using ^{13}C NMR and Proton Spin Diffusion Methods*, American Physical Society Meeting, St. Louis, March 1996.

D. L. VanderHart, *NMR Investigations of Polymer Morphology Using Proton Spin Diffusion*, Chemistry and Applied Science Department Seminar, William and Mary University, April 1996.

D. L. VanderHart, *Morphological Study of a Sulfonated Poly(styrene)/Poly(amide) Blend Using Solid State NMR*, 38th Rocky Mountain Conference on Analytical Chemistry, Denver, Colorado, July 1996.

Characterization of Polymer Morphology by Microscopy Techniques

C. L. Jackson

Objectives

The objectives are to utilize optical and electron microscopy to study the morphology of polymeric materials and to investigate the potential of new microscopy techniques, such as scanning force microscopy, cryo-TEM, and TEM with image processing, to solve problems in polymer morphology.

Technical Description

The characterization polymer morphology is important to better understand the relationship between structure and properties in many materials. Techniques used include transmission electron microscopy (TEM), scanning electron microscopy (SEM), optical and atomic force microscopy. The combination of microscopy techniques with other methods such as scattering,

diffraction or spectroscopic methods gives a more complete description of the structure of complex blends, composites or other multiphase materials. Many types of materials have been studied to date, including polymer blends, block copolymers, liquid crystalline polymers, and organic-inorganic hybrid materials.

External Collaborations

A collaboration with Dr. Henri Chanzy of CNRS in Grenoble, France has been initiated to add measurement capability in the area of cryo-TEM. This method allows solutions or suspensions of polymer aggregates, micelles or dendrimers, for example, to be imaged directly in vitrified solvent. This method has not been widely used on synthetic polymers. Preliminary work is being done at NIH in collaboration with Drs. F. Booy and A. Stevens.

Accomplishments

From TEM studies of graft copolymers of polystyrene (PS) and poly(methacrylic acid) (PMMA), the dried micelles were found to be about one-third the size of the solubilized micelles as measured by dynamic light scattering and small angle neutron scattering. This implies that the PS cores are swollen and the PMMA chains in the corona are almost fully extended in solution. From the TEM studies, the polydispersity of the micelles as well as the number of aggregates per micelle were determined.

Other recent studies have focused on phase separated polymer blends containing block copolymer as a compatibilizer where the kinetics of phase separation at constant and shallow quench depths was studied by light scattering techniques. As block copolymer is added, the kinetics of phase separation slows dramatically. TEM specimens were prepared under similar conditions to compare the real-space morphology on these complex ternary systems.

Outputs

Publications

C. L. Jackson, L. Sung, and C. C. Han, *Evolution of Phase Morphology in Compatibilized Polymer Blends at Constant Quench Depths: Complimentary Studies by Light Scattering and Transmission Electron Microscopy*, Polym. Eng. Sci., submitted.

C. L. Jackson, B. J. Bauer, A. I. Nakatani and J. D. Barnes, *Synthesis of Organic-Inorganic Materials from Interpenetrating Polymer Network Chemistry*, Chem. Mater., 1996, **8**, 727-733.

C. L. Jackson, L. Sung and C. C. Han, *Morphology and Phase Separation Kinetics of a Compatibilized Blend*, SPE Antec Proc., 1996, 1599.

Presentations

C. L. Jackson, *Vitrification and Crystallization of Organic Liquids Confined to Nanoscale Pores*, American Chemical Society, Orlando, FL, August, 1996.

C. L. Jackson, *Morphology Evolution and Phase Separation Kinetics in a Polymer Blend with Diblock Copolymer Additive*, Gordon Conference on Polymer Physics, Newport, RI, July 1996.

C. L. Jackson, *Morphology and Phase Separation Kinetics of a Compatibilized Blend*, Society of Plastics Engineers, Indianapolis, IN, May 1996.

C. L. Jackson, *Micellar Structure of a Model Ionic Graft Copolymer*, American Physical Society, St. Louis, MO, March 1996.

Structural Characterization of Polymers by Small Angle X-Ray Scattering

John D. Barnes

Objectives

A Small Angle X-Ray Scattering Facility is maintained both to serve as a user facility for outside industrial clients and to support research within the Polymers Division. The project objectives are focused on maintaining an up-to-date, state-of-the-art SAXS Facility that develops and incorporates improvements in analysis methods and instrumentation that expand the use of small angle x-ray scattering (SAXS) as a technique for characterizing materials and processes.

Technical Description

By maintaining a state-of-the-art SAXS facility, Polymers Division researchers are able to perform in house research relevant to ongoing programs as well as collaborative research with both industrial and academic scientists. Of particular interest is the two-dimensional capability of the NIST area detector and development of special techniques such as oblique incidence scattering, elevated temperature capabilities and deformation stages for studies. In addition, analytical capabilities are constantly upgraded and implemented as the need or opportunity arises.

External Collaborations

The SAXS facility was used during the year for projects with outside users that fall into three categories. First, there were several extensive collaborations with industrial research laboratories in which the results were of importance to the company and also resulted in technical publications. W.R. Grace uses the oblique incidence technique to describe the through thickness orientation of developmental films, the Dow Chemical Company examines the morphology of injection molded syndiotactic polystyrene, and Air Products Company studies the microstructure of high performance polyurethanes. The SAXS facility is also used for proprietary measurements when the industrial client, i.e. W.R. Grace, is interested in protecting sensitive data. Finally, the facility attracts collaborators from the academic community and here work was undertaken with Michigan Technological Institute in the study of the microstructure of block copolymers under shearing deformations.

Planned Outcomes

NIST researchers and external users from industry, government and academic laboratories will have available a state-of-the-art small angle x-ray facility operated by experts who can assist in collection and analysis of data.

Accomplishments

- Created a new Commission on Small Angle Scattering within the International Union of Crystallography. John Barnes is currently serving as its first chairperson. This group's agenda includes important initiatives for improved standardization of experimental methods and data handling for small-angle scattering.
- Best Paper Award from Society of Plastics Engineers, Engineering Properties and Structure Division for work on SAXS from syndiotactic polystyrene under DOW Chemical Company CRADA.
- Developed new measurement technique for studying microstructural changes in amorphous polymers due to pre-craze damage accumulation in stress relaxation experiments.
- Designed multi-cell hot stage for scattering measurements at high temperatures.

Outputs

Publications

C.L. Jackson, B.J. Bauer, A.I. Nakatani, and J.D. Barnes, *Synthesis of Hybrid Organic-Inorganic Materials from Interpenetrating Polymer Network Chemistry*, Chem. Mater., 1996, 8, 727-733.

J.D. Barnes, G.B. McKenna, B.G. Landes, R.A. Bubeck, and D.A. Banks, *Morphology of Syndiotactic Polystyrene as Examined by Small Angle X-Ray Scattering*, Proc. SPE Annual Technical Conference, 1996, 1532-1535.

R. Hu, W.S. Lambert, and J.D. Barnes, *Structure-Property Correlation in Stretched LLDPE Film Using Oblique Incidence SAXS*, Proc. SPE Annual Technical Conference, 1996, 1839-1843.

Nonlinear Viscoelasticity of Solid Polymers

G.B. McKenna, C.R. Schultheisz, D.M. Colucci, and P.A. O'Connell

Objectives

The objectives are to develop measurement methods and analytical approaches for the analysis of the nonlinear viscoelastic response of polymers. In addition, evaluations are made of constitutive

relationships, with the emphasis on material clock or reduced time models, that allow the description of the mechanical response to complex mechanical and thermal histories.

Technical Description

Improvements in measurement methods are sought through modifications of conventional testing techniques such as extension and compression measurements in stress relaxation, creep or torsional measurements, the latter including torsional dilatometry. The experimental design is based on concepts from finite elasticity theory of incompressible materials for evaluation in compressible, viscoelastic materials in order to use simple measurements in a single geometry to predict properties under other test geometries. Thermal histories and multiple step strain and stress histories are applied to the materials to evaluate viscoelastic constitutive models based on material clock or reduced time concepts. Furthermore, a complete database for a single, well defined, glassy polymer is being developed for publication as a reference for evaluation of material models. The material itself can be distributed as a research material to interested and qualified laboratories.

External Collaborations

The major interaction is with the General Motors/General Electric Advanced Technology Program project on "Thermoplastic Engineering Design" in which viscoelasticity data on the project's polycarbonate thermoplastic material are provided to the GM and GE researchers for use in Numerical Modeling being developed at GM and GE. In addition, collaborative work with the University of Leeds in Leeds, UK, demonstrated the ability to extend finite elasticity concepts to finite viscoelasticity as a means of determining material model parameters from simple tests (uniaxial extension) to predict the response in shear and equi-biaxial extension.

Planned Outcomes

- Comprehensive materials data base for the nonlinear viscoelastic properties of a single glassy polymer in multiple deformation geometries (torsion, tension and compression) and in creep and stress relaxation types of histories. This data base will be available for researchers to evaluate different constitutive models of nonlinear viscoelasticity of polymer glasses.
- Maintain a supply of the poly(carbonate) on hand for distribution as a research material to interested and qualified laboratories.
- Establish the range of validity of using incompressible finite elasticity concepts to describe compressible, viscoelastic materials.

Accomplishments

- Established that finite elasticity concepts can be used to determine the time-dependent strain potential function of polyvinyl chloride in the incompressible melt regime. Predictions from uniaxial extension tests in stress relaxation were within 25 % of the values measured in constant rate of extension in both pure shear and equibiaxial test

geometries.

- Established that the tension and compression responses of a commercial grade poly(carbonate) can be described within 15 % based on properties obtained from torque and normal force data in torsion. The result required development of a compressible form of Valanis-Landel Strain Energy Function.
- Discovered that poly(carbonate) in tension can undergo densification at long relaxation times. In compression, densification was found to continue to increase after application of a constant deformation. Both results are attributed to the non-equilibrium state of poly(carbonate) at room temperature.

Outputs

Publications

C. R. Schultheisz, D. M. Colucci and G. B. McKenna, *Experimental Evidence and Modeling of the Differing Time Scales of Structural Recovery and Mechanical Relaxation Observed During Aging of Glassy Polymers*, Proceedings of the Society for Experimental Mechanics, VIII International Congress on Experimental Mechanics, June 10-13, 1996, Nashville, Tennessee.

A.S. Wineman and G.B. McKenna, *Determination of the Strain Energy Density Function for Compressible Isotropic Nonlinear Elastic Solids by Torsion-Normal Force Experiments*, In Nonlinear Effects in Fluids and Solids, ed. By M.M. Carroll and M. Hayes, Plenum Press, New York, 1996.

J.J. Pesce and G.B. McKenna, *A Comparison of Torque and Normal Force Responses in Polycarbonate in One and Two Step Torsional Histories with a Material Clock Model*, in Mechanics of Plastics and Plastic Composites, 1995, ed by M.C. Boyce, American Society of Mechanical Engineers, 1995, MD-68 and AMD-215, 309-336.

C.R. Schultheisz, G. B. McKenna, Y. Leterrier and E. Stefanis, *A Comparison of a_σ and a_{ϵ} from Simultaneous Volume and Mechanical Measurements*, Proceedings of the Society of Experimental Mechanics, Spring Conference, June 12-14, 1995, Grand Rapids, MI.

C.R. Schultheisz, D.M. Colucci, G. B. McKenna, and J.M. Caruthers, *Modeling the Differing Time Scales of Structural Recovery and Mechanical Relaxation in Aging Experiments*, in Mechanics of Plastics and Plastic Composites, 1995, ed by M.C. Boyce, American Society of Mechanical Engineers, 1995, MD-68 and AMD-215, 251-282.

D.M. Colucci, P. A. O'Connell and G.B. McKenna, *Volume Changes in Thermoplastics in Creep and Stress Relaxation Experiments in Tension and Compression*, (1996) SPE ANTEC, 1543.

P. A. O'Connell and G.B. McKenna, *Large Deformation Response of Polycarbonate: Time-*

Temperature and Time-Aging Time Superposition. (1996) SPE ANTEC, 2262.

J.-J. Pesce and G. B. McKenna, *Prediction of the Sub-Yield Extension and Compression Responses of Glassy Polycarbonate from Torsional Measurements*, (J. Rheology, Submitted).

P.A. O'Connell and G.B. McKenna, *Large Deformation Response of Polycarbonate: Time-temperature and Time-Aging Time Superposition*, in Polycarbonate Science and Technology, ed. by D.G. LeGrand and J.T. Bendler, Marcel Dekker, New York, (Submitted).

S.A. Ketcham, J.M. Niemiec, and G.B. McKenna, *Extension and Compression of Elastomeric Butt Joint Seals*, J. Engineering Mechanics, 1996, 122, 669-677.

Presentations

P.A. O'Connell and G.B. McKenna, *Sub- T_g Time-Temperature Superposition in Polymers at Large Deformations*, Society of Rheology Annual Meeting, Sacramento, CA, October, 1995.

J.J. Pesce and G.B. McKenna, *Prediction of the Extension and Compression Response of Glassy Polycarbonate in the Nonlinear Range from Torsional Measurements*, Society of Rheology Annual Meeting, Sacramento, CA, October, 1995.

G.B. McKenna, *Structural Recovery and Nonlinear Viscoelasticity in Glassy Polymers*, IBM Almaden Research Center, San Jose, CA, October, 1995.

G.B. McKenna, *The Impact of Physical Aging and Nonlinear Viscoelasticity on the Performance of Polymers and Composites*, School of Chemical Engineering, Purdue University, Lafayette, IN, October, 1995.

D.M. Colucci, *A Thermoviscoelastic Approach in Modeling the Glass Transition Region*, University of Maryland, Baltimore Campus, Department of Mechanical Engineering, Baltimore, MD, November 1995.

J.J. Pesce and G.B. McKenna, *Comparison of Torque and Normal Force Responses of Polycarbonate in One and Two Step Torsional Histories with a Material Clock Model*, ASME Winter Annual Meeting, San Francisco, CA, November, 1995.

G.B. McKenna, *Measurement of Material Properties in Nonlinear Viscoelasticity of Solid Polymers*, Eindhoven University, Eindhoven, The Netherlands, February, 1996.

G.B. McKenna, *Time-Temperature, Time-Aging Time and Time-Strain Superposition in Polymers Below the Glass Transition*, Institut Charles Sadron, Strasbourg, France, February, 1996.

P.A. O'Connell and G.B. McKenna, *Sub- T_g Time-Temperature, Time-Aging Time and Time-*

Strain Superposition in Polymers at Large Deformations, Division of High Polymer Physics, American Physical Society March Meeting, St. Louis, MO, March, 1996.

W.H. Han, F. Horkay and **G.B. McKenna**, *Evaluation of Some Rubber Elasticity Models from Mechanical and Swelling Measurements*, Division of High Polymer Physics, American Physical Society March Meeting, St. Louis, MO, March, 1996.

G.B. McKenna, *The Need for Efficient Methods for the Determination of Material Parameters in Non-linear Materials*, Institute for Mechanics and Materials Think Tank on The Role of Theory and Experiment in the Physics and Mechanics of Solids, Houston, TX, March, 1996.

D.M. Colucci, C.R. Schultheisz, and G.B. McKenna, *A Thermoviscoelastic Analysis of the Differences in Time Scales Evidenced by Structural Recovery and Physical Aging*, American Physical Society Annual Meeting, March 1996, St. Louis, MI.

G.B. McKenna, *Efficient Experimental Methods for the Measurement of Nonlinear Material Parameters*, University of Nebraska-Lincoln, Lincoln, NB, April, 1996.

P.A. O'Connell and **G.B. McKenna**, *Large Deformation Response of Polycarbonate: Time-Temperature and Time-Aging Time Superposition*. SPE ANTEC, Indianapolis, IN, May, 1996.

D.M. Colucci, P.A. O'Connell, and G.B. McKenna, *Volume Changes in Thermoplastics in Stress Relaxation Experiments in Tension and Compression*, 1996 Society of Plastics Engineers Annual Meeting, May 1996, Indianapolis, IN

D.M. Colucci, *A Comparison of the Predictive Capabilities of Several Nonlinear Viscoelastic Constitutive Models*, Materials Lab Directorate, Wright Patterson Air Force Base, Dayton, OH, May 1996.

G.B. McKenna, D.M. Colucci and P.A. O'Connell, *Relaxation Behavior of Polycarbonate below the Glass Transition*, Thermoplastic Engineering Design Meeting with GM and GE, General Electric CRD, Schenectady, NY, May, 1996.

W.H. Han, Glenn Brown Award Lecture entitled *Computational Modelling of Orientation and Flow Instabilities, Textures, Rheology, and Optics of Shearing Nematic Liquid Crystalline Materials*, 16th Biennial International Liquid Crystal Conference, Liquid Crystal Institute, Kent State University, Kent, OH, June, 1996.

D.M. Colucci, P.A. O'Connell, and G.B. McKenna, *Experimental Investigation of the Nonlinear Viscoelastic Response and Subsequent Volume Changes of Two Engineering Polymers in Tension and Compression*, VII International Congress on Experimental and Applied Mechanics, Special Symposium: Time Dependent Materials, Nashville, TN, June 1996.

D.M. Colucci, P.A. O'Connell, and G.B. McKenna, *Single Step Stress Relaxation Responses of Polycarbonate: Biaxial Measurements*, 1996 American Society of Mechanical Engineers, Mechanics and Materials Conference, June 1996, Baltimore, MD

J.J. Pesce and G.B. McKenna, *Prediction of the Extension and Compression Responses of Glassy Polycarbonate in the Nonlinear Range from Torsional Measurements Using a Compressible Valanis-landel Analysis*, ASME Spring Meeting, Johns Hopkins University, Baltimore, MD June, 1996.

P.A. O'Connell and G.B. McKenna, *Sub- T_g Time-Temperature and Time-Strain Superposition in Polymers at Large Deformations*, ASME Spring Meeting, Johns Hopkins University, Baltimore, MD June, 1996.

Physical Aging of Polymers

G.B. McKenna, C.R. Schultheisz, D.M. Colucci, P.A. O'Connell, M. L. Cerrada

Objectives

The objectives are to develop new methods and incorporate known methods of measurement to determine the interrelationships between the thermodynamics and kinetics of glass formation and to relate these to the underlying microstructure of the glass through appropriate physical models.

Technical Description

Engineering polymers are generally used below their glass transition temperature with the result that their properties are constantly evolving due to the non-equilibrium state of the glassy phase. In addition, the actual path of pressure and temperature by which the polymer reaches the glassy state impacts the resulting mechanical properties. Therefore it is important to have a constitutive framework in which to cast the evolution of the material properties with history in order to predict the resulting material behavior both during and subsequent to processing. In this project, measurements of the volume recovery and mechanical response are made on both amorphous and semi-crystalline polymers. In the case of the amorphous polymers the procedures chosen are classical and torsional dilatometry and stress relaxation measurements after temperature jumps in order to establish the range of validity of the current models of structural recovery and physical aging. In addition, the physical aging data generated on poly(carbonate) are part of a larger data base of viscoelastic data for an amorphous, glassy polymer. Because the ideas currently used as the basis of understanding the structural recovery and physical aging are known to be inadequate, the experiments are designed to provide insight into where improvements in the models can be made. An example is the observation that the mechanical response of the polymer does not evolve at the same rate as does the volume, giving rise to questions about the validity of simple free volume descriptions of glassy kinetics.

PVT measurements of a glass forming polymer (poly(carbonate)) are also used to understand how

the glass transition and the glassy state depend on path. In particular, first time measurements that demonstrate the existence of an isochoric (constant volume) glass transition have been made.

To assess microstructural changes in amorphous polymers a new capability has been added to the Small Angle X-ray Scattering (SAXS) facility to permit studies of the wavelength dependence of the structural evolution of amorphous polymers after temperature jump experiments. Such experiments will determine the existence of differences in kinetics of structural recovery depending on microstructural size scale in a way that is consistent with free volume distribution models of the glassy state.

Models of the aging response of semi-crystalline polymers are even less successful than those for the amorphous polymers. To better describe such processes physical aging data are obtained on semi-crystalline films and injection molded syndiotactic polystyrene. New non-contact techniques based on laser extensometry are being developed to study anisotropic structural recovery in semi-crystalline films.

External Collaborations

The classical dilatometry studies on poly(carbonate) are part of collaborative work with the GM/GE ATP project on Thermoplastic Engineering Design. Similarly, the linear viscoelastic response of poly(carbonate) to physical aging is part of this project. The data produced here are given to GM and GE for incorporation into numerical models used in the program. The physical aging work on anisotropic films is performed in collaboration with researchers at Kodak. The work on the PVT response of poly(carbonate) and on isochoric glass transition was performed in collaboration with researchers from Wright Laboratories and Michigan State University.

Planned Outcomes

- Better predictions of the path dependence of the mechanical response of amorphous, glassy polymers by determination of the range of validity of classical concepts of structural recovery and physical aging will allow design of products to narrower tolerances.
- Development of a model of the physical aging and structural recovery response of semi-crystalline polymers that incorporates structural anisotropy will allow designers to take advantage of anisotropic mechanical properties of semicrystalline polymers in applications requiring dimensional stability.

Accomplishments

- Built a high temperature mercury dilatometry facility to obtain structural recovery data for a poly(carbonate) amorphous thermoplastic.
- Developed time-temperature and time-aging time shift data base for amorphous poly(carbonate) in torsion and in the linear viscoelastic range and shared data with researchers at GE.

- Modified current mechanical testing equipment to perform temperature jump experiments in stress relaxation for thin films and obtained time-temperature and time-aging time data for poly(ethylene terephthalate) and poly(ethylene naphthalate) thin films. Shared data with researchers at Kodak.
- Designed a multi-cell temperature control device for performing temperature jump experiments on the SAXS facility.
- Performed first measurements of an isochoric glass transition and showed that the isochoric glass transition occurs at the same pressure, volume and temperature as does the isobaric transition. However, the strength of the transition is much weaker than the isobaric one which leads to a different glassy structure for the isochorically formed glass.

Outputs

Publications

J. M. Niemiec, C.L. Schutte, C.R. Schultheisz and G. B. McKenna, *Time-Temperature and Time Aging Time Superposition in Polycarbonate Below the Glass Transition*, Proceedings ANTEC, SPE, 2402-2408 (1995).

J.-J. Pesce, J.M. Niemiec, M. Y. Chiang, C. L. Schutte, C.R. Schultheisz, and G.B. McKenna *Characterization of Polymers in the Glass Transition Range: Time-Temperature and Time-Aging Time Superposition in Polycarbonate*, in Current Research in the Thermo-Mechanics of Polymers in the Rubbery-Glassy Range, ed. by M. Negahban, American Society of Mechanical Engineers, New York, 1995, AMD-Vol. 203, pp 77-88.

I. Spinu and G.B. McKenna, *Physical Aging of Thin Films*, Proceedings ANTEC, SPE, 2684-2697 (1995).

G.B. McKenna, *Dynamics and Mechanics Below the Glass Transition: The Non-Equilibrium State*, J. Comp. Matls. Science, 1995, 4, 349-360.

J. Beckmann, G.B. McKenna, D.H. Banks, B.G. Landes and R.A. Bubeck, *The Physical Aging Response of Syndiotactic Poly(styrene)*, (1996) SPE ANTEC, 2272.

G.B. McKenna, *Comments on the paper 'Isobaric Volume and Enthalpy Recovery of Glasses II. A Transparent Multiparameter Model*, J. Polymer Science, Polymer Physics Edition, (In Press).

D.M. Colucci, C.R. Schultheisz and G.B. McKenna, *Dynamics of Structural Recovery and Mechanical Response of Polymeric Liquids Near to the Glass Transition*, Proceedings of the Materials Research Society 1995 Fall Meeting: Disordered Materials Symposium, Boston, MA.

D.M. Colucci, G.B. McKenna, A. Lee, D.B. Curliss, K.B. Bowman and J.D. Russell, *Isochoric*

and Isobaric Glass Formation: Similarities and Differences, J. Polymer Science, Physics Edition, (submitted).

Presentations

C.R. Schultheisz, D.M. Colucci and G.B. McKenna, "*Structural Recovery and Physical Aging: A Thermoviscoelastic Analysis of the Differences in Rates of Evolution*," 67th Annual Meeting of the Society of Rheology, Sacramento, California, October, 1995.

G.B. McKenna, "*Physical Aging and its implications for the long term performance of polymers and composites*," Golden Gate Polymer Forum, Mountain View, CA, October, 1995.

G.B. McKenna, "*Structural Recovery and Nonlinear Viscoelasticity in Glassy Polymers*," IBM Almaden Research Center, San Jose, CA, October, 1995.

G.B. McKenna, "*Structural Recovery and Its Implications for the Long Term Performance of Polymers and Composites*," Department of Chemical Engineering, University of Pittsburgh, November, 1995.

C.R. Schultheisz, D.M. Colucci, **G.B. McKenna** and J. M. Caruthers, "*Modeling of Different Time Scales of Structural Recovery and Mechanical Relaxation Observed in Aging Experiments*," ASME Winter Annual Meeting, San Francisco, CA, November, 1995.

D.M. Colucci, C.R. Schultheisz, and G.B. McKenna, "*Prediction of Torsional Dilatometry Responses Using a Thermoviscoelastic Constitutive Model*", American Institute of Chemical Engineers National Meeting, November 1995, Miami, FL.

D.M. Colucci, G.B. McKenna, and A. Lee, "*Observation of an Isochoric Glass Transition*", Materials Research Society Fall Meeting, November 1995, Boston, MA.

D.M. Colucci, C.R. Schultheisz, and G.B. McKenna, "*Dynamics of Structural Recovery and Mechanical Response of Polymeric Liquids Near to the Glass Transition*", Materials Research Society Fall Meeting, November 1995, Boston, MA.

P.A. O'Connell and **G.B. McKenna**, "*Time-Temperature and Time-Aging Time Superposition in Polymers Below The Glass Transition*," Materials Research Society, Winter Meeting, December, 1995.

G.B. McKenna, "*Time-Temperature, Time-Aging Time and Time-Strain Superposition in Polymers Below the Glass Transition*," Institut Charles Sadron, Strasbourg, France, February, 1996.

D.M. Colucci, "*Volume Change Measurements in Isotropic and Anisotropic Deformations of a Polymer Glass: A Comparison of Experiment with Statistical Mechanical and*

Phenomenological Models", National Institute of Standards and Technology, Gaithersburg, MD, February 1996.

G.B. McKenna, "*Physical Aging in Polymers and Its Implications for Long Term Performance of Polymers and Composites*," Lehigh University Department of Chemical Engineering, Bethlehem, PA, March, 1996.

D.M. Colucci and G.B. McKenna, "*Prediction of Pressure-Volume-Temperature Behavior Including the Glass Transition Temperature Using the Simha-Somcynsky and Gibbs-DiMarzio Equations of State*", American Physical Society Annual Meeting, March 1996, St. Louis, MO.

D.M. Colucci, C.R. Schultheisz, and G.B. McKenna, "*A Thermoviscoelastic Analysis of the Differences in Time Scales Evidenced by Structural Recovery and Physical Aging*", American Physical Society Annual Meeting, March 1996, St. Louis, MO.

G.B. McKenna, "*Viscoelasticity and Aging in Polymer Glasses: Questions of Measurement and Analysis*," Virginia Polytechnic and State University, Blacksburg, VA, April, 1996.

P.A. O'Connell and G.B. McKenna, "*Large Deformation Response of Polycarbonate: Time-Temperature and Time-Aging Time Superposition.*" SPE ANTEC, Indianapolis, IN, May, 1996.

J. Beckmann, G.B. McKenna, D. H. Banks, B.G. Landes and R.A. Bubeck, "*The Physical Aging Response of Syndiotactic Poly(styrene)*," SPE ANTEC, Indianapolis, IN, May, 1996.

C. R. Schultheisz, D. M. Colucci and G.B. McKenna, "*Experimental Evidence and Modeling of the Differing Time Scales of Structural Recovery and Mechanical Relaxation Observed During Aging of Glassy Polymers*," Society for Experimental Mechanics, VIII International Congress on Experimental Mechanics, June, 1996, Nashville, Tennessee.

C. R. Schultheisz and G. B. McKenna, "*Volume Changes in Polycarbonate Following Temperature Jumps*," American Society of Mechanical Engineers, 1996 Mechanics and Materials Conference, June, 1996, Baltimore, Maryland.

G.B. McKenna, "*The Dynamics of Polymers Below the Glass Transition*," Gordon Research Conference on Polymer Physics, Newport, RI, July, 1996.

C. R. Schultheisz and G.B. McKenna, "*Volume Evolution of Lexan LS-2 Polycarbonate*," Semiannual Meeting GE/GM Advanced Technology Project on Thermoplastic Engineering Design, October, 1996, Buffalo, New York.

Organizing Activity

G.B. McKenna and S.C. Glotzer co-organized a Symposium on "40 Years of Entropy and the Glass Transition," at the March Meeting of the American Physical Society, Division of High

Polymer Physics, St. Louis, MO, March, 1996.

Finite Element Analysis in Polymer Mechanics.I: Dimensional Stability

M.Y.M. Chiang

Objective

The objective is to determine the impact of specific parameters, e.g., deviations from material linearity, inhomogeneity of temperature, etc., on the residual stresses and resulting dimensional stability or warpage of polymer-based components.

Technical Description

The project implements nonlinear viscoelasticity into finite element codes that are used to analyze the impact of thermal history on the residual stresses in printed wiring board type composites and injection molded parts. Initially, a simplified micro-mechanical model is used in a linear thermo-viscoelastic finite element analysis to examine the role of material viscoelasticity (stress relaxation or creep) on dimensional changes. The analysis incorporates material properties determined in our laboratory for the thermo-viscoelastic response of an epoxy. The model, based on a unit representative cell and classical laminate theory, serves to demonstrate the time-dependency of the inner layer dimensions during the cooling process after the part is removed from the mold. Long term behavior is explored in a numerical simulation which includes stress relaxation below the glass transition temperature (T_g). In this model, the relaxation response at a given temperature, T , is described by substituting a temperature-dependent reduced time factor into a formerly temperature-independent relaxation function (time-temperature superposition, TTS).

In addition to considerations of time-temperature superposition behavior, it has been observed that polymeric materials undergo a continuous evolution of properties below the glass transition temperature and that the changes in viscoelastic properties can be well represented by a time-aging time superposition principle. Hence, the material response at different aging times may be treated rather than the response at different temperatures T . A circular plate geometry is chosen to predict the warpage caused by residual stresses, which are induced by the quenching from the temperature near T_g to room temperature. The plate is initially assumed to be stress free and viscoelastic. The analysis includes a heat transfer and subsequent stress analysis.

External Collaborations

This work has been performed in collaboration with participants in the GM/GE ATP project on Thermoplastic Engineering Design.

Planned Outcomes

- To have the physical aging and non-singular temperature dependence of the shift factors effects incorporated into the GM/GE project and into a commercial finite element code, such as ABAQUS.

Accomplishment

Non-exponential temperature dependence and physical aging shift factors were incorporated into ABAQUS finite element code in our laboratories and made preliminary calculations of warpage.

Outputs

Presentations

M.Y.M. Chiang and G.B. McKenna, *The Effect of Age Dependent Behavior on Shape Changes in a Polymeric Part Subjected to Non-uniform Cooling*, Materials Research Society, Winter Meeting, December, 1995.

M.Y.M. Chiang, *Effect of Time-Temperature Superposition on Dimensional Stability in Micro-mechanics Model*, Polymer Composite Laboratory, Korea Institute of Science and Technology, Seoul, Korea, September, 1996.

Finite Element Analysis in Polymer Mechanics. II: Fracture

M.Y.M. Chiang

Objective

The objective is to combine numerical solutions with experimental observations to determine the impact of material elastic-plastic and visco-plastic constitutive properties on strain localization in fracture of thin adhesive bonds. The effects of viscoelasticity and aging on the localization event are investigated.

Technical Description

This investigation combines experiments and finite element analysis with emphasis on the local deformation at the crack tip to establish fracture criteria which are independent of specimen geometry. In the experiments, the bond thickness is the prime variable, ranging from 25 μm to 420 μm . End-notched flexure and the Butterfly adhesive bonding test specimens are used to study constrained interfacial crack propagation. Experiments were performed using an epoxy adhesive; the crack tip region was observed with the aid of a high-magnification video system.

Large strain incremental plasticity finite element analysis was used to study numerically the same specimen geometry and test conditions as measured experimentally. The deformation and mechanism of fracture during the entire event of crack propagation, which includes the onset of crack propagation, was modeled.

External Collaboration

This work was carried out in collaboration with the Tel Aviv University, Israel.

Planned Outcome

- To establish through experiment and numerical analysis a geometry independent local failure criterion in adhesive joints that would be used in the design of structures involving adhesive joining.

Accomplishments

The local shear strains estimated from the finite element analysis and those measured experimentally are in reasonable agreement. The analysis provides quantitative insights into the mechanics of other failure modes observed in the experiments. The onset of a detrimental microdebond ahead of the crack tip is controlled by the bond-normal tensile stress. Hydrostatic tension seems responsible for the development of a large void at the crack tip which temporarily arrests the crack while the principal tensile stress at the crack tip seems to govern crack kinking. All of these failure modes are activated under large strains, which highlights the rule of plasticity in the fracture of polymer joints.

Outputs

Publications

M.Y.M. Chiang, *Modified Mohr-Coulomb Plasticity Model for Nonlinear Fracture Analysis of Polymeric Interlayer*, ANTEC '95, Society of Plastic Engineers, Boston.

H. Chai and M.Y.M. Chiang, *A Crack Propagation Criterion Based on Local Shear Strain in Adhesive Bonds Subjected to Shear*, J. of Mech. Phys. of Solids (submitted).

M.Y.M. Chiang and H. Chai, *A Large Strain Analysis of Constrained Interfacial Crack Propagation Based on Local Shear Deformation - Part I*, Int. J. Solids and Structures (submitted).

H. Chai and M.Y.M. Chiang, *A Large Strain Analysis of Constrained Interfacial Crack Propagation Based on Local Shear Deformation - Part II*, Int. J. Solids and Structures (submitted).

Presentations

M.Y.M. Chiang, *Finite Element Analysis of Strain Localization and Finite Strain Fracture in Adhesive Bonds*, North Carolina State University, MARS Mission research Center, Raleigh, NC, March, 1996.

M.Y.M. Chiang and H. Chai, *An Intrinsic Fracture Property for Highly Constrained Interlayer Subjected to Shear Loading*, 19th Technical Conference, The Adhesion Society, Myrtle Beach, SC, March, 1996.

M.Y.M. Chiang, *Study of Strain Localization of Thin Adhesive Bonds*, Martin Chiang Inst. of Applied Mechanics, National Taiwan University, Taiwan, September, 1996.

Viscoelastic Measurements in Plasticizing Environments

G.B. McKenna, F. Horkay, and W.H. Han

Objectives

The objectives are to develop measurement methodologies for determination of the creep response of polymers, including rubber and glasses, in plasticizing environments such as H₂O and CO₂. The test methods need to have the capability of measuring the material response to both constant activity (concentration) and transient conditions. In addition, the methods must include moderate pressure and temperature excursion capabilities to 10 MPa and 150 °C.

Technical Description

Small molecules are known to plasticize polymers and reduce the glass transition temperature T_g . Associated with such a decrease in T_g it is generally observed that the modulus decreases and the viscoelastic relaxation response shifts to shorter times. While such behavior anticipates that the concepts of reduced time, similar to time temperature superposition, should describe the response of polymer glasses to changes in small molecule concentration, it has not been fully demonstrated. A test methodology is under development in which the thermodynamic activity of a small molecule vapor or gas, specifically moisture and CO₂, can be controlled much as temperature can be. Then, the equivalence of changing the activity to changing the temperature can be investigated. Furthermore, because the change in T_g with concentration reduces the temperature difference from T_g in isothermal experiments, activity jumps should be treatable in the same manner as are temperature jumps. If this is true, then it becomes possible to use the reduced time concepts, developed in nonlinear viscoelasticity and time-temperature and time-aging time superposition, to describe the impact of moisture or CO₂ on polymer behavior.

The experimental procedure requires the ability to perform isothermal activity (relative humidity or pressure)-jump experiments on thin polymer samples and to determine the volume, mass and viscoelastic property changes after such a jump. The questions to be asked are: does the property evolution that results obey reduced time principles? do the observed reduced time variables (shift factors) obey the same kinetics as would result from temperature jump experiments? and can the behavior be modeled using the reduced time framework developed for volume and aging responses of polymers?

Accomplishments

- Designed modifications for four pressure vessels and built two relative humidity chambers for performing activity-jump experiments.
- Designed and built creep apparatuses to place in chambers to measure creep response of 60 μm thick films after activity jump.
- Performed preliminary T-jump and activity-jump experiments on films of epoxy and

poly(carbonate).

- Completed prior work in study of small molecules on the swelling and mechanical behaviors of network polymers.

Outputs

Publications

F.Horkay, W.K.Waldron, Jr., and G.B. McKenna, *The Effect of Molar Volume on the Swelling of Poly(Dimethyl Siloxane) in Fluorocarbon Fluids*, *Polymer*, 1996, 36, 4525. (In Press).

F. Horkay and G.B. McKenna, *Gels*, In Physical Properties of Polymers Handbook, ed. by J. E. Mark, AIP Press, American Institute of Physics, Woodbury, New York, 1996, 379-400.

G.B. McKenna and J.M. Crissman, *Temperature and Crosslinking Effects on the Swelling of Poly(isoprene) in Isopiestic Conditions*, *J. Polymer Science, Physics Ed.* (In Press).

F. Horkay, W.H. Han, G. B. McKenna, *A Comparison of Some Rubber Network Models with Stress-Strain Data on Dry and Swollen Polymer Rubbers*, *J. Mathematics and Mechanics of Materials* (submitted).

Chiang, M.Y.M. and McKenna, G.B., *Report on the NIST Workshop of Hygrothermal Effect on the Performance of Polymers and Polymeric Composites*, NISTIR 5826, April, 1996.

Presentations

W.H. Han and **G.B. McKenna**, *The Physical Aging Response of Epoxy in Relative Humidity Jump Experiments*, 6th International Workshop on Moisture in Electronic Packaging, U.S. Department of Commerce, NIST, Gaithersburg, MD, October, 1996.

Organizing Activity

M.Y.M. Chiang and G.B. McKenna co-organized a working group meeting with researchers from industry that followed up on issues identified in the Workshop on "Hygrothermal Effects on the Performance of Polymers and Polymeric Composites," held in FY 1995.

Measurement of Craze Initiation and Growth in Polymers

Principal Investigators: G.B. McKenna, J.D. Barnes, P.A. O'Connell, G. Gusler and M. Delin

Objectives

The objectives are to develop methods to measure the structural changes in polymers prior to crazing using small angle x-ray scattering techniques and to investigate the time evolution of such changes in poly(carbonate) and styrene-acrylonitrile copolymer. Instrumentation and methods are

devised to investigate the craze initiation and growth responses during physical aging.

Technical Description

It is well known that physical aging affects the viscoelastic response of polymers. However, there have been few studies of the impact of aging on failure and fewer on a common precursor to failure referred to as crazing. Methods are devised to study the impact of the aging response on crazing and to understand the accumulation of material changes that lead to the craze initiation event. An optical approach is being taken to study the initiation of crazes and the impact of aging on the craze initiation and growth. Although crazing is a macroscopic phenomenon in the sense that crazes are readily visible to the naked eye, the events that lead to crazing are not clear. Therefore, SAXS methods are developed to examine the ways in which microstructural damage accumulates in the polymer prior to the craze initiation. In particular, a stress relaxation method was devised to initiate crazing that is controlled in such a way as to be able to perform SAXS measurements of structural change as a function of deformation and time after application of the deformation.

External Collaboration

This work is being performed in collaboration with researchers from Chalmers Institute of Technology in Goteburg, Sweden.

Accomplishments

- An optical system has been implemented to record the initiation and growth of crazes.
- A special attachment for crazing samples under constant deformation (stress relaxation conditions) has been built for the SAXS facility to study the accumulation of microstructural change in polymers prior to craze initiation.

Outputs

Publications

G. M. Gusler and G.B. McKenna, *The Effect of Physical Aging on the Crazing Behavior of Polystyrene*, ACS Polymer Preprints, 1995, 36(2), 63-64.

G.M. Gusler and G.B. McKenna, *The Effect of Physical Aging on the Craze Response of Polystyrene and a Styrene-Acrylonitrile Copolymer*, (1996) SPE ANTEC, 1537.

G.M. Gusler and G.B. McKenna, *The Craze Initiation Response of A Polystyrene and a Styrene-Acrylonitrile Copolymer During Physical Aging*, Polymer Engineering and Science (submitted).

Presentations

G.M. Gusler, D.M. Colucci, and G.B. McKenna, *Impact of Physical Aging on Crazing in Polystyrene*, American Institute of Chemical Engineers National Meeting, November 1995, Miami, FL.

G.M. Gusler and **G.B. McKenna**, *Crazing in a Polystyrene and a Styrene-Acrylonitrile Copolymer: Does Physical Aging Have an Effect?* Materials Research Society, Winter Meeting, December, 1995.

G.M. Gusler and **G.B. McKenna**, *The Impact of Physical Aging on Craze initiation in Polystyrene and a Styrene-Acrylonitrile Copolymer*, Division of High Polymer Physics, American Physical Society March Meeting, St. Louis, MO, March, 1996.

G.M. Gusler and **G.B. McKenna**, *The Effect of Physical Aging on the Craze Response of Polystyrene and a Styrene-Acrylonitrile Copolymer*, SPE ANTEC, Indianapolis, IN, May, 1996.

DENTAL AND MEDICAL MATERIALS

The Dental and Medical Materials Program provides basic materials science, engineering, test methods, and standards to sectors of the health-care industry for the development of new or improved materials and delivery systems. The focus of this program is the development of improved dental restorative materials with greater durability, wear resistance and clinical acceptability.

Dental restorative composites are heterogeneous materials having three essential phases: (1) a polymeric matrix which comprises the continuous phase, (2) fillers of various types, sizes, shapes and morphologies which constitute the disperse phase and (3) an interfacial phase that, in varying degree, bonds the continuous and disperse phases into a unitary material rather than a simple admixture. While all three phases are important in determining the properties of the composites, this program is focused primarily on the interfacial and polymer matrix phases. Since the polymerization shrinkage that occurs in the matrix phase is one of the most commonly cited deficiencies of dental restorative composites, resources are allocated to develop high conversion, durable, low shrinkage polymeric materials for use in dental resin and composite applications. The polymeric matrix of a dental composite typically is formed by free radical polymerization of a resin which is one or more vinyl monomers, usually of the methacrylate class. Polymerization is started either by the formation of initiating radicals from chemical reduction-oxidation (redox) reactions or by photochemical redox reactions.

Although only a minor component of these composites, the interfacial phase that develops from the interaction of the silane coupling agent with the polymer matrix and the siliceous filler exerts a profound effect on the properties of the composites. Because these composites are used in an aggressive, aqueous environment that constantly challenges the vulnerable silane mediated polymer-filler bond, understanding of this critical interfacial phase is being acquired so that strategies can be developed for its improvement.

The occupational and environmental hazards associated with the use of mercury-containing dental alloys are a recurring source of public concern. Since dental amalgams have performed exceedingly well over more than one hundred years, the development of a direct filling material still based on the common constituents of dental amalgams, other than mercury, is desirable. The approach is based on three main premises: (1) the cold-welding of oxide-free silver; (2) the *in situ* formation of Ag_xSn_y intermetallics by the room temperature fast diffusion of silver and tin; and (3) the homogeneous precipitation of silver by Sn(II) in solution. This project is focused on acid-assisted consolidation of chemically precipitated silver powders and property measurements of hand consolidated test compacts prepared with the tools and procedures normally employed by dentists. The observed values of flexural strength for the silver compacts were equal or superior to mercury amalgams. Corrosion resistance, microleakage and marginal toughness values of the compacts were found to be superior to those of amalgams. Wear and biocompatibility studies on the hand consolidated compacts are in progress.

Dental research directions in support of the goals are established in collaboration with the American Dental Association (ADA), the National Institute of Dental Research, and guest scientists from the U.S. Navy and the U.S. Public Health Service. NIST has hosted research associates from ADA since 1928. Currently, the ADA Health Foundation sponsors 32 research associates at NIST. The collaborative relationship between that professional association and the federal government is unique, and continues to develop and transfer important new technologies to dentistry and medicine.

Significant Accomplishments

- Low shrinkage interpenetrating polymer networks were formed by coincident free-radical methacrylate polymerization and cationic double ring-opening polymerization.
- Demonstrated that the addition of urethane functional groups to fluorinated methacrylate monomers can provide polymers with significantly improved strength and minimal water uptake.
- An efficient method was developed to prepare hydroxy-functionalized methacrylates that can be used directly as dental bonding agents or further derivatized to give highly reactive crosslinkable monomers.
- Demonstrated that the microbond test could be used as a durability test for monitoring polymer-glass interfacial adhesion.
- Demonstrated by mass spectrometry that *N*-aryl- α -amino acids act as polymerization initiators for acrylic monomers.
- Demonstrated the feasibility of developing stress-bearing craniofacial implants from hydroxyapatite and bioresorbable polymers.
- Cooperative Research and Development Agreements were signed with six orthopaedic companies to evaluate the wear properties of orthopaedic joint materials.

Dental Polymers Designed with Minimal Polymerization Shrinkage, Residual Vinyl Content and Water Sorption

Jeffrey W. Stansbury

Objective

The objective is to develop dental composite restoratives that provide improved performance in specific areas where current dental materials have acknowledged deficiencies. Deficiencies include excessive polymerization shrinkage, the lack of long term durability, and susceptibility to moisture.

Technical Description

Through appropriate monomer design, the resin phase of the dental composites can undergo efficient photopolymerization with minimal shrinkage. A reduction in the volume contraction associated with polymerization is necessary to avoid excessive internal stresses that result in both micro and macro defects in dental composites. The lack of long-term durability of dental composites compared with amalgam restorations requires that material modifications be made in the polymeric and interfacial phases of composites, which are the weak links in this regard. There is need for more hydrophobic, more hydrolytically stable polymers and interfacial layers to enhance the resistance of composite restoratives to the challenging oral environment.

The use of ring-opening spiro orthocarbonate (SOC) monomers, which can produce expansion during polymerization, and monomers with bulky spacer groups that limit the density of reactive groups can provide photocurable resins that offer low shrinkage and good mechanical strength properties. The introduction of organofluorine substituents in the monomers allows the formation of inert polymers that repel not only water, but a wide range of chemicals that can potentially degrade or stain polymer-based dental restorations. Structural alterations to increase the hydrophobicity of the coupling agent used to fuse the resin matrix with the reinforcing filler particles can improve the strength and stability of dental composites.

External Collaborations

Dr. Kyung Choi is actively advancing the work with fluorinated resins and modified coupling agents under a National Institute of Dental Research-supported contract between NIST and the University of California, Irvine.

Planned Outcomes

- Development of visible light photocurable dental resins with less than half the polymerization shrinkage of conventional materials. Expect these new monomers to provide low shrinkage polymers with less residual stress and minimized polymerization-induced defects.

- Development of organofluorine containing dental composites with less than 1/10th the water uptake of conventional materials. Expect more durable composites that retain their excellent initial properties during prolonged exposure to challenging environments.
- Development of more hydrolytically stable coupling agents for use in dental composite restoratives. Expect more inert composites with improved initial properties and better retention of these properties upon long-term storage in water.

Accomplishments

An examination of the photopolymerization of SOC monomers (cured by a cationic mechanism) with methacrylate-based comonomers (cured by a free radical process) has provided details on the simultaneous formation of very low shrinkage interpenetrating polymer networks. Multifunctional SOC oligomers were used to produce highly crosslinked, ring-opened polymers with expansion.

A computer modeling study has been conducted to screen prospective monomers for predicted shrinkage based on the solvent excluded molecular volume of the monomers. Large differences in molecular volumes were found for monomers with very similar molecular weights. The predicted monomeric molecular volume proved to be a better indicator of actual polymerization shrinkage than monomer molecular weight.

A previous investigation demonstrated that very high strength, hydrophobic polymers can be prepared from urethane-based fluorinated monomers. The role of the urethane functionality to promote polymer mechanical strength (via extended hydrogen bonding networks) while minimizing the hydrophilic tendency of these polar groups was examined. A new coupling agent, which is more compatible with the fluorinated resins, was evaluated and found to provide surface coverage that is more hydrophobic and more durable than that obtained with the conventional silane coupling agent used in dental composites.

An efficient method to produce functionalized methacrylates was developed. The monomers obtained can be used directly as bonding agents for the adhesion of dental restoratives to dentin or they can be further modified through the hydroxy functional groups to produce new crosslinkable monomers that exhibit unusually high reactivity during photopolymerization.

Outputs

Publications

J.W. Stansbury, J.M. Antonucci, K.M. Choi, *High Strength Hydrophobic Composites from Urethane-containing Fluorinated Resins*. Proceedings of the International Association of Dental Research Meeting, J. Dent. Res., 75, 145 (1996).

K.M. Choi, J.W. Stansbury, *New Families of Photocurable Oligomeric Fluoromonomers for Use in Dental Composites*. Chem. Mater. (in press).

Presentations

J.W. Stansbury, J.M. Antonucci, K.M. Choi, *High Strength, Hydrophobic Composites from Urethane-containing Fluorinated Resins*. IADR meeting, San Francisco, CA, March 1996.

J.W. Stansbury, *Dental Resins Based on Alternative Monomers and Polymerization Pathways*. Advances in Materials Science: New approaches and developments symposium. IADR meeting, San Francisco, CA, March 1996.

J.W. Stansbury, *Current Dental Materials Research at NIST*. ASME Applied Mechanics Division and Materials Division Meeting at Johns Hopkins University, Biomaterials symposium, June 1996.

J.W. Stansbury, *Evaluation of Cross-linkable Double Ring-opening Monomer and Oligomer Systems*. The Science of Adhesion Gordon Conference, Tilton, NH, August 1996.

Dental Composites With Improved Interfaces

Joseph M. Antonucci

Objective

The objective is to develop polymeric dental composites with enhanced interfacial strength and durability.

Technical Description

It is expected that improvements in the quality of the interfacial phase along with similar improvements in the polymer matrix and filler phases will result in dental composites of improved performance and service life. In addition to the use of traditional mechanical tests as a means of measuring interfacial strength, two single-fiber tests, the single-fiber fragmentation and the microbond test, have also been used to assess interfacial behavior. Attempts to utilize the single-fiber fragmentation test to determine the strength and durability of the interface derived from dental polymers and variously treated glass fibers have generally met with limited success due to the premature fracture of the brittle polymeric matrices. By contrast, the microbond test has proved to be a useful method for assessing polymer-fiber shear bond strengths and, generally, for exploring the interaction of dental polymers and silane coupling agents with silica surfaces. Recent studies indicate that the microbond test can also be used as a durability test and can be adapted for use with substrates other than fibers.

Accomplishments

It was demonstrated that 10-methacryloxydecyltrimethoxysilane, a more hydrophobic silane coupling agent than the widely used 3-methacryloxypropyltrimethoxysilane (MPTMS), generates a more durable interface than MPTMS.

The microbond test was adapted for use with flat glass surfaces that are potentially more amenable for surface analysis than fiber glass substrates.

Facile methods for the synthesis of multifunctional acrylic substituted silsesquioxanes were developed. These novel hybrid organic-inorganic resins are expected to find use in composite, sealant and adhesive dental applications.

Outputs

Publication

W.G. McDonough, J.M. Antonucci, J. P. Dunkers, *Interfacial Shear Strengths of Dental Composites by the Microbond Test*, J. Dent. Res., 75,14 Abstract 1026 (1996).

Presentation

W. G. McDonough, J. M. Antonucci, J. P. Dunkers, *Interfacial Shear Strengths of Dental Composites by the Microbond Test*. IADR Meeting, San Francisco, CA, March 1996.

Improved Adhesive Systems for Bonding to Tooth Structure

Joseph M. Antonucci

Objectives

The overall objective of this project is to develop effective, less technique- sensitive adhesive systems for bonding to dentin and other dental substrates. An ancillary objective is to elucidate the mechanisms involved in bonding to dentin by means of *N*-aryl- α -amino acids and *N*-arylimino acids.

Technical Description

Previously, it was shown that the application of aqueous acetone solutions of *N*-phenyliminodiacetic acid (PIDAA) to dentin both etches and activates the dentinal surface for subsequent polymerization of photoactivated adhesive resins. With this simple two-step bonding protocol strong composite-to-resin bonds were routinely obtained. Recent studies indicate that this unique adhesive system can be modified by the addition of silane coupling agents without adversely affecting its adhesion to dentin. The presence of silane coupling agents has potential for mediating adhesion to other dental substrates such as porcelain. In a related study, the mechanism of initiating polymerization with *N*-aryl- α -amino acids was investigated by mass spectrometry. In addition, a study was initiated to investigate the mechanism of diffusion of primers into demineralized dentin and their role in dentin bonding.

External Collaboration

Drs. G. E. Schumacher and J. E. Code of the U. S. Public Health Service and P. S. Bennett of the American Dental Association Health Foundation's Paffenbarger Research Center collaborated in the bonding study. The mechanism study involved collaboration with Dr. M. Farahani of the Paffenbarger Research Center. Dr. T. Nikaido, a guest researcher from the Tokyo Medical and Dental University, also participated in the dentin bonding studies.

Accomplishments:

- Demonstrated that silane agents such as 3-methacryloxypropyltrimethoxysilane can be successfully incorporated in the two component PIDAA adhesive system to yield high composite-to-dentin shear bond strengths.
- Demonstrated by mass spectrometric analysis techniques that *N*-aryl- α -amino acids act as polymerization initiators when dissolved in acrylic monomers.
- Demonstrated the *N*-aryl- α -amino acids such as *N*-phenylglycine prevent the collapse of demineralized dentinal collagen, thereby promoting enhanced interfacial diffusion on adhesive resins.

Impact

A patent has been issued based on self-etching primers of the *N*-aryliminodiacetic acid type. The American Dental Association has licensed this invention and several companies have shown interest in this technology.

Outputs

Publications

J.E. Code, J.M. Antonucci, G.E. Schumacher, P.S. Bennett, *Silane-Modified Dentin Bonding Systems*, J. Dent. Res., 75, 126 Abstract #870 (1996).

G.E. Schumacher, J.M. Antonucci, T. Nikaido, J.E. Code, *Molar Efficiency of N-Phenyliminodiacetic Acid in Dentin Bonding*, J. Dent. Res., 75, 348 Abstract #2641 (1996).

J.M. Antonucci, G.E. Schumacher, J. E. Code, T. Nikaido. *Efficacy of N-Aryl and N-Alkyliminodiacetic Acids in Dentin Bonding*, J. Dent. Res., 75, 348 Abstract #2644 (1996).

T. Nikaido, J. M. Antonucci, *Stabilization Effect of NPG on Demineralized Dentin and Its Mechanism*, J. Dent. Res., 75, 126 Abstract #871 (1996).

M. Farahani, J.M. Antonucci, L.R. Karam, *Initiation of Methacrylate Polymerization by N-Aryl- α -amino acids. A Mass Spectrometric Study*, J. Dent. Res., 75, 46 Abstract #1032 (1996).

J.M. Antonucci, G.E. Schumacher, P.S. Bennet, *N-Phenyliminodiacetic Acid as an Etchant/Primer for Dentin Bonding*, J. Dent. Res., (in press).

Patent

J.M. Antonucci, P.S. Bennett, *A Method and Composition for Promoting Improved Adhesion to Substrates*. U.S. Patent #5498643, March 12, 1996.

Presentations

J.E. Code, J.M. Antonucci, G.E. Schumacher, P.S. Bennett, *Silane-Modified Dentin Bonding Systems*, IADR meeting, San Francisco, CA, March 1996.

G.E. Schumacher, J.M. Antonucci, T. Nikaido, J.E. Code, *Molar Efficiency of N-Phenyliminodiacetic Acid in Dentin Bonding*, IADR meeting, San Francisco, CA, March 1996.

J.M. Antonucci, G.E. Schumacher, J. E. Code, T. Nikaido. *Efficacy of N-Aryl and N-Alkyliminodiacetic Acids in Dentin Bonding*, IADR meeting, San Francisco, CA, March 1996.

T. Nikaido, J. M. Antonucci, *Stabilization Effect of NPG on Demineralized Dentin and Its Mechanism*, IADR meeting, San Francisco, CA, March 1996.

M. Farahani, J.M. Antonucci, L.R. Karam, *Initiation of Methacrylate Polymerization by N-Aryl- α -amino acids. A Mass Spectrometric Study*, IADR meeting, San Francisco, CA, March 1996.

J.M. Antonucci, *N-Phenyliminodiacetic Acid as an Etchant/Primer for Dentin Bonding*, Generic/Pentron, Wallingford, CT, April 1996.

Polymer-Modified Porous Ceramics: Interpenetrating Phase Composites for Dental Applications

Joseph M. Antonucci

Objective

The objective is to develop strong, tough interpenetrating phase composites by the *in situ* polymerization of resin-infiltrated porous ceramic structures that are easily formed by low temperature pyrolysis of ceramic powders coated with pre-ceramic polymers such as polysiloxanes.

Technical Description

Conceptually, interpenetrating phase composites are expected to have enhanced properties compared to either dental ceramics or traditional dental composites. Previously, it was shown that a polymer-reinforced interpenetrating composite (IPC) with high strength properties could be prepared by the *in situ* polymerization of methyl methacrylate (MMA) within a silanized, porous ceramic network formed by the low temperature pyrolysis (<750 °C) of feldspathic porcelain or alumina powders that had been coated with a poly(dimethylsiloxane) binder. During the current phase of this research, the effects of silanization versus no silanization of the porous ceramic and the influence of resin composition on the biaxial tensile strength of the IPCs were investigated.

External Collaboration

Dr. J. R. Kelly, of the Naval Dental Research Institute and the Naval Dental School, Bethesda, MD

Accomplishments:

- The use of the silane agent 3-methacryloxypropyltrimethoxysilane had a positive effect on the biaxial tensile strength of the IPCs, a result similar to that found with traditional dental composites.
- The polymerization of infiltrated thermosetting resin systems based on MMA and cross-linking difunctional methacrylates did not generally enhance the strength of alumina-polymer-based IPCs. (This suggests that the role of the polymer phase in IPCs and in conventional particulate-filled composites may not be equivalent.)

Impacts

Two patent applications have been filed and several companies have shown interest in the technology.

Outputs

Publication

M.G. Marks, J.R. Kelly, J.M. Antonucci, *Effect of Resin Composition on Polymer-Reinforced Ceramics*, J. Dent. Res., 75, 148 Abstract #1041 (1996).

Patent

J.R. Kelly, J.M. Antonucci, U. S. Patent Applications - 08,487,557 and 08,660,000.

Presentation

M.G. Marks, J.R. Kelly, J.M. Antonucci, *Effect of Resin Composition on Polymer-Reinforced Ceramics*, IADR meeting, San Francisco, CA, March 1996.

Bioresorbable Polymer-Reinforced Calcium Phosphate Cements

Joseph M. Antonucci

Objective

The object is to improve the load-bearing behavior of a biocompatible, self-setting calcium phosphate cement by the inclusion in its structure of a bioresorbable polymer in fiber mesh form.

Technical Description

Hydroxyapatite-forming calcium phosphate cements (CPC) derived from the reaction of tetracalcium phosphate and dicalcium phosphate in aqueous media have proven successful in healing small, non-stress bearing skeletal defects. However, because of its low tensile strength,

CPC is not an appropriate cement for stress-bearing applications. Polyglactin (a copolymer of glycolic and lactic acids of the type used in resorbable sutures) in knitted fiber mesh form was incorporated into the tensile surface of CPC discs during the setting process. Two sets of control discs were prepared: (1) unreinforced CPC and (2) heat cured PMMA, i.e., poly(methyl methacrylate) cements of the type used for ocular prostheses. The three types of discs were loaded in biaxial flexure (ring-on-ring) to simulate blunt loading of an edge-supported cranial prosthesis (mesh surfaces placed in tension). Work-to-fracture was measured for the discs at a defined strain following storage in artificial serum for (0 to 28) days at 37 °C.

External Collaborations

This project involved collaboration with Dr. Ann Sue von Gonten of the U. S. Army Dental Corps and Dr. J. Robert Kelly of the U. S. Navy Dental Corps, both of the Naval Dental School in Bethesda, MD.

Planned Outcomes

The technology developed in this study has the potential for extending the biomedical use of the highly biocompatible CPC developed at the American Dental Association Health Foundation Paffenbarger Research Center (ADAHF/PRC). A company involved in the commercialization of CPC has shown interest in this technology and, in part, because of the promising results of this study, has agreed to provide some financial assistance (through the ADAHF/PRC) for this type of research.

Accomplishments

The results of this study demonstrated the compatibility of polyglactin fibers with CPC. The 2-D oriented polyglactin fibers exhibited good adhesion to CPC and resisted biaxial tensile stresses prior to their hydrolytic degradation. Thus, CPC reinforced with polyglactin fiber mesh progressed to failure in a manner consistent with the inelastic behavior of oriented fiber composites, holding relatively high loads despite the occurrence of innumerable fracture events. Unreinforced CPC behaved as a simple brittle material with low fracture toughness. Not surprisingly the PMMA cement exhibited only minimal change in its work-to-fracture value after 28 days of immersion. For at least seven days the fiber mesh-reinforced CPC performed as well as PMMA. Thus, bioresorbable polymeric fiber-reinforced CPCs show potential for use in stress-bearing as well as non-stress bearing biomedical applications.

Outputs

Publication

A.S. Von Gonten, J.R. Kelly, J.M. Antonucci, *Load-bearing Behavior of a Simulated Craniofacial Structure Fabricated from Hydroxyapatite Cement and Bioresorbable Fiber Mesh*, J. Prosth. Dent. (Submitted).

Presentation

A.S. Von Gonten, J.R. Kelly, J.M. Antonucci, *Load-bearing Behavior of a Simulated Craniofacial Structure Fabricated from Hydroxyapatite Cement and Bioresorbable Fiber Mesh*, Winner: Graduate Student Research Award, American Academy of Maxillofacial Prosthodontists, Kansas City, MO, October 1996.

Measurement Methods for Process Control of Cell Encapsulation

Francis W. Wang

Objective

The objective is to develop measurement methods for monitoring the encapsulation of cells and enzymes.

Technical Description

In a commonly used process for encapsulating cells with sodium alginate, reaction conditions, such as temperature, reaction time, and amounts of reactants, are controlled to produce functionalized alginate with varying degrees of attachment of photopolymerizable functional groups. In addition, the extent of photo-induced cross-linking of the functionalized alginate is controlled to produce microcapsules of required porosity. The method of wavelength-shift fluorescence is used in this project to monitor the degree of functionalization. This is accomplished by: (1) synthesizing a mobility-sensitive fluorescent probe which becomes covalently attached to sodium alginate at a reaction rate similar to the rate for the attachment of photopolymerizable functional groups to sodium alginate; (2) adding a trace amount of the probe to the reaction mixture containing sodium alginate and other reactants; and (3) measuring the fluorescence spectrum of the probe as a function of the reaction time. Since the mobility of the probe molecules decreases upon their attachment to sodium alginate, the fluorescence wavelength of the probe decreases with the increase in the attachment of the probe molecules to sodium alginate. Consequently, the change in the fluorescence wavelength of the probe is a measure of the degree of attachment of the photopolymerizable functional groups to sodium alginate, if the probe has been designed such that its reactivity with the secondary hydroxy groups of sodium alginate is comparable to the reactivity of the reactant for attaching photopolymerizable functional groups to the secondary hydroxy groups of sodium alginate. Once a correlation is established between the change in the fluorescence wavelength and the degree of attachment determined by H-NMR, an absolute value for the degree of attachment can be obtained from the change in the fluorescence wavelength. Alternatively, the measured value of the fluorescence wavelength can be used to compare or maintain the degree of attachment throughout the functionalization process.

Photo-induced crosslinking of the functionalized alginate can be monitored in the manner similar to the method described for monitoring the functionalization. This will be accomplished by: (1) synthesizing a mobility-sensitive fluorescent probe with a photopolymerizable moiety which has the same reactivity as the photopolymerizable functional groups covalently attached to sodium

alginate; (2) adding a trace amount of the fluorescent probe to the reaction mixture containing the photo-crosslinkable alginate and other reactants; and (3) measuring the fluorescence spectrum of the probe as a function of the reaction time. Since the mobility of the probe molecules is reduced due to their reaction with the functional groups on sodium alginate, the fluorescence wavelength of the probe decreases with the increase in the degree of crosslinking of the alginate. Consequently, the change in the fluorescence wavelength of the probe is a measure of the degree of crosslinking. Once a correlation is established between the change in the fluorescence wavelength and the porosity of the microcapsules, the porosity can be obtained from the change in the fluorescence wavelength. Alternatively, the measured value of the fluorescence wavelength can be used to compare or maintain the porosity throughout the photo-induced crosslinking process.

External Collaboration

VivoRx

Planned Outcome

Technology transfer to VivoRx of process control methods for functionalization and cross-linking of sodium alginate for cell encapsulation.

Accomplishments

Mobility-sensitive fluorescent probes for monitoring functionalization and cross-linking of sodium alginate have been synthesized. It was demonstrated that, when the mobility-sensitive probe was dissolved in the reaction mixture for functionalization of sodium alginate, the peak fluorescence wavelength of the fluorescent probe decreased with the extent of functionalization.

Outputs

Patent

F.W. Wang, K.F. Lin, and R.E. Lowry, *Non-destructive Method for Determining the Extent of Cure of a Polymerizing Material and the Solidification of a Thermoplastic Polymer Based on Wavelength Shift of Fluorescence*, U.S. Patent Application Serial No. 08/389,823, allowed for July, 1996.

Bioactive Polymeric Dental Materials with Remineralization Potential Based on Amorphous Calcium Phosphate

Joseph M. Antonucci

Objective

The objective of this project is to develop bioactive polymeric composites with remineralization potential using various forms of amorphous calcium phosphates (ACP) as the filler phase.

Technical Description

Two modified ACP fillers were prepared by sol-gel precipitation techniques using tetraethoxysilane (silica modified ACP) and zirconyl chloride (zirconia modified ACP). Visible light activated acrylic composites based on these fillers prepared and compared with similar composites based on unmodified ACP as a filler. *In vitro* release of calcium and phosphate ions from the modified ACP composites was monitored by atomic absorption and UV spectroscopic methods respectively. Mechanical strength was evaluated by the biaxial flexure test.

Remineralizing polymer based ACP systems are expected to find use as adhesives, sealants and as base and lining materials.

External Collaborations

Dr. E.D. Eanes, Dr. D. Skrtic, Mr. A.W. Hailer of NIDR and Dr. S. Takagi of ADAHF/PRC.

Accomplishments

- Demonstrated that glass forming agents such as tetraethoxysilane and zirconyl chloride can be used to modify ACP fillers for bioactive composite applications.
- The new bioactive composites exhibited adequate release of calcium and phosphate ions for remineralization on exposure to oral-simulative environments.
- The biaxial tensile strengths of the modified ACP composites exceeded that of an unmodified ACP composite control.

Impact

A patent has been issued based on the use of amorphous calcium phosphate as a bioactive filler, and several companies have expressed interest in this technology.

Outputs

Publications

D. Skrtic, J.M. Antonucci, E.D. Eanes, *Modified Amorphous Calcium Phosphate Fillers for Bioactive Composite Applications*, J. Dent. Res., 75, 145 Abstract #1017 (1996).

J.M. Antonucci, D. Skrtic, E.D. Eanes, *Bioactive Polymeric Materials Based on Amorphous Calcium Phosphate - effect of coupling agents*, Chapter 20 in: **Hydrogels and Biodegradable Polymers for Bioapplications** (R. Ottenbrite, S. Huang and K. Park eds.); ACS Symposium Series 627, Washington, DC, pp.243-254 (1996).

D. Skrtic, A.W. Hailer, S. Takagi, J.M. Antonucci and E.D. Eanes, *Quantitative Assessment of the Efficacy of Amorphous Calcium Phosphate/Methacrylate Composites in Remineralizing Caries-like Lesions Artificially produced in Bovine Enamel*, J. Dent. Res. (in press).

Patent

J.M. Antonucci, D. Skrtic and E.D. Eanes, *Polymeric Amorphous Calcium Phosphate Compositions*. Patent issued April 16, 1996, (US Patent 5508342).

Presentations

D. Skrtic, J.M. Antonucci, E.D. Eanes, *Modified Amorphous Calcium Phosphate Fillers for Bioactive Composite Applications*, IADR meeting, San Francisco, CA, March 1996.

J.M. Antonucci, D. Skrtic, E.D.Eanes, *Bioactive Polymeric Materials Based on Amorphous Calcium Phosphate - effect of coupling agents*, Generic/Pentron, Inc., Wallingford, CT., April 1996.

Support for the Biomaterials Integrated Products Industries

J.A. Tesk, Steve Hsu¹

¹ Ceramics Division

Objective

The objective is to assess the standards and measurement needs of the U.S. industries that manufacture biomaterial integrated products.

Technical Description

The Objective will be met by forming cooperative relationships between industry, NIST, other government agencies (NIH and FDA), and standards bodies to identify needs and develop strategies to meet needs. This is done by sponsoring of workshops, development of CRADAs and other agreements, and active support of standards related activities.

External Collaborations

Biomet Inc. (Warsaw Ind.), Johnson & Johnson Professional, Inc. (Raynham, Mass.), Osteonics Inc. (Allendale, N.J.), Smith & Nephew Richards, Inc. (Memphis, Tenn.), Wright Medical Technology, Inc. (Arlington, Tenn.), and Zimmer, Inc., (Warsaw, Ind.), Poly Hi Solidur (Fort Wayne, Ind) Teledyne Allvac/Vasco (Monroe,NC), Polymer Technology Group (Emeryville, Ca.) American Association of Orthopaedic Surgeons, Hip and Knee Society, Ohio State University Department of Orthopaedic Surgery, Massachusetts General Hospital Department of Orthopaedic Surgery, Rush-Presbyterian - St Luke's Hospital Department of Orthopaedic Surgery, National Heart, Lung, & Blood Institute, Medical Devices Standards Board, Leadership roles with the Biomaterials Society.

Planned Outcomes

- Accelerated tests for evaluation of wear of orthopaedic joint materials.
- Reference materials for implantable materials and explanted devices.

- National and international standards for medical devices.

Accomplishments

Cooperative Research & Development Agreements (CRADAs) were signed with six (6) orthopaedic companies to form a consortium to identify accelerated methods for evaluation of the wear properties of orthopaedic joint materials.

Facilitating NIST-NIH-FDA-Private Industry collaboration for NIST dissemination of industry developed Polyetherurethane Reference Materials, useful in the development of cardiovascular devices.

Coordinating development of a memorandum of understanding between NIST, NIH & FDA for future development of reference materials for biomedical devices.

Outputs

Publications

J. Tesk, *What is a Standard Reference Material, What is any Reference Material?*, Biomaterials Newsletter "The Forum", April 1996.

J. Tesk, *International Standards and Reference Materials*, Proceedings of Workshop On Implant Retrieval and Analysis; Buffalo NY., June 1996.

Presentation

J. Tesk, *International Standards and Reference Materials*, Workshop on Implant Retrieval and Analysis, Buffalo, NY, June 1996.

Durability Assessment of Biomedical Materials/ Prostheses

John A. Tesk; J. Stansbury, J. Lechner (retired, Division 882); Collaborators: S.C. Saunders; H. Morris; K. Asaoka.

Objectives

The objectives are to explore the following: employment of cyclopolymerizable monomers as substitutes for poly(methyl methacrylate) in orthopaedic bone cement, models of the mechanical behavior of dental/medical materials, probabilistic methods which may be useful in the prediction of clinical survivability of biomedical implants and prostheses based on early time survival data, and screening tests for nanosized filler dental restoratives for which the coupling agents to the filler acts as the resin matrix.

Technical Description

Evaluate properties of mixtures of poly(methyl methacrylate) and cyclopolymerizable monomers; explore with NIH, NIST and Washington State University the feasibility/interest in workshop on implant reliability predictions using engineering statistical approaches; continue modeling collaborations with Tokushima University.

External Collaborations

J. Lechner (retired, Division 882); S.C. Saunders, Washington State University; H. Morris, Veterans Administration; K. Asaoka, Tokushiima University.

Accomplishments

Established informal collaboration with Ohio State University Department of Orthopaedic Surgery for evaluation of experimental bone cement formulations.

Outputs**Publication**

J.A. Tesk, and Asaoka, *On Computer Simulation of Stresses developed in Dental Investments During Burnout, Prior to Casting*, Dent. Mater. (submitted).

THEORY AND MODELING

Materials science and engineering are on the threshold of a fundamental transformation. New theoretical capabilities combined with spectacular advances in computer processor power, memory, and computational methodologies now allow researchers to simulate highly complex materials behavior and microstructures. MSEL theory and modeling efforts in FY96 continued their focus on the behavior and properties of materials over the entire range of length scales, from atoms to bulk materials. Molecular dynamics simulations were performed to study such phenomena as fracture in brittle materials, relaxation and glass formation in supercooled liquids, and propagation of dislocations in metals. Mesoscopic phase-field and reaction-diffusion models of metal alloys, polymers, and polymer/liquid-crystal blends permitted the study of phase behavior, stability, separation kinetics, and morphological evolution in these materials, complementing ongoing experimental efforts at NIST and elsewhere in the area of materials processing. Finite-element computer codes were developed to model a variety of materials processes, such as injection molding of automotive parts, solder geometry in microelectronic interconnects, physical aging in composite materials, and mechanical properties of ceramic microstructures.

To facilitate progress in the rapidly evolving field of computational materials science, MSEL established a distributed Center for Theoretical and Computational Materials Science (CTCMS) in 1994. Using the tremendous advances in electronic communication and collaboration, this infrastructure facilitates interactions between industry, academia, NIST and other government labs in the development and application of state-of-the-art theoretical and computational materials science techniques to industrially important materials and materials processing problems.

To use more effectively the Nation's talents and resources, the CTCMS integrates ongoing research at various institutions by forming temporary multi-disciplinary and multi-institutional research teams as required to attack key materials issues. The CTCMS has three principal activities, all operating interactively: planning, research, and technology transfer. Workshops are held as the first step in defining technical research areas with significant technological impact, identifying team members, and in building and designing the infrastructure for collaborative research. NIST, in its unique position as a "third party" liaison, is well suited to play a national role in this planning process. The CTCMS provides an infrastructure and support for its members, including an interactive World Wide Web information server, and modern computing and workshop facilities. In FY96, the CTCMS addressed critical technical issues in processing, characterization, behavior, and properties of multiphase, heterogeneous materials. Current programs include theory and simulation in the areas of microelectronic interconnect design, Green's functions and boundary element methods applied to mechanical properties, microstructure and dynamics of glass formation, standards in micromagnetics modeling, morphological control of polymer-based liquid crystal display materials, solidification and dendritic growth in casting of alloys, and object-oriented finite-element modeling of ceramic microstructures.

Significant Accomplishments

- Developed a relationship between the entropy of a glass forming polymer system and its viscosity in which the viscosity is determined by the configurational free energy, rather than the configurational entropy as originally anticipated.
- Introduced new and general analytic description of transport virial coefficients of particles having general shape and arbitrary property mismatch.
- Validated analytic model with numerous examples in three and two dimensions corresponding to bulk and thin film polymer materials.
- Development of new numerical first-passage time random walk method for solving for polymer solution transport properties.

Theory and Modeling in Polymer Physics

E.A. DiMarzio

Objective

The project objective is to develop a statistical mechanical basis for the non-Arrhenius temperature dependence of viscosity in glass forming polymers.

Technical Description

In this project the viscosity of glass forming polymers is examined within the context of the entropy theory of glasses. A simple statistical mechanical model is developed to account for the non-Arrhenius temperature dependence of the viscosity that is observed in polymer melts.

External Collaborations

Work on the effects of plasticizer on glass transition and on the fundamentals of the viscosity of glass forming liquids was performed in collaboration with researchers from Armstrong World Industries.

Accomplishments

Developed a statistical mechanics based relationship between the entropy of a glass forming polymer system and its viscosity. The model predicts that the viscosity is determined by the configurational free energy, rather than the configurational entropy as originally anticipated.

Outputs

Publication

E.A. DiMarzio and A.J.-M. Yang, *The Configurational Entropy Approach to the Kinetics of Glass Formation*, J. Res. NIST (In Press).

Presentation

E. A. Di Marzio, *The use of Kinetic Energy to Derive the Kinetic Properties of Glasses*, APS March Meeting, St. Louis, MO, March, 1996.

Theory and Modeling of the Properties of Polymer Blends, Suspensions and Solutions

J. Douglas

Objectives

- Develop general theory relating to the transport properties of polymer blends and solutions.
- Describe influence of complex-shaped additives on the transport properties of polymer

materials.

- Calculate equilibrium and transport properties of polymers having membrane-like and sponge-like connectivity.

Technical Description

- Perform numerical calculations of the hydrodynamic radius, capacity, and Smoluchowski rate constant for diffusion-limited reactions of polymers using a novel random walk algorithm for solving the associated boundary value problems.
- Calculate transport properties (electrical and thermal conductivity, dielectric constant, refractive index, shear modulus, magnetic permeability, shear viscosity) of polymer blends, polymer solutions and polymer materials with suspended additives by developing a perturbation expansion in the property mismatch, using numerical and Padé approximation methods.
- The critical exponents describing the average dimensions, friction coefficient and the intrinsic viscosity of polymeric random surfaces are calculated based on the Wiener sheet model with inclusion of excluded volume interactions. The growth of branched polymer structures under equilibrium and non-equilibrium diffusion-limited conditions is also treated within the same framework.

External Collaborations

Building Materials Division, NIST- Apply transport property calculations to cement modeling. finite element calculations of transport virial coefficients for complex shaped particles having a wide range of property mismatch to validate analytical model.

Biotechnology Division and Center for Advanced Research in Biotechnology- Collaborate on development of new random walk based algorithms for calculating transport properties of complex-shaped particles.

Accomplishments

- Introduced new and general analytic description of transport virial coefficients of particles having general shape and arbitrary property mismatch.
- Validation of analytic model with numerous examples in three and two dimensions corresponding to bulk and thin film polymer materials.
- Development of new numerical first-passage time random walk method for solving for polymer solution transport properties.

- Introduced new model describing the average size and transport properties of polymers, membranes and sponge-like structures in good and poor solvents.

Publications

J. F. Douglas and E. J. Garboczi, *Intrinsic Viscosity and Polarizability of Particles Having a Wide Range of Shapes*, *Advances in Chemical Physics*, 91, 85 (1995).

E. J. Garboczi and J. F. Douglas, *Intrinsic Conductivity of Objects Having Arbitrary Shape and Conductivity*, *Physical Review E* 53, 6169 (1996).

J. F. Douglas, *A Dynamic Measure of Order in Glasses*, *Comp. Mat. Sci.* 4, 292 (1995).

J. F. Douglas, *Swelling and Growth of Polymers, Membranes, and Sponges*, *Physical Review E*, 54, 2677 (1996).

J. F. Douglas, C. Guttman, A. Mah, T. Ishinabe, *Spectrum of Self-Avoiding Walk Exponents*, *Physical Review E*, (to appear).

J. Given, J. B. Hubbard, J. F. Douglas, *A First-Passage Algorithm For Calculating the Friction and Capacity of Polymers*, *Journal of Chemical Physics*, (submitted).

Presentations

J. F. Douglas, *Transport Properties of Suspensions, Polymer Solutions, and Polymer Blends*, *Polymers Gordon Conference*, Newport, Rhode Island, July 1996.

J. F. Douglas, *Polymers and Superfluids?*, *Physics Division Lecture Series*, NIST, March 1996.

OTHER PROGRAMS

In response to requests from other federal agencies the Division conducts research on a reimbursable basis to solve specific needs of the requesting agency. The nature of these activities changes from year to year depending on national priorities. Specific projects include assistance to the Bureau of Consular Affairs, Department of State to evaluate candidate security laminates and a long term activity with the National Institute of Dental Research to develop improved dental restorative materials. The last mentioned project is included in the report on the Dental and Medical Materials Program.

Diffusion of Gases in Polymeric Materials

Charles Guttman and William Blair

Objectives

The objectives are to develop and apply measurement techniques capable of quantifying the adsorption characteristics of polymeric materials in the presence of flowing gas streams.

Technical Description

The experimental apparatus used in this research measures the reductions in the concentration of permeable gases caused by passing the gas stream over the polymeric material. A luminescence detection method provides sufficient sensitivity for detection of changes in concentrations of oxides of nitrogen and sulfur of the order of $\mu\text{L/L}$.

Accomplishments

- An experimental apparatus has been constructed and successfully used to detect small changes in $\mu\text{L/L}$ and nL/L concentrations of pollutant gases, NO , NO_2 and SO_2 in air with varying humidity.
- Preliminary studies have shown absorption of SO_2 gas at $400 \mu\text{L/L}$ in air by polyimide films, but none by poly(vinylidene fluoride) films at the same gas concentrations.

Development and Use of Test Methods for Qualification of Passport Laminates

W.G. McDonough and D.L. Hunston

Objectives

The objectives are to perform testing and provide consultation to assist the Bureau of Consular Affairs at the U.S. Department of State in selecting and purchasing the plastic laminate that is used to protect the photograph and descriptive information on the U.S. Passport. Also, the work includes testing and providing consultation on the development of next generation materials for the U.S. Passport.

Technical Description

NIST's responsibilities include performing evaluation tests as part of the solicitation process, examining new materials and security concepts that become available, and developing new test methods as required by progress in the field. The area of the passport that contains the photograph and descriptive information is called the data page. The laminates must protect this page from dirt, spills and abrasions that may occur in normal use. In addition, these laminates must resist attempts to tamper with the photograph or data page. When new laminating material is needed, the Department of State issues a solicitation inviting manufacturers to submit products for evaluation. NIST has a continuing cooperative program with the State Department to assist in this activity. NIST's responsibilities include: (1) consulting on the plan for evaluation tests included in the solicitation, (2) performing these tests as part of the solicitation process, (3) examining new materials and security concepts that become available, and (4) developing new test methods as required by progress in the field. Finally, where appropriate, NIST and the State Department provide feedback to the manufacturers on the performance of their technology in the evaluation. This assists the companies in making better materials for the future and thereby helps the Government improve the security of the passport.

Accomplishments

The current plan for evaluation tests includes ten different measurements and NIST conducts nine of these. In past work, a number of the tests have been refined and improved by NIST in consultation with the State Department as part of this project. The measurements assess susceptibility to attack by common fluids, durability and processability of the materials, and resistance to tampering. The results are provided to the State Department who combines them with cost and other data to make a final procurement decision.

During the past year, a number of new concepts in lamination technology were evaluated and compared as a guide to future directions for this field. The results were reported to the State Department.

Outputs

Reports on the work are provided to the State Department on a periodic basis. This work has enabled the State Department to implement new security measures in passports. The two key factors are that NIST's technical expertise has enabled the development of test methods that compare laminates with very different approaches to security, and NIST has the impartiality to gain industries' respect.

POLYMERS DIVISION

CHIEF

Leslie E. Smith
Phone: (301) 975-6762
e-mail: leslie.smith@nist.gov

DEPUTY CHIEF

Bruno M. Fanconi
Phone: (301) 975-6762
e-mail: bruno.fanconi@nist.gov

NIST FELLOW

Charles C. Han
Phone: (301) 975-6771
e-mail: charles.han@nist.gov

GROUP LEADERS

Electronic Packaging and Interconnects
G. Thomas Davis
Phone: (301) 975-6725
e-mail: george.davis@nist.gov

Polymer Blends & Processing
Eric J. Amis
Phone: (301) 975-6681
e-mail: eric.amis@nist.gov

Polymer Composites
Richard S. Parnas
Phone: (301) 975-5805
e-mail: richard.parnas@nist.gov

Structure and Mechanics
Gregory B. McKenna
Phone: (301) 975-6752
e-mail: gregory.mckenna@nist.gov

Polymer Characterization
Bruno M. Fanconi
Phone: (301) 975-6762
e-mail: bruno.fanconi@nist.gov

Dental & Medical Materials
Francis W. Wang
Phone: (301) 975-6726
e-mail: francis.wang@nist.gov

RESEARCH STAFF

Amis, Eric J.
eric.amis@nist.gov

- o Neutron, x-ray and light scattering
- o Strong interactions in polymer/solvent systems
- o Polyelectrolytes
- o Viscoelastic behavior of polymers
- o Dendritic polymers

Antonucci, Joseph M.
joseph.antonucci@nist.gov

- o Synthetic and polymer chemistry
- o Dental composites, cements and adhesion
- o Antioxidants

Barnes, John D.
john.barnes@nist.gov

- o Gas and vapor transport in polymers
- o X-ray scattering
- o Computer applications in polymer measurements

Bauer, Barry J.
barry.bauer@nist.gov

- o Polymer synthesis
- o Neutron, x-ray and light scattering
- o Dendrimers
- o Thermal characterization

Beck Tan, Nora⁺
nora.becktan@nist.gov

- o Polymer Interfaces
- o Structural Characterization of Polymers and Polymer Blends

Blair, William R.
william.blair@nist.gov

- o Polymer analysis by size exclusion chromatography
- o Diffusion and absorption of gases in polymeric matrices
- o Mass spectrometry

Bloss, Peter
peter.bloss@nist.gov

- o Charge distribution
- o Thermal diffusivity

Bowen, Rafael L.*
rafael.bowen@nist.gov

- o Adhesion
- o Dental composites
- o Novel Monomer Synthesis

Briber, Robert M.⁺
robert.briber@nist.gov

- o Structure and morphology of polymers
- o Electron microscopy
- o X-ray scattering

Broadhurst, Martin G.⁺
martin.broadhurst@nist.gov

- o Dielectric measurements
- o Piezoelectric and pyroelectric modeling and theory

- | | |
|---|---|
| Bur, Anthony J.
anthony.bur@nist.gov | o Equation of state of polymers
o Ionic conduction |
| Campbell, Jr., Gordon C. ⁺ | o Dielectric properties of polymers
o Fluorescence and optical monitoring of polymer processing
o Piezoelectric, pyroelectric polymers
o Viscoelastic properties of polymers |
| Carey, Clifton M.*
clifton.carey@nist.gov | o Solid state NMR of polymers
o Off-resonance proton irradiation techniques |
| Cerrada, Maria ⁺
maria.cerrada@nist.gov | o Dental plaque
o Microanalytical analysis techniques
o Phosphate chemistry
o Ion-selective electrodes |
| Chang, Shu Sing ⁺ | o structure property relations
o physical aging |
| Cherng, Maria*
maria.cherng@nist.gov | o Thermal properties of polymeric and composite materials
o Composite process monitoring
o Electronic packaging materials
o Polymer phase transitions
o Precision electrical and temperature measurements |
| Chiang, Chwan K.
c.chiang@nist.gov | o Calcium phosphate biomaterials |
| Chiang, Martin Y.
martin.chiang@nist.gov | o Electroluminescent polymers
o Residual stress
o Impedance spectroscopy |
| Chiang, Martin Y.
martin.chiang@nist.gov | o Computational mechanics (finite element analysis)
o Strength of materials
o Engineering mechanics of polymer based materials |
| Chin, Pearl S. ⁺ | o Surface energies |
| Choi, Kyung Moon ⁺
kyung.choi@nist.gov | o Polymer composites |

- Colucci, Dina M.
dina.colucci@nist.gov
- o Nonlinear viscoelasticity
 - o Physics and modeling of polymer glasses
- Chow, Laurence C.*
laurence.chow@nist.gov
- o Calcium phosphate compounds
 - o Dental and biomedical cements
 - o Solution chemistry
 - o Topical dental fluorides
- Davis, G. Thomas
george.davis@nist.gov
- o Electronic packaging
 - o Polymer crystallization
 - o X-ray diffraction of polymers
 - o Polarization distribution
 - o Piezoelectricity in polymers
- DeReggi, Aime S.
aime.dereggi@nist.gov
- o Polarization-depth profiles in polymers
 - o Space charge in dielectrics
 - o Ferroelectric polymers
 - o Polymeric piezo- & pyroelectric devices
- Delin, Mats⁺
delin@nist.gov
- o polymer crazing
 - o polymer mechanics
 - o physical aging
- Dickens, Brian
brian.dickens@nist.gov
- o Polymer oxidation
 - o Monomer design and free radical curing
 - o Automation
 - o Photoacoustic spectroscopy
- Dickens, Sabine*
sabine.dickens@nist.gov
- o Clinical dentistry
 - o Dental composites
 - o Dental adhesives
 - o Transmission electron microscopy
- Di Marzio, Edmund A.
edmund.dimarzio@nist.gov
- o Statistical mechanics of polymers
 - o Phase transitions
 - o Glasses
 - o Polymers at interfaces
- Douglas, Jack F.
jack.douglas@nist.gov
- o Theory on polymer solutions and blends
 - o Transport properties of polymer solutions and suspensions
 - o Polymers at interfaces
 - o Scaling and renormalization group calculation

Dunkers, Joy P.
joy.dunkers@nist.gov

- o Polymer characterization
- o Infrared microspectroscopy of polymers
- o Fiber optics spectroscopy
- o Process monitoring and control

Eanes, Edward D.*
edward.eanes@nist.gov

- o Structure of bones and teeth
- o Calcium phosphate compounds as dental materials
- o Effects of solution and biological molecules on precipitation of calcium phosphates
- o Liposome studies

Eichmiller, Frederick C.*
frederick.eichmiller@nist.gov

- o Clinical dentistry
- o Composites
- o Dentin adhesives

Eidelman, Naomi N.*
naomi.eidelman@nist.gov

- o Prevention of calcification in the cardiovascular system
- o Effect of phosphonates, cholesterol and phospholipids on calcium phosphate formation
- o Characterization of calcified deposits by FTIR microscopy

Ermi, Brett D.+
brett.ermi@nist.gov

- o Neutron and light scattering
- o Polymer characterization
- o Strong interactions in polymer solvent systems
- o Polyelectrolytes

Ettegui, Emile E.+
emile.ettegui@nist.gov

- o Light emitting polymers
- o Surface physics
- o Fluorescence spectroscopy

Fanconi, Bruno M.
bruno.fanconi@nist.gov

- o Infrared & Raman spectroscopy of polymers
- o Structure of polymers
- o Polymer fracture
- o Process monitoring of polymer composites

Farahani, Mahnaz*
mahnaz.farahani@nist.gov

- o Radiation chemistry/physics
- o Analytical chemistry

Feng, Yi+

- o Temperature jump light scattering
- o Phase separation kinetics of polymer blend

Flaim, Glenn M.*
glenn.flaim@nist.gov

- o Fabricating dental composites

- Flynn, Kathleen M.
kathleen.flynn@nist.gov
- o Permeability Measurements
 - o Flow Visualization Experiments
- Fowler, Bruce O.*
bruce.fowler@nist.gov
- o Infrared and laser Raman structural analysis of calcium phosphates
- George, Laurie A.*
laurie.george@nist.gov
- o Glass-ceramics
- Gettinger, Constance L.
constance.gettinger@nist.gov
- o Neutron and light scattering
 - o Ion containing polymers and copolymers
- Giuseppetti, Anthony A.*
anthony.giuseppetti@nist.gov
- o Casting of dental alloys
 - o Mercury-free amalgam alternative
- Gruber, John
john.gruber@nist.gov
- o Polymer processing
 - o Fluorescence and optical monitoring of polymer processing
 - o Polymer coatings
 - o Solution properties of polymers
 - o Size exclusion chromatography
 - o Semicrystalline polymer chain configurations
 - o Mass spectroscopy of polymers
 - o Diffusion and absorption of gases by polymers
- Guttman, Charles M.
charles.guttman@nist.gov
- Hailer, Arthur W.*
art.hailer@nist.gov
- o Chemical reactions, chemical analysis
- Han, Charles C.
charles.han@nist.gov
- o Phase behavior of polymer blends
 - o Phase separation kinetics of polymer blends
 - o Polymer characterization and diffusion
 - o Shear mixing/demixing and morphology control of polymer blends
 - o Static, time resolved, and quasi-elastic scattering of light and neutron
- Han, Won Hee⁺
won.han@nist.gov
- o Moisture effects on polymers
 - o Plasticization
 - o Physical aging
 - o Liquid crystal rheology
- He, Jing⁺
- o Toughened epoxy
 - o Fracture analysis

Hobbie, Eric K.⁺
erik.hobbie@nist.gov

- o Light scattering and optical microscopy
- o Dynamics of complex fluids
- o Shear induced structure in polymer blends and solutions

Holmes, Gale A.
gale.homes@nist.gov

- o Composite interface science
- o Chemical structure-mechanical property relationships for polymers
- o Polymer chemistry
- o Mass spectroscopy

Hoffman, Kathleen M.*
kathleen.hoffman@nist.gov

- o Amalgam alternative material
- o Scanning electron microscopy
- o Nuclear magnetic resonance spectroscopy

Hunston, Donald L.
donald.hunston@nist.gov

- o Adhesion science and technology
- o Fracture behavior of polymers
- o Processing and failure behaviors of polymer composites
- o Flow behavior of dilute high polymer solutions
- o Macromolecular-small molecule binding

Huynh, Hai⁺

- o Rubber recycling
- o Mechanical properties of concrete

Ishikawa, Kunio*

- o Calcium phosphate compounds

Jackson, Catheryn L.
catheryn.jackson@nist.gov

- o Structure and morphology of polymers
- o Transmission and scanning electron microscopy
- o Finite-size effects on crystalline melting and glass transition temperatures
- o Liquid crystalline polymers
- o Microcellular foams morphology

Johnsonbaugh, David S.
david.johnsonbaugh@nist.gov

- o Fluorescence and optical monitoring of polymer processing
- o Microbiology
- o Phase behavior of polymer blends

Karim, Alamgir
alamgir.karim@nist.gov

- o Thin film phase behavior of polymer blends
- o Morphology of thin polymer blend films
- o Neutron and x-ray reflection, scattering, AFM and optical microscopy
- o Grafted polymer systems

Kelly, J. Robert⁺
robert.kelly@nist.gov

- o Bioceramics
- o Clinical-laboratory test correlation
- o Dental ceramics
- o Failure analysis; dental prostheses
- o Finite element analysis
- o Weibull analysis

Khoury, Freddy A.
freddy.khoury@nist.gov

- o Crystallization, structure and morphology of polymers
(including polymer blends)
- o Analytical electron microscopy of polymers
- o Wide angle and small angle x-ray diffraction
- o Structure and mechanical property relationships

Kim, Sanghoon⁺
sanghoon.kim@nist.gov

- o Small angle light scattering and optical microscopy
- o Shear induced phase transition
- o Phase separation kinetics

Kryder, Samuel J.⁺

- o Electronic circuit design and construction
- o Electronic troubleshooting and repair

Kurakawa, Hidenobu⁺

- o Polymer solution thermodynamics
- o Small angle neutron scattering

Lee, Benjamin P.
benjamin.lee@nist.gov

- o Theory of polymer blends
- o Theory of phase separation kinetics

Lenhart, Joseph L.⁺

- o Sensors
- o Interphase structure

Li, Shuiqiang⁺
shuiqiang.li@nist.gov

- o Instrument design and building for light scattering and
microscope with twin screw extruder

Liao, Hongyan^{*}
hongyan.liao@nist.gov

- o Statistical data analysis
- o Experimental design

Liao, Kin⁺
kin.liao@nist.gov

- o Fatigue, damage, and NDE of composites
- o Environmental durability of composites
- o Behavior of ceramic composites

Lin, Nam S.^{*}
nam.liao@nist.gov

- o Synthesis and testing of dental adhesives

Lin, Eric K.
eric.lin@nist.gov

- o Statistical mechanics
- o X-ray and neutron reflectivity

- Liu, D.-W.
da-wei.liu@nist.gov
- o Polymer synthesis
 - o Polymer characterization - thermal gravimetric analysis, differential scanning calorimetry, gel permeation chromatography, infrared spectroscopy, nuclear magnetic resonance, scanning electron microscopy
- Lowry, Robert E.⁺
robert.lowery@nist.gov
- o Applications of fluorescence spectroscopy to polymeric systems
 - o Synthesis of chromophore-labeled polymers
- Ly, Agnes K.^{*}
agnes.ly@nist.gov
- o Clinical dental assistant
 - o Adhesion measurements
- Mager, Carie⁺
- o Toughening Bioceramics
 - o Fracture mechanics
- Marjenhoff, William A.^{*}
william.marjenhoff@nist.gov
- o Research Administration
- Markovic, M.⁺
milenko.markovic@nist.gov
- o Calcium phosphate chemistry
 - o Biomineralization (normal and pathological)
 - o Crystal growth and dissolution kinetics
 - o Heterogeneous equilibria
- Mathew, Mathai^{*}
mathai.mathew@nist.gov
- o Crystallography
 - o Calcium phosphate compounds
- Maurey, John M.⁺
john.maurey@nist.gov
- o Ultracentrifugation
 - o Rayleigh light scattering
 - o Osmometry
 - o Densimetry
 - o Refractometry
 - o Intrinsic viscosity
- McDonough, Walter G.
walter.mcdonough@nist.gov
- o Processing and cure monitoring polymer composites
 - o Failure and fracture of polymers
 - o Polymer composite interfaces
- McKenna, Gregory B.
gregory.mckenna@nist.gov
- o Failure, yield and fracture of polymers
 - o Nonlinear viscoelasticity
 - o Molecular rheology
 - o Physics of polymer glasses
 - o Rubber thermodynamics and mechanics
 - o Mechanics of composites

- McKinney, John E.⁺
o Tribiology of dental composites, cements and alloys
- Migler, Kalman
kalman.migler@nist.gov
o Effects of shear and pressure on phase behavior
o Fluorescence and optical monitoring of polymer processing
o Liquid crystals
o Surface rheology
- Misra, Dwarika N.*
dwarika.misra@nist.gov
o Surface chemistry
o Adhesion
o Chemisorption
o Adsorption from solutions
- Mopsik, Frederick L.
frederick.mopsik@nist.gov
o Dielectric measurements and behavior
o Automated measurement design
o Computerized data analysis and programming
o Electrical properties of polymers
- Nakatani, Alan I.
alan.nakatani@nist.gov
o Polymer blends and solution properties under shear
o Small angle neutron scattering
o Phase behavior of polymer blends
- Neff, Raymond A.
raymond.neff@nist.gov
o Processing of thermoset polymers
o Cure monitoring and sensors
o Rheology
- O'Connell, Paul A.
paul.oconnell@nist.gov
o Nonlinear viscoelasticity
o Physical aging
o Torsional testing
- Parnas, Richard S.
richard.parnas@nist.gov
o Flow through porous media with heterogeneous structure
o Surface rheology
o Polymer dynamics
o Evanescent wave optical fiber fluorescence monitoring
o Control of the liquid molding process
- Parry, Edward E.*
edward.parry@nist.gov
o Dental appliance and crown and bridges fabrication
o Machine shop applications
- Peterson, Richard C.
richard.peterson@nist.gov
o Interface mechanics
o Permeability
- Phelan, Jr., Frederick R.
o Resin transfer molding: modeling and processing

frederick.phelan@nist.gov

studies

- o Viscoelastic flow modeling
- o Flow in porous media

Raghavan, Dharmaraj T.⁺
Dharmaraj.Raghavan@nist.gov

- o Rubber recycling
- o Interface chemistry
- o Mechanical properties of concrete

Reed, Benjamin B.*
benjamin.reed@nist.gov

- o Synthetic and polymer chemistry
- o Polymerization expanding monomers
- o Laboratory automation

Rolnick, Robert A.

- o Network administrator (Blends Group)
- o Computer maintenance

Rose, Karen J.*
karen.rose@nist.gov

- o Topical fluoridation for professional application

Roth, Steven C.
steven.roth@nist.gov

- o Piezoelectric polymer transducers-fabrication and applications
- o Vacuum deposition of metals
- o Calibration of polymer transducers
- o Microcomputer interfacing
- o Fluorescence measurements

Rouiller, Vincent⁺
vrouil@enh.nist.gov

- o Viscoelasticity
- o Polyurethane creep

Rupp, Nelson W.*

- o Clinical dentistry
- o Amalgams
- o Direct golds
- o Composites
- o Microleakage
- o Dentin adhesives

Sanin, Norman D.*
norman.sanin@nist.gov

- o Topical dental fluorides
- o Calcium phosphate cements

*Research Associate

⁺Guest Scientist

Schen, Michael A.
michael.schen@nist.gov

- o Non-linear optical polymer
- o Optical spectroscopy
- o Microelectronics packaging materials
- o Photonics
- o Coefficient of thermal expansion
- o National technology roadmaps in electronics

Schultheisz, Carl R.
carl.schultheisz@nist.gov

- o Failure of composites
- o Experimental mechanics
- o Torsional dilatometry
- o Physics of polymer glasses

Schumacher, Gary E.*
gary.schumacher@nist.gov

- o Clinical dentistry
- o Composites
- o Dentin adhesives

Sieck, Barbara A.*
barbara.sieck@nist.gov

- o Calcium phosphate compounds
- o Chemical analysis
- o Remineralization

Skrtic, Drago*
drago.skrtic@nist.gov

- o Calcium phosphates as dental materials
- o Liposome studies

Smith, Leslie E.
leslie.smith@nist.gov

- o Adsorption of polymers
- o Polymer degradation reactions

Spaid, Michael A.
michael.spaid@nist.gov

- o Fluid mechanics
- o Lattice Boltzmann methods
- o Flow in porous media

Stansbury, Jeffrey W.
jeffrey.stansbury@nist.gov

- o Synthetic chemistry
- o Polymers and polymer composites
- o Polymerization of expanding monomers
- o Fluorinated polymers

Takagi, Shozo*
shozo.takagi@nist.gov

- o Crystallography
- o X-ray diffraction
- o Calcium phosphate biomaterials
- o Topical fluoridation
- o De- and remineralization

Tesk, John A.
john.tesk@nist.gov

- o Biomaterials-industrial relations
- o Bond strength characterization
- o Casting of alloys

- o Strength of dental systems
 - o Thermal expansion and properties of dental materials
 - o Finite element studies
 - o Porcelain-metal systems
 - o Weibull analysis
 - o Processing of dental ceramics, effects of
 - o Wear testing, orthopaedic materials
- Topp, Andreas
andreas.topp@nist.gov
- o Small angle neutron scattering
 - o Dendrimers
- Tung, Ming A.*
ming.tung@nist.gov
- o Chemistry of calcium phosphate compounds
 - o Remineralization studies
 - o Standard reference materials
- VanderHart, David L.
david.vanderhart@nist.gov
- o Measurement of orientation in polymer fibers and films
 - o Solid state NMR of polymers
 - o Measurement of polymer morphology at the 2-50 nm scale
 - o Pulsed field gradient NMR
- Van Zanten, John H.
- o Complex fluids
 - o Polymer interfaces
 - o Scattering of light, neutrons & x-rays
 - o Biophysics
 - o Interfacial phenomena
 - o Scanning probe microscopy
- Valachovic, Diane E.+
diane.valachovic@nist.gov
- o Light and neutron scattering
 - o Polyelectrolytes
 - o Polymer characterization
 - o Dendrimers
- Vogel, Gerald L.*
gerald.vogel@nist.gov
- o Dental plaque chemistry, chemistry of calcium phosphates
 - o Microanalytical techniques
- Waldron, William K.+
william.waldron@nist.gov
- o Nonlinear viscoelasticity
 - o Mechanics and thermodynamics of rubber
- Wallace, William E.
william.wallace@nist.gov
- o Surface and interface behavior
 - o Ion beam and electron spectroscopies
 - o X-ray and neutron reflectivity
 - o MALDI mass spectrometry

Wang, Francis W.
francis.wang@nist.gov

- o Photophysics and photochemistry of polymers
- o Fluorescence spectroscopy
- o Thermodynamic and frictional properties of macromolecules

Woerdeman, Dara⁺

- o Permeability
- o Composite process monitoring
- o Evanescent wave optical fiber fluorescence monitoring

Wu, Wen-li
wen-li.wu@nist.gov

- o Neutron and x-ray scattering and reflectivity
- o Electron microscopy
- o Mechanical behavior of polymers and composites
- o Polymer surfaces and interfaces

Xu, Huakun^{*}
hockin.xu@nist.gov

- o Silver alloy alternative to amalgam
- o Wear and fatigue
- o Ceramic-reinforced composite resin
- o Polymer blend characterization
- o Dye labeling
- o Small angle light scattering and fluorescence microscope

Yu, Jae-Woong⁺
jwyu@enh.nist.gov

- o Polymer synthesis
- o Light x-ray and neutron scattering, reflection
- o Polymer blends containing specific interactions
- o AFM and optical microscopy

Zhou, Chunlin⁺
clzhou@enh.nist.gov

Zhang, Zhen^{*}
jane.zhang@nist.gov

- o Microanalysis of dental plaque

Wang, Liang
Wang, Liang
Wang, Liang
Wang, Liang

Wang, Liang
Wang, Liang
Wang, Liang
Wang, Liang

Wang, Liang
Wang, Liang
Wang, Liang
Wang, Liang

Wang, Liang
Wang, Liang
Wang, Liang
Wang, Liang

Wang, Liang
Wang, Liang
Wang, Liang
Wang, Liang

Wang, Liang
Wang, Liang
Wang, Liang
Wang, Liang

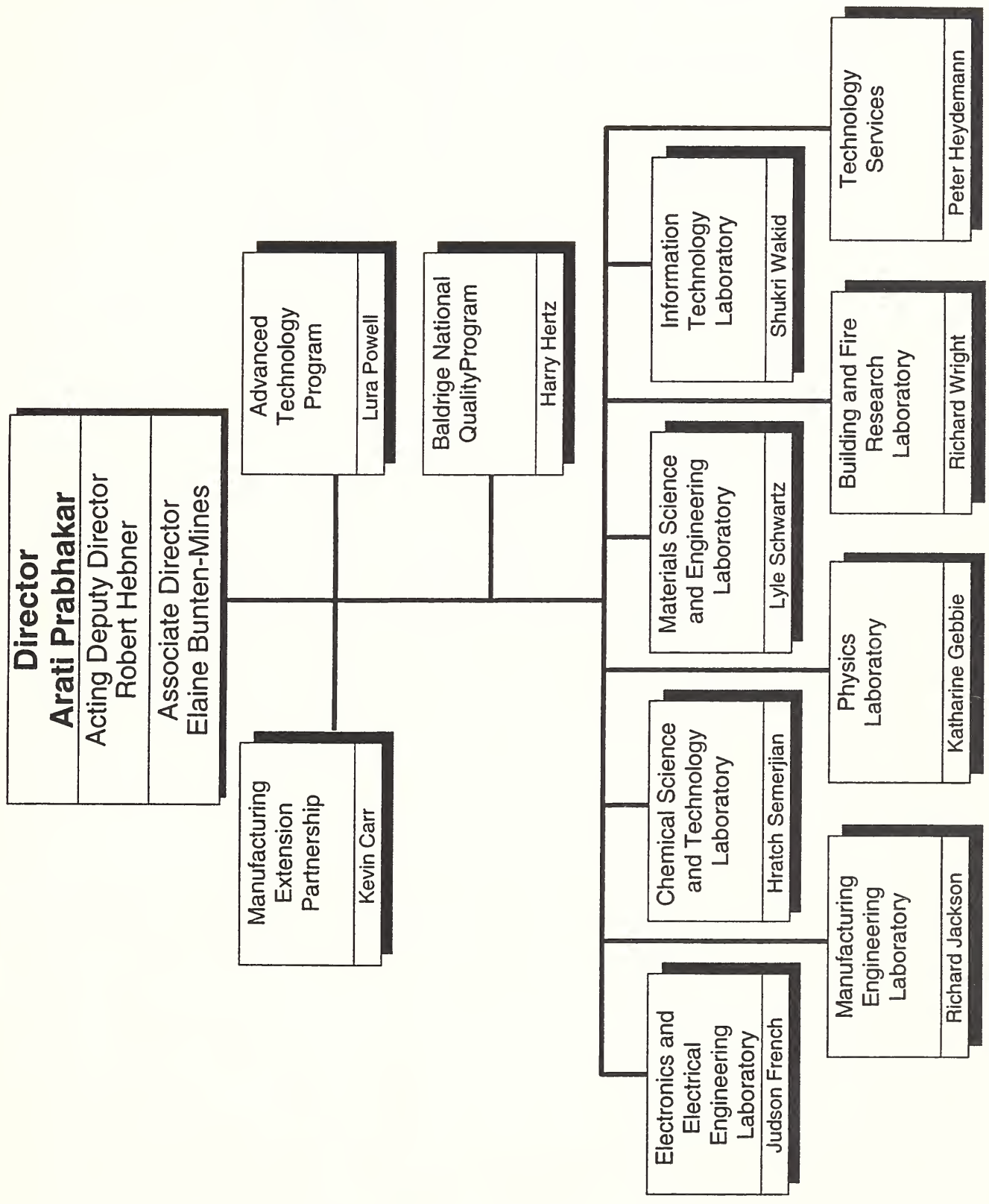
Wang, Liang
Wang, Liang
Wang, Liang
Wang, Liang

Wang, Liang
Wang, Liang
Wang, Liang
Wang, Liang

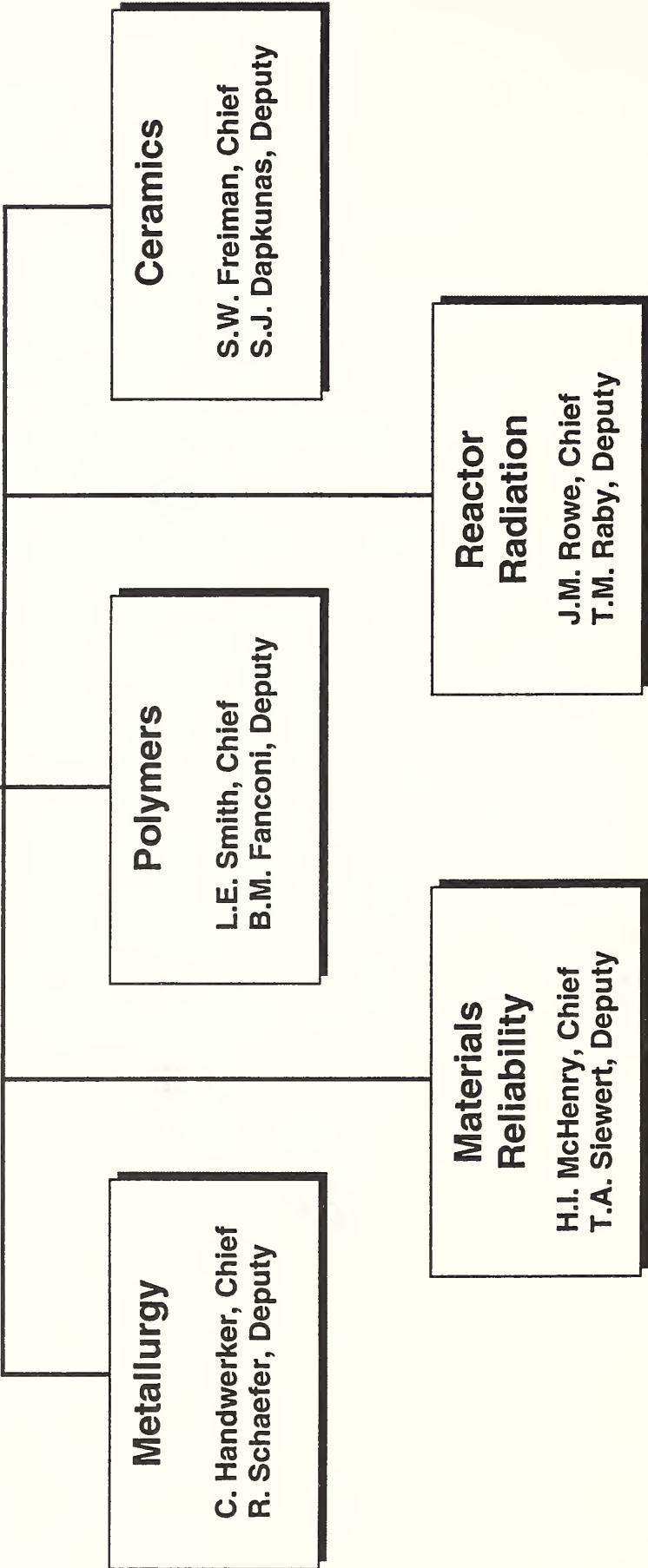
Wang, Liang
Wang, Liang
Wang, Liang
Wang, Liang

National Institute of Standards and Technology

Organizational Chart



**MATERIALS SCIENCE AND
ENGINEERING LABORATORY**
L.H. Schwartz, Director
D. Hall, Acting Deputy Director



POLYMERS DIVISION

Smith, Leslie E., Dr., Chief

Fanconi, Bruno M., Dr., Deputy Chief

Han, Charles C., Dr., NIST Fellow

Lightbody, Sonja C., Mrs., Admin. Offcr.

Green, Janice M., Mrs., Secretary

ELECTRONICS APPLICATIONS

Davis, G. Tom, Dr., Ldr.

Webb, Bronny, Mrs., Secy.

Beck Tan, Nora C., Dr.

DeReegi, Aime S., Dr.

Dickens, Brian, Dr.

Mopsik, Frederick I., Dr.

Roth, Steven C., Mr.

Schen, Michael A., Dr.

Wallace, William E., Dr.

Wu, Wen-li, Dr.

Guest Scientists

Bloss, Peter, Dr.

Chin, Pearl S., Ms.

Edelman, Seymour, Mr.

Kramer, Edward, Dr.

VanZanten, John H., Dr.

POLYMER BLENDS & PROCESSING

Amis, Eric J., Dr., Leader

Burton, June S., Ms., Secretary

Bauer, Barry J., Dr.

Bur, Tony J., Dr.

Douglas, Jack F., Dr.

Gettinger, Constance L., Dr.

Jackson, Catheryn L., Dr.

Johnsonbaugh, David S., Mr.

Karim, Alangir, Dr.

Liu, Da-Wei, Mr.

Migler, Kalman, Dr.

Nakatani, Alan I., Dr.

Research Associates

Landry, Michael, Dr.

Lohse, David, Dr.

Marr, David, Dr.

North, Diane, Ms.

Pearson, Scott, Dr.

Thudium, Richard N., Mr.

Viswanathan, Ravi, Dr.

Yuan, Haojie, Ms.

Guest Scientists

Arcarese, Elizabeth B., Mrs.

Balsara, Nitash P., Dr.

Barnes, Kathleen A., Ms.

Briber, Robert M., Dr.

Choi, Sangwook

Chunlin, Zhou, Mr.

Dadmun, Mark D., Dr.

Ermi, Brett D., Mr.

Feng, Yi, Mr.

Hess, Diana B., Ms.

STRUCTURE AND MECHANICS

McKenna, Gregory B., Dr., Leader

Hollingsworth, Karen B., Mrs., Secretary

Barnes, John D., Dr.

Chiang, Martin Y., Dr.

Colucci, Dina M., Dr.

DiMarzio, Edmund A., Dr.

Gusler, Gloria M., Dr.

VanderHart, David L., Dr.

Verdier, Peter H., Dr.

Research Associates

Kearsley, Elliott A., Dr.

Yang, Arthur J., Dr.

Guest Scientists

Castellano, Claudio, Mr.

Chai, Herzl, Dr.

Gornick, Fred, Dr.

Han, Won Hee, Dr.

Horkay, Ferenc, Dr.

Humphrey, Jay D., Dr.

Kryder, Samuel J., Mr.

Lee, Andre Y., Dr.

O'Connell, Paul A., Dr.

Spinu, Ionel M., Dr.

Stiehler, Robert D., Dr.

Waldron, William K., Dr.

POLYMER CHARACTERIZATION

Fanconi, Bruno M., Dr., Leader

Webb, Bronny, Mrs., Secretary

Blair, Bill R., Mr.

Broadhurst, Martin J., Dr.

Guttman, Charles M., Dr.

Khoury, Freddy A., Dr.

Maurey, John R., Dr.

Guest Scientists

Florin, Roland E., Dr.

Flynn, Joseph H., Dr.

Wu, En S., Dr.

DENTAL & MEDICAL MATERIALS

Wang, Francis W., Dr., Leader

Hollingsworth, Karen M., Mrs., Secretary

Antonucci, Joseph M., Dr.

Stansbury, Jeffrey W., Dr.

Tesk, John A., Dr.

Research Associates

Eanes, Edward A., Dr.

Fowler, Bruce O., Mr.

Hailer, Arthur W., Mr.

Guest Scientists

Choi, Kyung Moon, Dr.

Code, James E., Dr.

Kelly, J. Robert, Cmdr.

Markovic, Milenko, Dr.

McKinney, John E., Mr.

Nikaido, Toru

Schumacher, Gary E.

Skrtic, Drago

Tateosian, Louis H.

American Dental Association

Eichmiller, Fred, Dr., Director

Bowen, Rafael L., Dr.,

Carey, Clifton M., Dr.

Chalkley, Margaret W., Mrs.

Cheng, Maria, Dr.

Chow, Laurence C., Dr.

Dickens, Sabine, Dr.

Eidelman, Naomi, Dr.

Farahani, Mahnaz, Dr.

George, Laurie A., Mrs.

**POLYMER BLENDS &
PROCESSING**

Guest Scientists

Ho, Li-Te, Mr.
Hobbie, Erik K., Dr.
Kent, Michael S., Dr.
Kim, Sanghoon, Dr.
Kitade, Shinichi, Mr.
Li, Shuiqiang, Mr.
Lin, Cheney, Mr.
Liu, Xiaodu, Mr.
McCrackin, Frank L., Dr.
Morrison, Faith A., Dr.
Mullins, Carol A., Mrs.
Pitcher, Matthew B., Mr.
Register, Richard A., Dr.
Reichart, Glenn C., Mr.
Sung, Li-Piin, Dr.
Valachovic, Diane, Miss
Yu, Jae-Woong, Dr.
Zhou, Chunlin, Mr.

**DENTAL & MEDICAL
MATERIALS**

American Dental Association

Gibson, Heather H., Dr.
Giuseppetti, Anthony A., Mr.
Hoffman, Kathleen M., Miss
Liao, Hongyan, Mrs.
Ly, Agnes K., Dr.
Marjenhoff, William A., Dr.
Mathew, Mathai, Dr.
Mistra, Dwarika N., Dr.
Parry, Edward E., Mr.
Ratzker, Menahem B., Mr.
Reed, Benjamin B., Mr.
Rose, Karen J., Dr.
Rupp, Nelson W., Dr.
Sanin, Norman D., Mr.
Sieck, Barbara A., Ms.
Smythers, Christine, Ms.
Stangel, Ivan, Dr.
Stephenson, Maurice A.S., Dr.
Takagi, Shozo, Dr.
Tomazic, Branko B., Dr.
Tung, Ming S., Dr.
Vogel, Gerald L., Dr.
Zhang, Zhen, Mrs.

