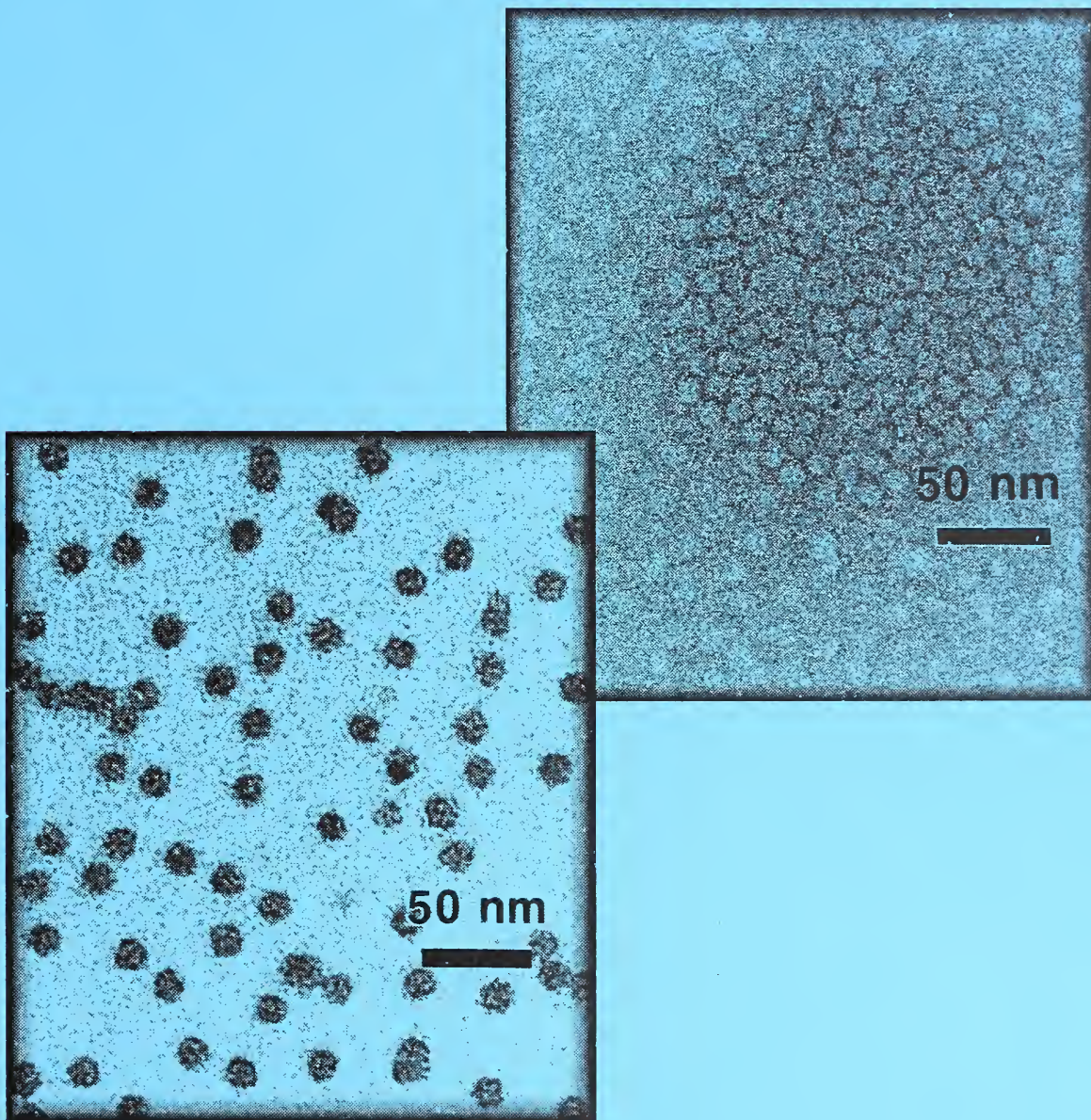




POLYMERS



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Department of Commerce
Quality Administration
Institute of Standards
Technology

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1997

Technical Activities 1997

Polymers

Electron micrographs of dendritic polymers, where each object is an individual molecule. The micrograph (bottom) was obtained using conventional biological-type transmission electron microscopy staining methods in which the solvent is removed. The micrograph (top) is of molecules imaged in vitrified solvent at very low temperature and should be a more accurate representation of dendrimers in solution. Under the latter condition, the dendrimer molecules appear to have more polyhedral shapes, rather than strictly spherical, and sometimes assemble into clusters.

MSEL

Materials Science and Engineering Laboratory

POLYMERS

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

NISTIR 6065
U.S. Department of Commerce
Technology Administration
National Institute of Standards
and Technology

Technical Activities 1997



U.S. DEPARTMENT OF COMMERCE
William M. Daley, Secretary
TECHNOLOGY ADMINISTRATION
Gary Bachula, Acting Under Secretary for Technology
NATIONAL INSTITUTE OF STANDARDS
AND TECHNOLOGY
Robert E. Hebner, Acting Director

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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 1997 fiscal year. It is organized according to the program structure by which we plan our work and 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 from both extensive informal visits to and from our customers and from the following formal workshops:

- NIST hosted a three day joint scientific workshop with the Hashimoto Phasing Project of the Exploratory Research and Technology Organization (ERATO) of Japan, which was attended by over 65 representatives of U.S. industry, ERATO, and NIST. In addition to further developing the scientific interactions between these two research groups, the workshop provided U.S. industrial researchers a direct view of the ERATO-supported project.
- In April 1997, SEMATECH, the Semiconductor Research Corporation and NIST conducted a workshop on *Interfaces and Adhesion in Electronic Packaging and Assembly* involving experts from industry, academia and government. The workshop explored new scientific opportunities for enhancing the understanding and robustness of material interfaces in semiconductor devices. As the size of microelectronic devices shrink, and their complexities increase, industry has identified material “interfaces and adhesion” as a critical area where substantial advancements within the semiconductor industry are needed.
- In October 1996, the U.S. Air Force Rome Laboratory and NIST sponsored the 6th *International Conference on Moisture in Microelectronics* at NIST's Laboratories in Gaithersburg, MD. Drawing over ninety individuals from industry, academia and government, this workshop was held to allow researchers and engineers, in the microelectronics industry, to exchange new insights and knowledge on how moisture impacts the performance and reliability of today's microelectronic products and packaging

materials. Moisture is universally seen as the single largest environmental factor which threatens the manufacturability and reliability of electronic packages and interconnects.

- An industry/NIST workshop on interfacial micromechanics in May, 1997 brought together leading researchers in the field and important industrial users of composites. The important problems in interface testing were identified and routes to solving some of them agreed upon. For example, an international program on interface test standardization under the auspices of VAMAS was announced to solve the problem of poor intercomparison.

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's technology transfer activities were recognized by the NIST Slichter Award to A. Bur, K. Migler and F. Wang and by the Federal Laboratory Consortium Award for Excellence in Technology Transfer to A. Bur. These awards recognize that our industrial collaborators have adopted NIST technology in their processing and R&D facilities.

This year the Polymers Division joined four industrial laboratories in the Participating Research Team (PRT) for the Advanced Polymer Beamline at Brookhaven National Synchrotron Light Source. Data taken during the commissioning phase showed a wavevector range and resolution much superior to lab based facilities. When completed this beamline will provide real-time simultaneous small and wide angle x-ray scattering with high incident flux and multiple area detectors for dynamic measurements. Beam time available through PRT membership will complement our in-house SAXS facilities and significantly enhance the capabilities available for our internal research and for our industrial and academic collaborators.

In a significant step toward increased development of biomaterial reference materials and standards, the three government agencies with responsibilities in this area - NIST (Polymers Division and Standard Reference Materials Program), the Food and Drug Administration, and the National Institute of Health - signed a Memorandum of Understanding (MOU) establishing a coordinating committee for the development of reference materials. The first step will be to transfer to NIST the reference materials previously developed by the National Heart, Lung, and Blood Institute for dissemination through our Standard Reference Materials Program. This will provide the community with one central source for such materials.

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

ELECTRONICS PACKAGING, INTERCONNECTS & ASSEMBLY

- For dielectric measurements, a coaxial sample holder has been designed and tested and measurement protocols instituted which eliminate discrepancies in the overlap regions of frequency in the several different instruments required to cover the range from DC to 1 GHz. The new holder reduces the measurement error in capacitance and loss at 30 MHz from 8% using a conventional four terminal holder to 0.1%. The same configuration can be used at frequencies up to 1 GHz where the uncertainty is about 1%. These techniques will allow the accurate measurement of dielectric constant and loss of thin film materials being evaluated for interlayer dielectrics in the microelectronics industry.
- Density profile and coefficient of thermal expansion (CTE) of ultra-thin (~100 nm) spin-on glass films have been determined by x-ray reflectivity and reported in collaboration with Dow-Corning Corp. Spin-on glass film is a primary candidate for interlayer dielectrics in future multi-level chips. Density profile and CTE are critical data needed for chip design and are not accessible with any other conventional measurement technique.
- A three terminal capacitance cell has been designed and constructed of nichrome-coated fused quartz electrodes that is capable of measuring the out-of-plane coefficient of thermal expansion of films as thin as 5 μm with a standard uncertainty of 0.1% over a 100 °C interval for polymeric materials whose properties are sufficiently stable. This measurement technique is expected to supplement the standard test method for coefficient of thermal expansion which is inadequate for providing reliable data on the thin polymer films encountered in the design of flexible circuits and microelectronic packaging.
- A new technique using twin neutron reflectivity has been developed which enables the determination of the density of thin films on many substrates including silicon wafers with a relative uncertainty of $\pm 1\%$. Density of thin films, especially in the ultra-thin range (≤ 100 nm), provides important insights about the structure of such films that has not been previously determined with an accuracy of $\pm 1\%$.

POLYMER BLENDS and PROCESSING

- The capability of NIST-developed on-line instrumentation, using light scattering and optical microscopy to measure *in-situ* domain size and shape during extrusion of incompatible and reactively compatibilized blends was demonstrated. In addition to morphology studies, the instrumentation can measure velocity profiles and characterize multiphase mixing. Industrial partners, including 3M and Rohm & Haas, have begun work using this instrument to investigate effects of polymer processing aids.

- NIST's on-line microscopy extruder instrument has revealed new droplet morphologies in the high shear stress regime which are tentatively attributed to normal forces. For two component systems, with a high viscosity ratio, droplets with negative surface curvature or structures elongated orthogonal to the flow direction, were observed. This result demonstrates the power of on-line measurements to complement typical post processing studies.
- In collaboration with Packard Electric, the determination of specific changes in the spectrum of a fluorescent probe provided simultaneous measurement of temperature and crosslinking in a polyethylene/polyvinyl acetate copolymer. This measurement can be used to control and monitor continuous extrusion of wire insulation during which crosslinking is activated by raising the temperature in the later stages of processing. During the early stages of the extrusion, limited crosslinking is allowed so that the rheology remains uniform.
- Dendrimer molecules of convergent types have been characterized with a combination of small angle neutron scattering, small angle x-ray scattering, and transmission electron microscopy. Four critical observations arise from the solution characterization which contrast dendrimers with other classes of polymers: Dendrimers are spherical in shape and have a narrow size distribution even at relatively low molar mass; the segment density distribution profile is nearly uniform within the dendrimer; the terminal units of the dendrimer are located within a relatively narrow shell toward the periphery of the molecule; and with increasing concentration the dendrimers appear to collapse and pack in a random close packing arrangement with little interpenetration. These characteristics suggest possible applications as size and molecular mass calibration standards for SANS, SAXS, TEM, AFM, MALDI, SEC, and filtration.
- In collaboration with Exxon, large pressure induced demixing in metallocene polyolefin blends was demonstrated through optical cloud point measurements. The observed linear dependence of the demixing temperature on pressure is $0.24\text{ }^{\circ}\text{C}/\text{MPa}$. High pressures are typical in most polymer processing, including polyolefins, and the strong dependence on pressure will greatly shift phase boundaries.

POLYMER COMPOSITES

- A database of permeability and other reinforcement properties was released in collaboration with the NIST Standard Reference Data Division. This data will aid the composites industry in designing liquid molding processes by providing critical input to mold filling simulation software.
- A Lattice-Boltzmann microflow simulation was compared to experimental data for flow in a model of the porous tows of composite reinforcements. The formation of voids and their

subsequent size reduction was successfully recreated, and the permeability of the model porous medium was accurately predicted. The Lattice-Boltzmann method is much more computationally efficient than conventional finite element methods for multiphase flows in complex geometries, enabling the rapid assessment of fiber architecture effects on composite processing and void formation.

- The ability of Optical Coherence Tomography to image internal fabric architecture and residual porosity distribution was demonstrated for refractive index-matched glass reinforced epoxy and vinylester composites. This new technology uses visible and near infrared light, is fast, and may be a low cost alternative to X-ray imaging, at least for 1 cm thicknesses, in a number of commercially important composite systems.
- The ability of an optical fiber sensor system to use existing thermocouple ports in structural reaction injection molding equipment used by the automotive industry was demonstrated. The ability to collect data without disrupting production equipment is an important step towards more widespread use of sensors in industry.

POLYMER CHARACTERIZATION PROGRAM

- Recertification of SRM 1482, a polyethylene narrow molecular mass standard, was completed and a report issued. The standard is intended for use in calibration and performance evaluation of instruments used to determine molecular mass and its distribution by size exclusion chromatography.
- Nearly 100 different procedures for preparing samples of synthetic polymers for analysis by matrix assisted laser desorption ionization mass spectrometry (MALDI-MS) were taken from the literature and placed on the World Wide Web for use by practitioners of MALDI-MS.
- The influence of the static magnetic field on spectral resolution in ^{13}C NMR under magic angle spinning conditions was quantified and the findings reported to the NMR user community to facilitate design of experiments that optimize resolution.
- A statistical procedure was developed to characterize uncontrolled systematic errors and noise effects on Small Angle Scattering (SAS) data. Modeling studies and real data demonstrate that adequate characterization of the precision of SAS data is not possible unless both noise and systematic error are presented to the end user. This finding will provide important input into the development of standardized data reduction and data transport tools for the SAS community.
- An international round robin was initiated to study the thermoviscoelastic behavior of a research grade polycarbonate. The co-leader on the project is Prof. J.M. Hutchinson of

the Aberdeen University in Scotland with eight confirmed participants and five tentative participants. This round robin will help to resolve the fundamental issues involved in the reports from various laboratories of different (or not) fictive temperatures for different processes in glass forming liquids.

- A transition in craze growth rate under stress relaxation conditions was observed for a styrene-acrylonitrile copolymer. The logarithmic craze growth rate decreases by approximately a factor of five in going from below to above the transition aging time. If this is a universal behavior for all polymers it implies that the long term performance may be enhanced due to the aging process stabilizing the material against craze growth.
- A hybrid viscoelastic constitutive model was developed that can predict multi-step stress relaxation and creep results for polyurethane elastomers to within approximately 10% when the history is primarily one of increasing deformation or stress. This approach to nonlinear viscoelasticity will lead to simple test methods for characterizing the non-linear material parameters needed in computer simulations of, for example, blow molding processes.

DENTAL & MEDICAL MATERIALS

- The acid catalysts that bring about the desired ring-opening polymerization of spiro orthocarbonate (SOC) monomers were shown to also cause the rapid hydrolytic degradation of the monomers. The efficient competition between these two processes will affect how the SOC resins can be used as potential dental materials with minimal polymerization shrinkage.
- N-phenyliminodiacetic acid (PIDAA) was shown to be a multi-functional dental primer with the ability to etch dentin and at the same time stabilize collagen in demineralized dentin, thereby facilitating adhesive resin infiltration. In addition, PIDAA has the ability to initiate interfacial polymerization. This unique combination of properties in one adhesive agent permits the development of simplified, highly effective dental adhesive systems.
- Facile syntheses were developed for acrylic organosilsesquioxanes from readily available silane coupling agents. These reactive oligomers are readily polymerized and have potential for use in dental composites, sealants and adhesives. Other applications, e.g. in electronic packaging, that require fast-curing resins yielding polymers with high thermal stabilities and low dielectric properties also may be feasible.
- The microbond test was successfully adapted to probe adhesion to a variety of flat substrates, e.g., quartz, dentin, enamel. This new technique facilitates the evaluation of a variety of adhesive agents with diverse substrates.

TECHNICAL ACTIVITIES

ELECTRONIC PACKAGING, INTERCONNECTION AND ASSEMBLY PROGRAM

Today's U.S. microelectronics and supporting infrastructure industries are in fierce international competition to design and produce new smaller, lighter, faster, more functional electronics products more quickly and economically than ever before.

Recognizing this trend, in 1994 the NIST Materials Science and Engineering Laboratory (MSEL) began working very closely with the U.S. semiconductor packaging, electronic interconnection, assembly, and materials supply industries. These earlier efforts led to the development of an interdivisional MSEL program committed to addressing industry's most pressing materials measurement and standards issues central to the development and utilization of advanced materials and material processes within new product technologies, as outlined within leading industry roadmaps¹. The vision that accompanies this program - to be the key resource within the Federal Government for materials metrology development for commercial microelectronics manufacturing - may be realized through the following objectives:

- develop and deliver standard measurements and data
- develop and apply *in situ* measurements on materials and material assemblies having micrometer- and submicrometer-scale dimensions
- quantify and record 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

With these objectives in mind, the program presently consists of nearly twenty separate projects that examine key materials-related issues, such as: electrical, thermal, and mechanical characteristics of polymer and metal thin films; solders, solderability and solder joint design²; interfaces and adhesion; electromigration and stress voidage; and built up stress and moisture in plastic packages. These projects are always conducted in concert with partners from industrial consortia, individual companies, academia, and other government agencies. The program is strongly coupled with other microelectronics programs within government and industry, including the National Semiconductor Metrology Program (NSMP)³. The NSMP is a national resource responsible for the development and dissemination of new semiconductor measurement technology.

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

(<http://www.msel.nist.gov/epia1996/contents.htm>). Copies may be obtained by contacting Michael Schen at (301) 975-6741 or michael.schen@nist.gov.

¹ *National Technology Roadmap for Semiconductors*, Semiconductor Industry Association, San Jose, CA, 1994, 1997 (in draft); *National Technology Roadmap for Electronic Interconnections*, Institute for Interconnecting and Packaging Electronic Circuits, Lincolnwood, IL, 1995, 1997 (in draft); *National Electronics Manufacturing Technology Roadmap*, National Electronics Manufacturing Initiative, Inc., Herndon, VA, 1996.

²<http://www.ctcms.nist.gov/programs/solder>

³<http://www.eeel.nist.gov/810.01/index.html>

Significant Accomplishments

- For dielectric measurements, a coaxial sample holder has been designed and tested and measurement protocols instituted which eliminate discrepancies in the overlap regions of frequency in the several different instruments required to cover the range from DC to 1 GHz. The new holder reduces the relative measurement error in capacitance and loss at 30 MHz from 8% using a conventional four terminal holder to 0.1%. The same configuration can be used at frequencies up to 1 GHz where the relative uncertainty is about 1%. These techniques will allow the accurate measurement of dielectric constant and loss of thin film materials being evaluated for interlayer dielectrics in the microelectronics industry.
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- A new technique using twin neutron reflectivity has been developed which enables the determination of the density of thin films on many substrates including silicon wafers with a relative uncertainty of $\pm 1\%$. Density of thin films, especially in the ultra-thin range

(≤ 100 nm), provides important insights about the structure of such films that has not been previously determined with an accuracy of $\pm 1\%$.

- Using twin neutron reflectivity, the density of polystyrene thin films (10 to 100 nm thick) was found not to differ significantly from that of the bulk state. This finding is in contrast to a commonly held notion of thin film density depending on the type of substrate and film thickness. Density is an important parameter defining the structure of ultra-thin polymer films.
- Neutron reflectometry measurements confirm that polymer diffusion is impeded in an interfacial region of thickness equal to about 3 radii of gyration of the polymer away from a native oxide silicon surface. The interaction range between polymer chains and solid substrates is critical to our understanding of many technically important issues such as adhesion and lubrication.
- The thermal pulse instrumentation for measuring charge and/or polarization distribution and thermal diffusivity of thin polymer films as well as the heat transfer coefficient between film and substrate has been improved so that films as thin as 1 μm can be measured with a depth resolution of 10 nm. Thermal property data on thin films and interfaces are required for the accurate design for thermal management of the heat generated by next generation integrated circuits.
- Demonstrated that the modulus and in-plane coefficient of thermal expansion of spin-on polymer films can be deduced from measurements of the residual stress between the film and two different substrates using an instrument designed for measuring wafer bending. These data are required for the accurate modeling of reliability of packaged integrated circuits when subjected to thermal cycling.
- In April 1997, SEMATECH, the Semiconductor Research Corporation, and NIST conducted a workshop on *Interfaces and Adhesion in Electronic Packaging and Assembly* involving experts from industry, academia and government. The workshop explored new scientific opportunities for enhancing the understanding and robustness of material interfaces in semiconductor devices. As the size of microelectronic devices shrink, and their complexities increase, industry has identified material “interfaces and adhesion” as a critical area where substantial advancements within the semiconductor industry are needed.
- In October 1996, the U.S. Air Force Rome Laboratory and NIST sponsored the 6th *International Conference on Moisture in Microelectronics* at NIST’s Laboratories in Gaithersburg, MD. Drawing over ninety individuals from industry, academia and government, this workshop was held to allow researchers and engineers, in the microelectronics industry, to exchange new insights and knowledge on how moisture impacts the performance and reliability of today’s microelectronic products and packaging

materials. Moisture is universally seen as the single largest environmental factor which threatens the manufacturability and reliability of electronic packages and interconnects.

Improved Measurement Technique for Hydrothermal Expansion of Polymer Thin Films

F. I. Mopsik, C. Snyder and G. T. Davis

Objectives

The objectives are: *i.* Determine accuracy and precision of NIST-designed capacitor cell technique for measuring out-of-plane expansion of thin polymer films. *ii.* Investigate the dimensional stability of electronics packaging materials with temperature and humidity changes. *iii.* 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

Dr. Edward Shaffer of Dow Chemical Co. collaborates by preparing and supplying thin films of polymers of interest to his company which have been measured by other techniques. He will also prepare spin coated films of well-characterized polymers for studies of constrained films.

Dr. Luu Nguyen of National Semiconductor Corp. collaborates by supplying plaques of molding compound used in the measurement of expansion due to absorption of moisture.

Planned Outcomes

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

Accomplishments

- A three terminal capacitance cell has been designed and constructed of nichrome-coated fused quartz electrodes that is capable of measuring the out-of-plane coefficient of thermal expansion of films as thin as 5 μm with a relative standard uncertainty of 0.1% over a 100 $^{\circ}\text{C}$ interval for polymeric materials whose properties are sufficiently stable. This measurement technique is expected to supplement the standard test method for coefficient of thermal expansion which is inadequate for providing reliable data on the thin polymer films encountered in the design of flexible circuits and microelectronic packaging.
- The humidity chamber has been automated and the control over temperature and humidity improved beyond that as-received. A gas dryer and purge has been added to help maintain environments at less than 0.1 % relative humidity as well as help stabilize conditions at other settings.

- Measurements of both expansion and mass uptake of water were made on a cresol-novolac epoxy molding compound that has been examined by NMR in other work in this program. At 40 °C, the material expands with increasing humidity up to 60 % RH, but at a rate much smaller than implied by the bulk volume of the absorbed moisture. At 80 % relative humidity, there was a small volume contraction from the value at 60 % relative humidity even though there was an increased weight uptake of moisture. Also, the material was slowly creeping under load. Upon reduction of the humidity level, the volume was seen to expand back towards the value at 60 % relative humidity and the creep ceased. Upon increasing humidity at a constant temperature of 80 °C, the creep increased significantly starting at 40% RH so that a maximum could not be seen.
- The out-of-plane thermal expansion of a 10 μm-thick film of polybenzocyclobutene was measured. The in-plane expansions had been previously determined elsewhere. The measurements at NIST showed that the out-of-plane expansion was twice that of the in-plane expansion and therefore the film was not isotropic as originally assumed.

Thermal Properties Measurement

A. S. DeReggi and P. Bloss¹

¹University of Leipzig, Leipzig, Germany

Objective

The objective is to develop a laser pulse-based electrothermal method of measuring simultaneously: *i.* the thermal diffusivity and conductivity of dielectric films on substrates; *ii.* the thermal resistance of the interface or adhesive layer between film and substrate, and *iii.* the electric charge profile.

Technical Description

Laser pulse heating generates a pyroelectric-like response from a voltage-biased dielectric specimen that first expands inhomogeneously and then contracts to its original thickness as heat is transferred to the substrate. The electrical response depends on the thermal properties, charge profile, and thermal contact. Theoretical modeling of the problem and deconvolution of the electrical response using advanced numerical techniques allow fitting the response and determining the relevant thermal and electrical properties simultaneously.

External Collaborations

Prof. Tom Avedesian at Cornell University on an SRC-sponsored project on techniques for measuring thermal properties of materials.

Dr. E. Hartmann of the Institute of Surface Modification, Leipzig, Germany on electron beam cured nanocomposites.

Planned Outcome

- New thin film thermal and electrical metrology methods.
- Development of reference thermal properties specimens.
- Reliable thermal data on polymeric electronic packaging materials.

Accomplishments

- The thermal pulse instrumentation for measuring charge and/or polarization distribution and thermal diffusivity of thin polymer films as well as the heat transfer coefficient between film and substrate has been improved so that films as thin as 1 μm can be measured with a depth resolution of 10 nm. Thermal property data on thin films and interfaces are required for the accurate design for thermal management of the heat generated by next generation integrated circuits.
- Very sharp and strongly bound near-surface (<200 nm deep) charge layers have been discovered in several polyimide samples not previously subjected to an externally applied electric field.
- The thermal diffusivity of underfill epoxy layers containing inorganic powder additives to promote heat dissipation has been measured by the thermal pulse method in collaboration with Cornell University and the Semiconductor Research Corporation.
- Atmospheric moisture absorbed by the free surface of a polyimide film spun on a silicon substrate has been found to affect both the thermal conductivity shown by the film and the heat transfer coefficient between the film and substrate.
- The polarization profile and thermal properties of electron-beam cured, particulate nanocomposite (barium titanate in tripropylene glycol diacrylate) films were investigated in collaboration with the Institute of Surface Modification in Leipzig. The technique is used to quantify the effects of filler content and internal electric field on these radiation processed films.

Outputs

Publications

P. Bloß, A.S. DeReggi and H. Schäfer, *Simulation and experimental validation of the thermal diffusion problem in thin film planar electronics packaging materials*, Proc. Pacific Rim /ASME International Intersociety Electronic and Photonic Packaging Conference, InterPACK '97, Hawaii, USA, June, 1997, in *Advances in Electronic Packaging* EEP, 19, 2011 (1997).

P. Bloß, A.S. DeReggi and H. Schäfer, *In-situ measurements of thermal properties of dielectric films in metal-dielectric-substrate structures*, Proc. Materials Research Society, Fall 1996 Meeting, Boston, MA, December 1996.

P. Bloß, A.S. DeReggi, H. Schäfer, *Thermal properties and electric field profile in metallized dielectric film adhesively bonded to substrate*, 1996 Ann. Report Conf. on Electrical Insulation and Dielectric Phenomena (CEIDP), San Francisco, October, 1996, IEEE Pub. No. 96 CH35985, pp.721-725.

Presentations

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A.S. DeReggi, P. Bloß and H. Schäfer, *Simulation and Experimental Validation of the Thermal Diffusion Problem in Thin Film Planar Electronics Packaging Materials*, InterPack '97, Mauna Lani, HI, June 1997.

A.S. DeReggi, P. Bloß and G.T. Davis, *Investigations of Effects of Humidity on Thermal Properties of Polyimide Film on Si Wafer*, Next Generation Design Workshop, Hilton Head, SC, June 1997.

P. Bloß, A.S. DeReggi and H. Schäfer, *In-situ Measurements of Thermal Properties of Dielectric Films in Metal-Dielectric-Substrate Structures*, Materials Research Society 1996 Fall Meeting, Boston, MA, December 1996.

P. Bloß, A.S. DeReggi and H. Schäfer, *Thermal Properties and Electric Field Profile in Metallized Dielectric Film Adhesively Bonded to Substrate*, Conf. on Elec. Insul. & Dielec. Phenomena, San Francisco, CA, October 1996.

P. Bloß, *Investigations of Thin Dielectric Films by Using the Thermal Pulse Method*, Technical University Darmstadt, Darmstadt, Germany, May 21, 1997. Martin Luther University Halle/Wittenberg, Germany, June 1997.

P. Bloß, *Simultaneous Determination of Thermal and Electrical Properties of Thin Dielectric Films*, Research Center Rossendorf, Rossendorf, Germany, September 9, 1997.

Industry Coordination and Workshops in Electronic Packaging, Interconnection and Assembly

Michael Schen

Objectives

The objects are: *i.* enhance NIST's role and effectiveness in metrology for electronics packaging, interconnection and assembly by coordinating and cooperating with U.S. industry, academia and other government agencies in technology planning, infrastructure research and development, and

implementation of industry established technology roadmap priorities, *ii.* assist industry and NIST by conducting industry-led workshops to identify highest priority needs and gaps in metrology for electronic packaging and to provide a forum for the exchange of technical developments and information, *iii.* coordinate MSEL's program in electronic packaging, interconnection and assembly programs within MSEL and NIST.

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 include the following:

- 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 technology benchmarking exercises,
- 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 1997, significant coordination and workshop collaborations took place with the following organizations.

- Academia Georgia Tech, Packaging Research Center
University of Maryland, CALCE Center
- Associations Institute for Interconnecting and Packaging Electronic Circuits
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)
Plastic Packaging Consortium

- 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
NIST Advanced Technology Office
Office of Science and Technology Policy
United States Air Force, Rome Laboratory
- Standards Institute for Interconnecting and Packaging Electronic Circuits

Accomplishments

- 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 and through SEMATECH's partnerships in NIST workshop activities.
- 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 next century and in their standards activities. NIST is a member of the IPC Roadmap Steering Committee and participated substantially to their new 1997 *National Technology Roadmap for Electronic Interconnects*. NIST is also a member of the IPC's Test Methods Subcommittee (7-11) and made major contributions to enhance the quality of new IPC test methods.
- During this fiscal year, the Packaging program and the NIST Advanced Technology Program (ATP) teamed up in an effort to raise the microelectronics industry's awareness of opportunities for technology development partnerships with the NIST ATP. This consisted of numerous briefings and meetings with industry representatives at national technical conferences and workshops, and culminated in a two day workshop in which NIST facilitated industry's creation of a draft focus program white paper. As a result of these efforts, the NIST ATP is strongly considering launching a new focus program in microelectronics manufacturing in FY 1998.
- The Packaging program believes that workshops are an extremely important tool for NIST to not only understand industry's greatest needs but also to 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 the program, NIST has conducted six workshops, including in the past year:

- *Advanced Technology Workshop in Microelectronics Manufacturing*, sponsored by NIST Advanced Technology Program, July 24-25, 1997, Dallas, TX.
- In April 1997, SEMATECH, the Semiconductor Research Corporation, and NIST conducted a workshop on *Interfaces and Adhesion in Electronic Packaging and Assembly* involving experts from industry, academia and government. The workshop explored new scientific opportunities for enhancing the understanding and robustness of material interfaces in semiconductor devices. As the size of microelectronic devices shrink, and their complexities increase, industry has identified material "interfaces and adhesion" as a critical area where substantial advancements within the semiconductor industry are needed.
- NIST continues to distribute 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 and 1997 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. To date over 3000 copies have been distributed. The document is also available on the World Wide Web at <http://www.msel.nist.gov/epia1996/contents.htm>.
- NIST took a leadership role this year in reviewing and enhancing the technical quality of draft IPC test methods for moisture and insulation resistance of polymeric solder mask and conformal coatings. NIST is a member of the IPC Test Methods Subcommittee. Recent discussions between NIST and the IPC has paved the way for enhanced future involvement by NIST in the Printed Wiring Board, PWB, standards setting bodies.
- Through efforts in conjunction with the U.S. microelectronics and supporting infrastructure industries, and the NIST Advanced Technology Program (ATP), the NIST ATP is considering launching a new focused program entitled *Microelectronics Manufacturing Infrastructure Initiative*. If launched, this program will help this industry establish a systems-wide U.S. infrastructure capable of applying new, innovative technologies to electronics products well into the 21st Century.

Outputs

Publications

M.A. Schen, W. Wu, W.E. Wallace, N.C. Beck Tan, D.L. VanderHart and G.T. Davis, *Molecular Insight of Interfacial Properties and Moisture Uptake of Plastic Packaging Materials*, International Journal of Microelectronics and Electronic Packaging, **20**, No. 3 (1997).

Presentations

M.A. Schen, W. Wu, W. E. Wallace, N.C. Beck Tan, D.L. VanderHart and G.T. Davis, *Molecular Insight of Interfacial Properties and Moisture Uptake of Plastic Packaging Materials*, 3rd International Symposium on Advanced Packaging Materials, Braselton, GA, March 1997.

M.A. Schen, C. Furlani and J. Gudas, *Opportunities for Partnership with the NIST ATP*, at the following meetings and locations:

NEMI Implementation Team, Reston, VA, February 1997.

IMAPS Packaging Materials Conference, Braselton, GA, March 1997.

IPC Printed Circuits Expo 97, San Jose, CA, March 1997.

IMAPS Passive Components Conference, Braselton, GA, March 1997.

Plastic Packaging Consortium, Longmont, CO, March 1997.

University of Maryland CALCE Members Meeting, College Park, MD, March 1997.

IMAPS Multichip Module Conference, Denver, CO, April 1997.

SRC/NIST/SEMATECH Interfaces & Adhesion Workshop, Gaithersburg, MD, April 1997.

Ultra-thin Polymer Films

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

Objectives

The objectives are: *i.* Determine the role of interfaces on the properties of polymers by measuring the properties of ultra-thin polymer films adjacent to well-characterized substrates. *ii.* Compare experimental 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. Both supported polymer films with a free surface and buried layers having no free surfaces are investigated. For single-component supported films, the physical properties measured include the coefficient of thermal expansion, glass transition temperature, and density. For liquid crystal materials, the density profiles are determined and correlated with an isotropic liquid crystal transition zone near the interface. For buried polymer layers, the effects of polymer/substrate interaction on interdiffusion dynamics and interfacial segregation are measured. The aforementioned effects on interdiffusion can be examined under the influence of shear

displacement. A new technique, total reflection-x-ray fluorescence, has been introduced to characterize the surface roughness of thin films. This technique complements existing method that uses a combination of off-specular reflectivity and atomic force microscopy for surface roughness characterization. Typical materials considered include polystyrene, poly(methyl methacrylate), poly(vinyl pyridine), polyimides, and epoxies. By varying the film thickness, the type of polymer, its molecular mass, the sample temperature and environment and the film substrate surface, fundamental physical insight is gained into the behavior of polymer molecules adjacent to substrates. The experimental results are compared with self-consistent mean field calculations to build a theoretical framework for future predictions of polymer film properties. Another new technique, twin neutron reflectivity, has been developed to aid in measuring the subtle properties of polymer thin films.

External Collaborations

H.C. Liou of Dow Corning collaborates on density profile and coefficient of thermal expansion of spin-on glasses.

Dr. Barry Arkles of Gelest, Inc. and Professors Russ Composto and Don Berry of the University of Pennsylvania collaborate by preparing beta-chloroethyl-polysilsesquioxane and converting it to spin-on glass by UV irradiation. Composition and density of the resultant glass is determined by x-ray reflectivity at NIST.

Prof. Mark Dadmun and Gary Lin of the University of Tennessee collaborate on the effect of interfaces on phase transitions in liquid crystals.

Dr. N.C. Beck Tan of the Army Research Laboratory collaborates on studies of the composition of epoxy resins at a silica interface as determined by inelastic neutron scattering.

Dr. Michael Kent of Sandia National Laboratories collaborates on the measurement of moisture at an epoxy/silica interface using deuterated water and inelastic neutron scattering.

Accomplishments

- A new technique using twin neutron reflectivity has been developed at NIST which enables the determination of the density of thin films on many substrates including silicon wafers with a relative uncertainty of $\pm 1\%$. Density of thin films, especially in the ultra-thin range (≤ 100 nm), provides important insights about the structure of such films that has not been previously determined with an accuracy of $\pm 1\%$.
- Using twin neutron reflectivity, the density of polystyrene thin films (10 to 100 nm thick) was found not to differ significantly from that of the bulk state. This finding is in contrast to a commonly held notion of thin film density depending on the type of substrate and film thickness. Density is an important parameter defining the structure of ultra-thin polymer films.
- Neutron reflectometry measurements confirm that polymer diffusion is impeded in an interfacial region of thickness equal to about 3 radii of gyration of the polymer away from a native oxide silicon surface. The interaction range between polymer chains and solid substrates is critical to our understanding of many technically important issues such as adhesion and lubrication.

- Density profile and coefficient of thermal expansion (CTE) of ultra-thin (~100 nm) spin-on glass films have been determined by x-ray reflectivity and reported in collaboration with Dow-Corning Corp. Spin-on glass film is a primary candidate for interlayer dielectrics in future multi-level chips. Density profile and CTE are critical data needed for chip design and are not accessible with any other conventional measurement techniques.
- A total reflection x-ray fluorescence technique has been developed to measure the surface micro-roughness of thin polymer films with a detection sensitivity surpassing that of AFM for micro-roughness with a lateral correlation length less than ~100 nm.
- The composition and density of a novel spin-on glass, β -chloroethyl silsesquioxane, has been measured as a function of processing temperatures and UV radiation exposure in conjunction with Gelest, Inc. and University of Pennsylvania.

Outputs

Publications

N.C. Stoffel, C.A. Dai, E.J. Kramer, T.P. Russel, V. Deline, W. Volksen, W.L. Wu and S. Satija, *High Resolution Profiling of the Polyimide/Polyimide Interface*, *Macromolecules*, **29**, 6880 (1996).

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*, **38**, 2583 (1997).

N.C. Beck Tan, W.L. Wu, W.E. Wallace, G.T. Davis, *Interface Effects on Moisture Absorption in Ultrathin Polymeric Films*, *J. Polym. Sci., Poly. Phys.*, in press.

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E.K. Lin, W.L. Wu and S.K. Satija, *Measuring Polymer Dynamics Near the Polymer-Solid Interface using Neutron Reflectometry*, *Proc. American Chemical Society PMSE* **77**, 626 (1997).

N.C. Beck Tan, B.J. Bauer, J. Plestil, J.D. Barnes, D. Liu, L. Matejka, K. Dusek and W.L. Wu *Epoxy Network Structure. 7. Small Angle X-ray Scattering from Bimodal Networks*, *Macromolecules*, submitted.

W.L. Wu and H.C. Liou, *Study of Ultra-thin Hydrogen Silsesquioxane Films Using X-ray Reflectivity*, *Thin Solid Films*, in press.

W.L. Wu and W.E. Wallace, *Microroughness of Polymer Thin Films Studied by Total Reflection X-ray Fluorescence*, *J. Appl. Phys.*, submitted.

W.E. Wallace, N.C. Beck Tan and W.L. Wu, *Mass Density of Polystyrene Thin Films Measured by Twin Neutron Reflectivity*, J. Chem. Phys., submitted.

Presentations

W.L. Wu, *Thermal Properties of Polymer Thin Films*, American Chemical Society Workshop on Polymer Surfaces and Interfaces, Tampa, FL, October 1996.

W.L. Wu, *Off-specular X-ray Reflectivity of Polymer Thin Films*, American Physical Society March Meeting, Kansas City, MO, March 1997.

W.L. Wu, *Diffusion of Polymer Chains near An Attractive Surface*, American Crystallographic Association Meeting, St. Louis, MO, July 1997.

W.L. Wu, *Microroughness of Polymer Coatings Using AFM and Grazing Angle X-ray Fluorescence*, International Society for Optical Engineering Meeting, San Diego, CA, July 1997.

W.L. Wu, *Moisture Detection in Plastic Packaging Materials*, IMAPS Meeting, Washington Chapter, Columbia, MD, September 1997.

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W.E. Wallace, *Toward Improved Thin Film Density Measurements: Novel Applications of X-ray and Neutron reflectivity*, Materials Research Society Meeting, San Francisco, CA, April 1997.

W.E. Wallace, *Applications of X-ray and Neutron Reflectivity to Microelectronics*, Intel Corp. Santa Clara, CA, April 1997.

W.E. Wallace, *Novel Applications of X-ray Reflectivity to Thin Films*, SRC/NIST/SEMATECH Workshop on Interface and Adhesion in Electronics Packaging and Assembly, Gaithersburg, MD, April 1997.

E.K. Lin, *Neutron Reflectivity Study of Polymer Dynamics near an Attractive Surface*, American Chemical Society Workshop on Polymer Surfaces and Interfaces, Tampa, FL, October 1996.

E.K. Lin, *Polymer Interdiffusion near an Attractive Surface*, American Physical Society March Meeting, Kansas City, MO, March 1997.

E.K. Lin, *Measuring Polymer Dynamics near The Polymer-Solid Interface*, American Chemical Society, Las Vegas, NV, September, 1997.

Dielectric Measurements of Thin Films from DC to 1 GHz

F. I. Mopsik

Objective

The objective is to establish measurement protocols and sample configurations for the accurate determination of dielectric constant and loss for frequencies from DC to 1 GHz suitable for thin polymeric films of importance to the electronic packaging industry.

Technical Description

Commercially available Inductance-Capacitance-Resistance Bridges (LCR meters) are designed for accurate measurements over discrete ranges of frequencies with constraints on the sample configuration. 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 regions of overlap and extend the frequency range beyond that of a particular LCR meter. Sample configurations and data reduction methods will be developed to optimize the measurements.

Planned Outcomes

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 should provide consistent results for both producers and users of polymeric resins used in electronic packaging. Current standards are primarily in the lower frequency ranges.

Accomplishments

- A 30 MHz LCR meter was repaired and recalibrated. Comparison with previous measurements on a variety of standards established that a relative accuracy of up to 0.1%, as measured directly at its terminals is possible.
- Reproducibility from sample to sample taken from the same polypropylene sheet is within 1%. This includes all sources, including sample variation, variations in metallization geometry and sample insertion. The film was completely metallized on one side and a circular sample punched out followed by evaporating metal through a mask creating a central 5 mm spot on the other side.
- For dielectric measurements, a coaxial sample holder has been designed and tested and measurement protocols instituted which eliminate discrepancies in the overlap regions of frequency in the several different instruments required to cover the range from DC to 1 GHz. The new holder reduces the measurement error in capacitance and loss at 30 MHz from 8% using a conventional four terminal holder to 0.1%. The same configuration can be used at frequencies up to 1 GHz where the uncertainty is about 1%. These techniques will allow the accurate measurement of dielectric constant and loss of thin film materials being evaluated for interlayer dielectrics in the microelectronics industry.

Publications

F. I. Mopsik, *Low Frequency Dielectric Sensing*, in Sensing for Materials Characterization, Processing, and Manufacturing, G. Birnbaum and B.A. Auld, eds., American Society of Nondestructive Testing, to appear December, 1997.

R. Zorn, F.I. Mopsik, G.B. McKenna, L. Willner and D. Richter, *Dynamics of Polybutadienes with Different Microstructures. 2. Dielectric Response and Comparisons with Rheological Behavior*, J. Chem. Phys. **107**, 3645 (1997).

Residual Stress in Polymer Films Adhered to Silicon Substrates

C. K. Chiang, A. S. DeReggi and G. T. Davis

Objectives

The objectives are: *i.* Evaluate wafer bow technique for deducing the residual stress in polymer-coated silicon wafers resulting from differential contraction after cure. *ii.* Develop the stress measurement as a thin-film characterization method.

Technical Description

Differences in coefficient of thermal expansion, CTE, between two materials can lead to interfacial stress when subjected to temperature changes and these regions of high stress often lead to delamination. A common example is the cooling of a polymer coating processed at high temperature adhered to a lower CTE substrate such as silicon. A measure of interfacial stress is obtained using a commercial instrument which measures the angle of reflection of a laser beam from a wafer as it is scanned along the wafer diameter. From the reflection angles, a radius of curvature is calculated and used in the Stoney equation to deduce the stress on the wafer. In addition to information about the residual stress between a wafer and a thin film coating, the wafer bow technique can be used to obtain estimates of the coefficient of thermal expansion and modulus of constrained polymeric coatings. This can be achieved by preparing identical films on two or more substrates with differing thermal and mechanical properties and measuring the temperature dependence of the stress deduced from wafer curvature. For this purpose, silicon wafers were used in crystal orientation $\langle 110 \rangle$ and $\langle 111 \rangle$ which have slightly different biaxial moduli together with GaAs wafers for which both the CTE and modulus differ from that of silicon. The procedure was originally used for investigating the properties of refractory films by Retajczyk and Sinha, (Appl. Phys. Letters **36** 162 (1980)).

External Collaborations

Dr. David Feiler and Dr. Wei Xia of Rockwell Semiconductor Systems have been collaborating on the effect of processing conditions on the stress between silicon and spin-on glasses.

Dr. David Babb of Dow Chemical Co. in Freeport, TX and Drs. Edward O. Shaffer and Jay Im in Midland, MI have been collaborating on the properties and resultant residual stress of spin-on polymer films.

Accomplishments

- Contour maps of stress on a wafer coated with spin-on glass reveal that measurements taken from the coated side show a much wider variation in calculated stress and a less uniform distribution of stress than measurements taken from the uncoated side. (Properly integrated average stress over the whole wafer is not calculated at present.) This wider variation is attributed to the quality of the film and its influence on the position of the reflected laser probe beam. Since the polymer precursor is in liquid form, data for the initial heating must be obtained with the coated side of the wafer “up” and hence reflection occurs after passing through the coating.
- Demonstrated that the modulus and in-plane coefficient of thermal expansion of spin-on polymer films can be deduced from measurements of the residual stress between the film and two different substrates using an instrument designed for measuring wafer bending. These data are required for the accurate modeling of reliability of packaged integrated circuits when subjected to thermal cycling.

Outputs

Presentations

C.K. Chiang and A.S. DeReggi, *Investigation of Thermomechanical and Viscoelastic Phenomena in the Curing of Rigid-Rod Polyimide Thin Films*, American Physical Society March Meeting, Kansas City, MO, March 1997.

C.K. Chiang, A.S. DeReggi, G.T. Davis and D.A. Babb, *Residual Stress Measurement of Perfluorocyclobutane Aromatic Ether Polymer Thin Film on Silicon*, Materials Research Society, Boston, MA, December 1997.

Moisture Effects in Electronic Packaging Polymers

M.A. Schen, D.L. VanderHart and G.T. Davis

Objective

The objective is to develop metrology that will document the effect of moisture on the reliability performance characteristics of industrially important plastics used in electronic packagings.

Technical Approach

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 effect 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.

Solid state proton NMR is being used to characterize the quantity and physical state of moisture absorbed by a polymeric molding compound under a variety of humid or wet environments. The NMR spectrum due to moisture is obtained by subtracting that arising from the molding compound in the dry state and the physical state of the moisture is deduced from the width of the resonance lines. Liquid-like water, giving rise to very narrow spectra indicative of high mobility, is presumed to be located within voids in the material while less mobile moisture characterized by a broad resonance peak is presumed to be hydrogen-bonded to the matrix or filler particles.

External Collaborations

Dr. Luu Nguyen of National Semiconductor Corp. has supplied plaques of cured molding compound for this investigation. Results have been regularly communicated to members of 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 and Leading Technology Corp.)

Planned Outcomes

Provide industry with convenient metrology tools to examine moisture ingress into mold compounds on a molecular scale, rather than simple mass uptake. Provide experimental data which will enable evaluation of the appropriateness of commonly used conditioning treatments for the accelerated testing of moisture sensitivity of mold compounds. NIST will work with standards bodies, such as The Institute for Interconnecting and Packaging Electronic Circuits and the Joint Electronic Devices Engineering Council, and individual companies to refine current practices and standards.

Accomplishments

Previously, it was concluded that liquid-like water was present in the cresol-novolac molding compound only after immersion for long times in liquid water. Exposure to humid environments as high as 89% RH at 29 °C for 50 d resulted only in moisture bound to the matrix or filler particles. More recently, the same samples were exposed to conditions simulating the highly accelerated stress test, periods of 3 d to several weeks at 100% RH and 121 °C in a sealed glass tube. After such extreme conditions, the samples, when quickly returned to room temperature and removed from the sealed tube, exhibited water levels in the matrix comparable to levels in the sample immersed in water. However, there was no evidence for liquid-like water which is associated with condensation within voids in the material. Unfortunately, the NMR measurements cannot be made on the resin while exposed to a saturated environment at 121 °C. This means the analysis does not necessarily capture the state of or distribution of water under the aging conditions. For example, water could have been in the voids before decompression and temperature reduction but a major distribution of water may have taken place during the cooling and decompression. In addition, there may have been water loss or gain depending upon the change in equilibrium uptake at 100% RH at 121 °C versus 23 °C. Also, transient departures from 100% RH during cooling and decompression may have caused some water loss. By cooling

and decompressing on a time scale of a few minutes, it may be possible to minimize these latter effects, but it is impossible to ascertain that they've been eliminated.

Outputs

Publications

D.L. VanderHart, M.A. Schen and G.T. Davis, *Partitioning of Water between Voids and the Polymer Matrix in a Molding Compound by Proton NMR*, 6th International Workshop on Moisture in Microelectronics, Gaithersburg, MD, NISTIR, in press.

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Presentations

M.A. Schen, W. Wu, W.E. Wallace, N.C. Beck Tan, D.L. VanderHart and G.T. Davis, *Molecular Insight of Interfacial Properties and Moisture Uptake of Plastic Packaging Materials*, 3rd International Symposium on Advanced Packaging Materials, Braselton, GA, March 1997.

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G.T. Davis and B. Dickens, *Near Infrared Spectroscopy Examination of Water in Polyimide*, 6th International Workshop on Moisture in Microelectronics, Gaithersburg, MD, October 1996.

Interfacial Energy between Solids

W. Wu, R. Kolb¹ and G.T. Davis

¹ University of Hamburg, Hamburg, Germany

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 an interface. The JKR technique has been demonstrated to be 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 completed to automate the data acquisition process. In addition, the instrument has been modified to allow the measurements to be conducted in a controlled humidity environment and a program to study the humidity effects on adhesion has been initiated.

External Collaboration

Rainer Kolb from the University of Hamburg recently joined us to continue the work of Pearl Chin who 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

- Automation has been completed to enable the simultaneous acquisition of contact area and displacement.
- Humidity control capability has been added to the instrument so that the effect of humidity on adhesion can be studied.

Outputs

Publications

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, in press.

Aging of Light Emitting Polymers

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

Objective

The objective is to determine physical and/or chemical changes which correlate with the loss of electroluminescent intensity from polymeric light emitting devices.

Technical Description

One of the major barriers to the commercial development of light emitting devices based upon electroluminescent polymers is their useful lifetime. Others have shown that the lifetime of some such devices can be greatly extended by operating in an inert environment under dry box conditions. However, even under ideal conditions, the light intensity gradually decreases and some discrete regions become totally dark. Investigations are underway to determine the location and nature of the changes responsible for the loss of intensity with time and the origins of the dark spots. AC impedance measurements over a wide range of frequency are conducted and interpreted in terms of bulk and interface properties as a device ages. Optical microscopy as well as SEM and AFM are employed to examine device morphology and its influence on device performance. Photoluminescent spectra from the polymer are also followed as the device ages.

External Collaborations

Prof. Frank Karasz, Dr. Bin Hu and students at the University of Massachusetts, Amherst, MA collaborate by synthesizing and supplying electroluminescent polymers and preparing some of the polymeric light emitting devices used in the study.

Prof. Alan Heeger of the Uniax Corporation, Santa Barbara, CA has collaborated by supplying samples of polymer LEDs before and after subjecting to accelerated aging conditions.

Accomplishments

- An only partially reversible decrease in photoluminescent intensity from a film of poly[1,8-octanedioxy-2,6-dimethoxy-1,4-phenylene-1,2-ethenylene-1,4-phenylene-1,2-ethenylene-1,4-phenylene-1,2-ethenylene-3,5-dimethoxy-1,4-phenylene] (referred to as POPV3P) was observed following the deposition of about 2 nm of gold. This can be interpreted as due to the formation of interfacial electronic states resulting in the creation of quenching centers and the subsequent loss of electroluminescent intensity in a light emitting device.
- AC impedance spectroscopy from 0.1 Hz to 10 MHz performed on devices made from poly[2-methoxy-5-{2'-ethyl-hexyloxy}-1,4 phenylene vinylene] (referred to as MEH-PPV) both before and after subjecting to accelerated aging conditions reveal two clearly defined arcs when the out-of-phase component of impedance is plotted against the in-phase component (Cole-Cole plot). Upon aging, the smaller, high frequency arc with an impedance of about 15 Ω is unchanged while the larger arc at low frequency increases from 125 Ω to 1285 Ω . These results are interpreted to indicate that the electrical properties of the polymer remain essentially unchanged, but the impedance of the interface between polymer and metal cathode has greatly increased.
- A reflectance microscope has been adapted with a CCD imaging system, an excitation light source and optical filters to facilitate studies of electroluminescence and photoluminescence from highly localized regions of a polymer light emitting device.

Outputs

Publication

E.E. Etedgui, G.T. Davis, B. Hu and F.E. Karasz, *Degradation of Polymer Based Light Emitting Diodes during Operation*, Synthetic Metals, 90-73 (1997).

Presentations

C.K. Chiang, E.E. Etedgui, G.T. Davis, B. Hu and F.E. Karasz, *AC Impedance Spectroscopy of Light-Emitting Diodes*, Materials Research Society Meeting, San Francisco, CA, April 1997.

E.E. Etedgui, G.T. Davis, B. Hu and F.E. Karasz, *Evolution of the Optical Properties of Conjugated Polymers Following Metal Deposition*, Materials Research Society Meeting, San Francisco, CA, April 1997.

E. E. Schuppert, Jr. (1911-1987) was a prominent American architect and educator. He was born in St. Louis, Missouri, and graduated from the University of Missouri in 1933. He worked for the architectural firm of Skidmore, OWing, Merrill & Knapp (SOM) in New York City, where he became a partner in 1948. He was also a professor at the University of Missouri and the University of Illinois at Chicago. He is best known for his design of the Federal Reserve Bank Building in St. Louis, which is a prime example of modernist architecture. He also designed the St. Louis Convention Center and the St. Louis Gateway Arch. He died in St. Louis in 1987.

POLYMER BLENDS AND PROCESSING PROGRAM

Applications of polymer blends and multiphase polymer materials 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 more precise definition of material 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 additives 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: (1) measurement technology for on-line characterization of temperature, phase behavior, and shear deformation; (2) shear effects on phase diagrams and phase morphology; (3) activity of additives, compatibilizers, and fillers; and (4) 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. Industrial collaborators include: Aristech Chemical, Dendritech, DSM, 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 also promotes initiatives which cut across research projects to improve opportunities for industrial collaborators to use NIST measurement capabilities.

Significant Accomplishments

- The capability of NIST-developed on-line instrumentation, using light scattering and optical microscopy to measure *in-situ* domain size and shape during extrusion of incompatible and reactively compatibilized blends was demonstrated. In addition to morphology studies, the instrumentation can measure velocity profiles and characterize multiphase mixing. Industrial partners including 3M and Rohm & Haas have begun work using this instrument to investigate effects of polymer processing aids.
- NIST's on-line microscopy extruder instrument has revealed new droplet morphologies in the high shear stress regime which are tentatively attributed to normal forces. For two component systems, with a high viscosity ratio, droplets with negative surface curvature or structures elongated orthogonal to the flow direction, were observed. This result demonstrates the power of on-line measurements to complement typical post processing studies.
- In collaboration with Packard Electric, the determination of specific changes in the spectrum of a fluorescent probe provided simultaneous measurement of temperature and crosslinking in a polyethylene/polyvinyl acetate copolymer. This measurement can be used to control and monitor continuous extrusion of wire insulation during which crosslinking is activated by raising the temperature in the later stages of processing. During the early stages of the extrusion, limited crosslinking is allowed so that the rheology remains uniform.
- Dendrimer molecules of divergent types have been characterized with a combination of small angle neutron scattering, small angle x-ray scattering, and transmission electron microscopy. Four critical observations arise from the solution characterization which contrast dendrimers with other classes of polymers: Dendrimers are spherical in shape and have a narrow size distribution even at relatively low molecular mass; the segment density distribution profile is nearly uniform within the dendrimer; the terminal units of the dendrimer are located within a relatively narrow shell toward the periphery of the molecule; and with increasing concentration the dendrimers appear to collapse and pack in a random close packing arrangement with little interpenetration. These characteristics suggest possible applications as size and molecular mass calibration standards for SANS, SAXS, TEM, AFM, MALDI, SEC, and filtration.
- Measurements on thin film blends have established that nucleation and growth at the late stage of phase separation is dominated by a coalescence mechanism rather than by Ostwald ripening. Studies by bulk scattering techniques are not able to distinguish between coalescence mechanisms and Ostwald ripening because the time dependence is identical.
- A combination of time resolved light scattering and video microscopy together with transmission electron microscopy was used to observe the influence of block copolymer additives on phase separation kinetics and morphology development. A new compatibilization mechanism via the break-up of discrete domains in the late stage of spinodal decomposition was seen. We believe that this mechanism is responsible for some of the properties of compatibilized polymer blends which could now be tailored by process design.

- In collaboration with Exxon, large pressure induced demixing in metallocene polyolefin blends was demonstrated through optical cloud point measurements. The observed linear dependence of the demixing temperature on pressure is $0.24 \text{ }^{\circ}\text{C}/\text{MPa}$. High pressures are typical in most polymer processing, including polyolefins, and the strong dependence on pressure will greatly shift phase boundaries.
- Dynamic and steady shear viscoelastic properties of elastomer blends were correlated with the domain structure observed in shear mixing experiments with light scattering and optical microscopy. These correlations provide understanding and guidance for elastomer mixing and milling processes.
- The equilibrium and non-equilibrium phase behavior of a series of blends containing varying amounts of hydrogen bonding components were studied by small angle neutron scattering. Results can be explained by a two length scale model, with a thermal fluctuation length and a chemical barrier length due to the hydrogen bonding. This system has a fractal microstructure during phase separation and consequently should exhibit low or zero shrinkage.
- NIST hosted a three day joint scientific workshop with the Hashimoto Phasing Project of the Exploratory Research and Technology Organization (ERATO) of Japan, which was attended by over 65 representatives of U.S. industry, ERATO, and NIST. In addition to further developing the scientific interactions between these two research groups, the workshop provided U.S. industrial researchers a direct view of the ERATO-supported project.

Phase Behavior and Pair Interaction Parameters in Polymer Blends

C. C. Han, S. Kim¹, H. Jeon², C. Jackson, J. F. Douglas, B. Lee and S. Glotzer

¹University of Wisconsin, Madison, Wisconsin

²Polytechnic University, Brooklyn, New York

Objectives

The objectives are to develop techniques and methods to characterize phase behavior and interaction parameters of polymer blends and to provide measurements and data in support of other activities of the program.

Technical Description

Characterize the flow effect on multi-phase polymer blends at high shear rates and study the relationship between viscoelastic response of the phase morphology and the flow instability or the possibility of re-entrant of phase separation at higher shear rate.

- Investigate the influence of block copolymer additives on the phase stability and kinetics of phase separation by correlating time dependent light scattering and video microscopy results.
- Study effects of copolymer additives on the static phase diagrams and on the enhanced composition fluctuations.

External Collaborators

- R. Stadler, University of Bayreuth, Bayreuth, Germany - Collaboration and supply of polycaprolactone (PCL) and PCL block polymers.

Accomplishments

- A combination of time resolved light scattering and video microscopy together with transmission electron microscopy was used to observe the influence of block copolymer additives on phase separation kinetics and morphology development. A new compatibilization mechanism via the break-up of discrete domains in the late stage of spinodal decomposition was seen. We believe that this mechanism is responsible for some of the properties of compatibilized polymer blends which could now be tailored by process design.
- At fixed molecular mass of copolymer additives, the temperature dependence of thermodynamic properties, such as susceptibility and correlation length, becomes weaker (or smaller) as copolymer concentration increases. Also, deviation from mean-field scaling behavior (for a typical binary polymer blend) becomes greater.

Outputs

Publications

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S.A. Langer and S.C. Glotzer, *Morphogenesis in Liquid Crystal/Polymer Blends: Theory and Simulation*, CPIP '96 Conf. Proceedings, Pattern Formation in Fluids and Materials, Physica A, in press.

S.C. Glotzer and S.A. Langer, *Morphogenesis in Liquid Crystal/Polymer Blends*, Proc. from International Conference on Pattern Formation in Polymers, in press.

Presentations

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C.L. Jackson, L. Sung and C.C. Han, *Morphology Evolution and Phase Separation Kinetics in a Polymer Blend with Diblock Copolymer Additive*, NIST-ERATO Joint Meeting on "Multicomponent Polymers and Polyelectrolytes", NIST, Gaithersburg, MD, June 1997.

C.C. Han, J.-W. Yu, S. Kim, E.K. Hobbie and J.F. Douglas, *Homogenization of Polymer Blends by Shear Flow*, American Physical Society March Meeting, Kansas City, MO, March 1997.

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C.L. Jackson, *Surface Topology and Organization of Single Crystals from Polystyrene-Polycaprolactone (PS-*b*-PCL) and PS-Polybutadiene-PCL (PS-*b*-PB-*b*-PCL) Block Copolymers*, American Chemical Society, Las Vegas, NV, September 1997.

Structure Formation by Shear in Polymer Blends

C. C. Han, S. Kim¹, J.-W. Yu¹, H. Jeon², D. Johnsonbaugh; A. I. Nakatani, E. K. Hobbie³ and J. F. Douglas

¹University of Wisconsin, Madison, Wisconsin

²Polytechnic University, Brooklyn, New York

³University of Pennsylvania, Philadelphia, Pennsylvania

Objective

The objective is to develop the framework for controlling polymer blend morphology as a function of shear rate and compatibilizer concentration and, working in collaboration with industry, demonstrate application of characterization methods to determine parameters for specific systems.

Technical Description

- Determine the compatibilization effect on polymer blends by the corresponding block copolymers under shear flow by the small angle neutron scattering measurement.
- Characterize the structure change of polymer blends by combined time resolved light scattering and video microscopy techniques.
- Investigate the shear mixing, structural change and flow instability of polymer blends which possess a strong elastic effect.

External Collaborators

- Exxon Research and Eng. Co. - Collaboration and supply of polyolefins for shear mixing and morphology studies.
- Goodyear Rubber and Tire Co. - Collaboration and supply of polybutadienes and polyisoprenes of various microstructure for the elastomer blend study.
- Nagoya University - Examination of shear behavior of block copolymer solutions by SANS.
- Kyoto Institute of Technology - Examination of phase behavior of labeled polystyrene/poly(vinyl methyl ether) blends as a function of the isomeric state of the label.

Accomplishments

- Shear induced mixing of low vinyl polybutadiene/low vinyl polyisoprene LCST blends (LPB/LPI) and low vinyl polybutadiene/high vinyl polyisoprene UCST (LPB/HPI) blends demonstrates a change of droplet aspect ratio as a function of shear rate. This change was related to a shift of the phase diagram.
- Dynamic and steady shear viscoelastic properties of elastomer blends were correlated with the domain structure observed in shear mixing experiments with light scattering and optical microscopy. These correlations provide understanding and guidance for elastomer mixing and milling processes.
- The relationship between the structural change of two-phase elastomer blends under shear (droplet deformation, breaking, elongation, homogenization and instability) was compared and correlated with the corresponding steady state and dynamic rheological properties.
- SANS experiments on two types of samples, PSD/PB/PSD-PB and PSH/PB/PSD-PB, were performed as a function of shear rate, temperature and copolymer concentration. It has been shown that copolymers act to enhance miscibility, at low concentrations of copolymer, with and without the application of shear. Above a certain copolymer concentration, the copolymer destabilizes the single phase region during shear. In the quiescent state, the miscible region is expanded compared to the blend without copolymer.

Outputs

Publications

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Y. Takahashi, S. Kitade, N. Ochiai, I. Noda, Y. Matsushita, M. Imai, A.I. Nakatani, H. Kim and C.C. Han, *Order-Disorder Transition of Symmetric Styrene-2-Vinylpyridine Diblock Copolymers in Melts and Solutions*, Polymer Journal (Japan), submitted.

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S. Kim, E.K. Hobbie, J.-W. Yu and C.C. Han, *Droplet Breakup and Shear-Induced Mixing in Critical Polymer Blends*, Macromolecules, submitted.

S. Kim, E.K. Hobbie, J.-W. Yu and C.C. Han, *Pattern Formation and Scaling in Critical Polymer Mixtures Under Simple Shear Flow*, Proceedings of International Conference on the Morphology and Kinetics of Phase Separating Complex Fluids, Messina, Italy (to be published in Il Nuovo Cimento D).

Presentations

A.I. Nakatani, *Phase Behavior of Compatibilized Blends During Shear*, University of Wisconsin, Department of Chemistry, November 1996.

A.I. Nakatani, *SANS of Compatibilized Blends During Shear*, Gordon Research Conference Polymers (West), Ventura, CA, January 1997.

A.I. Nakatani, *SANS of Compatibilized Polymer Blends During Shear*, NIST-ERATO Joint Meeting on "Multicomponent Polymers and Polyelectrolytes", NIST, Gaithersburg, MD, June 1997.

A.I. Nakatani, *Small Angle Neutron Scattering of Polymer Blends Under Shear*, NIST- ERATO Joint Meeting on "Multicomponent Polymers and Polyelectrolytes", NIST, Gaithersburg, MD, June 1997.

S. Kim, E.K. Hobbie, J.-W. Yu and C.C. Han, *Droplet Breakup and Shear-Induced Mixing in Critical Polymer Blends*, NIST-ERATO Joint Meeting on "Multicomponent Polymers and Polyelectrolytes", NIST, Gaithersburg, MD, June 1997.

E.K. Hobbie, *Pattern Formation And Scaling in Critical Polymer Mixtures Under Simple Shear Flow*, Dept. of Physics, University of Pennsylvania, October 1996.

C.C. Han, *Homogenization and Critical Temperature Shift of Polymer Blends Under Shear Flow*, Materials Research Society, San Francisco, CA, April 1997.

C.C. Han, *Morphology of Two-Phase Polymer Mixture Under Shear Flow*, NIST Workshop on Characterization and Modeling of the Polymer/Polymer Interface/ Interphase Region, June 1997.

C.C. Han, S. Kim, E.K. Hobbie, J.-W. Yu, *Pattern Formation and Scaling in Critical Polymer Mixtures Under Simple Shear Flow*, International Conference on The Morphology and Kinetics of Phase Separating Complex Fluids, Messina, Italy, June 1997.

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C.C. Han, *Morphology of Two Phase Blends Under Shear Flow*, Gordon Research Conference on Elastomers, Networks and Gels, July 1997.

C.C. Han, *Critical Scaling and Pattern Formation of Polymer Blends Under Shear Flow*, International Workshop on Structure and Dynamics of Complex Fluids Under Shear Flow, Max-Planck-Institute for Polymer Research, Mainz, Germany, September 1997.

On-Line Morphological Characterization of Polymer Blends

K. Migler, E. Hobbie¹, B. Bauer, D.-W. Liu, D. Johnsonbaugh, C. Han and E. Amis

¹University of Pennsylvania, Philadelphia, Pennsylvania

Objective

The objective is to demonstrate effectiveness of light scattering and phase contrast microscopy measurements of polymer blend morphology and flow profiles for on-line characterization of processing in a slit-die extruder.

Technical Description

- An extrusion slit die with optical access for *in-situ* microscopy and light scattering enables measurement of polymer blend morphology and polymer flow profiles.
- Optical microscopy permits measurements of structures in the 2 μm to 200 μm range while light scattering can measure structures at length scales down to 0.1 μm .
- Identify key processing variables in the control of material structure. Examine the influence of processing on the development of morphology for representative classes of polymer blends.
- Demonstrate the ability to measure polymer flow profiles across the slit die using particle tracing microscopy.
- Measure real time changes in domain size during reactive extrusion.
- Measure the effects of strong shear stress on domain shape and size.

External Collaborations

- 3M - velocity profile measurements with polymer processing additives
- Rohm & Haas - velocity profile measurements with polymer processing additives
- Exxon Research and Engineering Co. - morphology of polyolefin blends during extrusion

Accomplishments

- The capability of NIST-developed on-line instrumentation, using light scattering and optical microscopy to measure *in-situ* domain size and shape during extrusion of incompatible and reactively compatibilized blends was demonstrated. In addition to morphology studies, the instrumentation can measure velocity profiles and characterize multiphase mixing. Industrial partners including 3M and Rohm & Haas have begun work using this instrument to investigate effects of polymer processing aids.
- Direct measurement of flow profiles in a slit die during extrusion, including transition from Poiseuille flow to plug flow, as a function of mass flow.
- Light scattering measurements during reactive extrusion show dramatic reduction in domain size and ellipticity due to decrease of blend interfacial tension.
- NIST's on-line microscopy extruder instrument has revealed new droplet morphologies in the high shear stress regime which are tentatively attributed to normal forces. For two component systems, with a high viscosity ratio, droplets with negative surface curvature or structures elongated orthogonal to the flow direction, were observed. This result demonstrates the power of on-line measurements to complement typical post processing studies.
- Direct observation of coarsening in dilute uncompatibilized blend following cessation of flow during extrusion.
- *In-situ* measurement of the dramatic change in domain size and elongation as a function of distance to the wall utilizing light scattering in conjunction with a purge - feed technique. Correlation of this effect with independently measured flow profile, provides a physical understanding of the skin-core effect.

Outputs

Publications

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E.K. Hobbie, K.B. Migler, C.C. Han and E.J. Amis, *Light Scattering and Optical Microscopy as in-line Probes of Polymer Blend Extrusion*, Advances in Polymer Technology, in press.

Presentations

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E.K. Hobbie, *Droplet Coalescence and Coarsening in Extruded Polymer Blends*, 71st American Chemical Society Colloid and Surface Science Symposium, University of Delaware, July 1997.

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Fluorescence Monitoring of Polymer Processing

A. Bur, K. Migler, S. Roth, J. Gruber and E. Amis

Objectives

The objectives are to develop sensors based on optical and fluorescence measuring techniques for monitoring important polymer processing parameters, such as temperature, temperature gradients, pressure, strain rate and molecular orientation and to develop models describing sensor behavior.

Technical Description

- Methods use fluorescent dyes which exhibit changes in their spectrum with temperature and pressure and which orient with applied stress.
- Dye spectra are analyzed using statistical methods in order to establish correlations with temperature and pressure and to support model descriptions of dye behavior.
- Sensors are designed to fit into standard instrument ports in processing machines.
- A temperature profile sensor employs confocal optics in order to isolate the point of measurement and yields a temperature profile by scanning the point of focus through the resin.
- A fluorescence anisotropy sensor containing polarizing optics is used to measure molecular orientation.

- Ultrasonic sensors are also being developed to complement the fluorescence measurements and are used to monitor temperature and resin modulus during extrusion and injection molding.
- An optical sensor for injection molding is used to monitor crystallization kinetics by measuring light transmission through the crystallizing resin.
- Applications of these sensors include the measurement of temperature profiles during resin extrusion, measurement of molecular orientation in stretched films, kinetics of resin crystallization and glass formation during injection molding and measurements of machine residence time during extrusion.

External Collaborations

- DuPont - measurements of temperature profiles during extrusion.
- Mobil Chemical - measurement of molecular orientation during biaxial stretching of polypropylene films.
- DELPHI Packard Electric - measurement of temperature and crosslinking during the extrusion of polyethylene wire insulation.
- General Electric - measurement of temperature and resin solidification kinetics during injection molding.
- 3M Co. - measurement of residence time profiles during extrusion using the confocal optics sensor.
- University of Utah - development of high temperature ultrasonics transducers for extrusion and the application of fluorescence confocal temperature measurements during injection molding.
- NIST Information Technology Laboratory - analysis of fluorescence spectra using statistical methods to identify correlations with temperature and pressure and to develop models describing dye behavior.

Accomplishments

- Demonstrated the feasibility of measuring strain rate by the method of fluorescence recovery after photobleaching.
- Employed the polarizing optics sensor to measure fluorescence anisotropy in films of polypropylene doped with a fluorescent dye and to scan over the surface of large area films to measure anisotropy as a function of position.
- Developed a model to describe light transmission through crystallizing polypropylene during injection molding.
- In collaboration with Packard Electric, the determination of specific changes in the spectrum of a fluorescent probe provided simultaneous measurement of temperature and crosslinking in a polyethylene/polyvinyl acetate copolymer. This measurement can be used to control and monitor continuous extrusion of wire insulation during which crosslinking is activated by

raising the temperature in the later stages of processing. During the early stages of the extrusion, limited crosslinking is allowed so that the rheology remains uniform.

- A patent was awarded for the confocal optics sensor for temperature profile measurements.

Impact

The technology developed in this project is being used by 3M Co., Mobil Chemical Co. and DELPHI Packard Electric in R&D studies of polymer processing. This technology is the subject of ongoing collaborations with 3M Co., DuPont Co., DELPHI Packard Electric, Mobil Chemical Co. and General Electric. 3M Co. is employing our technology to adjust the process parameters based on measurements of residence time in process machines. Mobil Chemical Co. is using fluorescence anisotropy as a measure of orientation in biaxially stretched polypropylene films. DELPHI Packard Electric is using fluorescent dyes to obtain temperature and crosslinking data for wire insulation. General Electric is collaborating with NIST in order to study resin crystallization kinetics and resin shrinkage during injection molding. These companies have sought NIST technology because existing process monitoring methods are inadequate.

Outputs

Publications

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Interfacial Interactions in Multi-Phase Systems

A. Karim, B. Bauer, H. Jeon¹, J. Douglas, D. Liu, B. Ermi² and E. Amis

¹Polytechnic University, Brooklyn, New York

²University of Southern California, Los Angeles, California

Objective

The objective is to characterize interfacial interaction parameters necessary to control and stabilize dispersions in a polymer matrix of particles, polymer droplet phases and dendritic molecules for thin film coatings and in bulk.

Technical Description

- Investigate frustrated coalescence phenomena in chemically reactive blend films.
- Compare interdiffusion promoted by chemical reaction in reactive blends with thermally diffusive mechanisms in non-reactive blends.

- Measure interfacial broadening in strongly interacting polymer/random copolymer bilayers and compare with theoretical predictions. Determine miscibility window for wide composition range of random copolymer.
- Characterize layer formation and determine control conditions necessary for preparing uniform and reproducible dendrimer monolayer films.
- Study surface properties of dendrimers and dendrigraft/polymer bilayers utilizing atomic force microscopy (AFM), X-ray reflectivity (XR), neutron reflectivity (NR) and optical microscopy (OM).
- Investigate compatibilization effects of added block and graft copolymer on the morphology and kinetics of phase separation in thin polymer blend films using AFM, OM and NR.

External Collaborations

- Dr. Dusty Majumdar, GE Plastics - Research collaboration including preparation of deuterated materials and joint research on strong interactions between polymer pairs.
- Dr. Donald Paul and Glen Merfeld, U. Texas, Austin - Research collaboration on unique materials with a graduate student working part-time at NIST .
- Raychem Corporation - Joint feasibility tests of *in-situ* AFM on phase separating polymer blend films with surfactant additives.
- Dendritech - Supply of materials for thin film dendrimer studies.

Accomplishments

- Copolymer composition study establishes that interfacial widths in bilayers of deuterated polyphenylene oxide (dPPO)/styrene (acrylonitrile (AN) or maleic anhydride (MA)) follow theoretically predicted trends as function of composition. However, the detailed shape of profile is asymmetric about bilayer interface, rather than predicted symmetric shape.
- Neutron reflectivity was used to determine bilayer interface thickness and shape. The interfaces are substantially thicker than estimated theoretically, and in addition, have an asymmetric shape about the joining boundary. This is expected to affect fracture toughness and adhesion strength.
- Uniform spin coated monolayer films of PAMAM dendrimers from generations 3 to 6 were prepared and characterized by XR and AFM. A film collapse transition was observed in films from generation 6 through 10.
- Wetting of polyethyloxazoline dendrigraft thin films yield novel patterns for higher branching content dendrigrafts that resemble floral shapes. These have not been observed previously in dewetting of linear polymers, possibly due to difference in entanglement behavior.

- Discovered that blend films of low molecular mass poly(styrene/butadiene) were stabilized by segregation of high molecular mass diblock copolymers to film boundaries, preventing lateral phase separation. Only transient stability was observed for small diblocks in a high molecular mass matrix.
- Demonstrated suppression of coalescence in polystyrene/polyvinylmethylether (PS/PVME) blend films by surfactant additives.

Outputs

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Stabilization of Blends by Strong Interactions

C. C. Han, C. Zhou¹, H. Gruell², C. Gettinger, B. Bauer, A. Karim, R. Xie³, E. K. Hobbie⁴, F. Ikkai⁵ and J. F. Douglas

¹Fudan University, Shanghai, China

²Alexander von Humboldt Foundation, Germany

³University of Connecticut, Storrs, Connecticut

⁴University of Pennsylvania, Philadelphia, Pennsylvania

⁵Kyoto Institute of Technology, Kyoto, Japan

Objectives

The objectives are to measure the effects of strong interactions, including hydrogen bonding and metal ion complexation, on the phase behavior of polymer blends in bulk and surfaces and to explore applications of compatibilizers based on strong interactions.

Technical Description

- Study the wettability of silicon oxide substrates by polymers with a combination of X-ray reflectivity, optical and atomic force microscopies.
- Sulfonated polystyrene ionomers (SPS) with varying sulfonation level and different metal counterions are used to control wetting and the patterns formed during de-wetting.
- End labeled polystyrene, PS-eOH and polybutylmethacrylate, PBMA-eOH are used together to study the influence of symmetry, thickness and hydrogen bonding effects on the phase separation and roughening of thin films on a silicon substrate.
- Hydrogen bonding is used to control miscibility, the structure of the phase separated polymer blends and also surface wetting.
- The influence of cross-linking density, temperature and degree of ionization on structural inhomogeneities in a weakly charged gel consisting of (N-isopropylacrylamide-co-acrylic acid) (NIPA-AAc) copolymers is studied by SANS and the results are analyzed by recent theories.
- Investigate the influence of cross-linking density on structural inhomogeneities in an ion-exchange resin having sulfonic acid groups and compare results with measurements on precursor polymers. Study the kinetics of microstructure development in NIPA-AAc gels after discrete temperature jumps through the critical point.

External Collaborations

- Bob Weiss, University of Connecticut - Collaboration and supply sulfonated polymers with various counterions.
- Kyoto Institute of Technology - Collaboration to prepare NIPA-AAc copolymer gels.

Accomplishments

- The wettability of low molecular mass sulfonated polystyrene ionomers (PS, $M_w=4,000$ g/mol) (SPS) with various levels of functionalization and metal counterion (Li^+ , Zn^{2+}) on inorganic silicon oxide substrates has been characterized by using a combination of x-ray reflectivity, optical and atomic force microscopy measurements.
- It was shown that inter and intra molecular complexation, in addition to long range electrostatic polymer-surface interactions, are important in retarding the dewetting process.
- A slowing down with increasing film thickness of the phase separation kinetics has been observed by x-ray reflectivity and AFM for a hydrogen bonding blend on a silicon surface covered with polymer grafts.
- The equilibrium and non-equilibrium phase behavior of a series of blends containing varying amounts of hydrogen bonding components were studied by small angle neutron scattering.

Results can be explained by a two length scale model, with a thermal fluctuation length and a chemical barrier length due to the hydrogen bonding. This system has a fractal microstructure during phase separation and consequently should exhibit low or zero shrinkage.

- Structure inhomogeneity as a function of crosslinking density was evaluated for a series of charged polymer gels as a function of crosslinking conditions, temperature, and charge density.

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Pattern Formation by Polymer Blends in Coatings and Adhesive Layers

A. Karim, B. Ermi¹, H. Gruell², J. Douglas, B. Lee, S. Glotzer, D. Liu, E. Amis and C. Han

¹University of Southern California, Los Angeles, California

²Alexander von Humboldt Foundation, Germany

Objectives

The objectives are to develop techniques and methodology for controlling surface adhesion, wetting, and pattern formation in polymer films through phase separation, layer thickness, and surface reaction.

Technical Description

- Investigate theoretical and experimental aspects of finite size effects on phase separation of fluid mixtures with particular emphasis on the influence of surface interactions.
- Experimentally characterize the effect of reduced dimensionality on the growth of pattern size and morphology type in thin film blends phase separation.
- Directly observe pattern formation and measure kinetics of pattern formation in real space in off-critical blend films.
- Demonstrate capacity to control surface pattern formation in phase separating blends through surface templates which vary the surface interaction.
- Determine how characteristic pattern size, chemical nature, and geometry of substrate boundaries affect detailed local geometry of phase separating mixtures.

External Collaborations

- Harvard U. - collaboration to prepare chemically patterned self assembled monolayer (SAM) substrates.
- Penn State U. and U. Maryland - collaboration on SANS of thin blend films.
- Exxon Chemicals - collaboration on and synthesis of chemically end-functionalized deuterated polymers.
- Goodyear Tire Company - materials supplied for phase separation studies.

Accomplishments

- Kinetics of phase separation was characterized in off-critical composition PS/PVME blend films.

- Measurements on thin film blends have established that nucleation and growth at the late stage of phase separation is dominated by a coalescence mechanism rather than by Ostwald ripening. Studies by bulk scattering techniques are not able to distinguish between coalescence mechanisms and Ostwald ripening because the time dependence is identical.
- Dissolution of phase separated surface structures demonstrated the thermodynamic reversibility of confined phase separated structures.
- Demonstrated alignment and healing of substrates pattern defects in phase separating thin blend films deposited on chemically patterned striped substrates.
- Aligned phase separated blends were shown to stabilize through control of substrate patterning dimensions. Existence of upper limit on chemical pattern length scale necessary for blend alignment was determined.
- Simulations of fluid phase separation in 2 and 3-D with a variety of patterned and regular surfaces demonstrated the development of checkerboard morphology.
- Confirmed trapping of an unfavorable solvent layer by a polymer brush from an off-critical binary solvent mixture due to presence of an attractive wall.
- Measured surface segregation in thin PS/PVME and PS/PB blend films. Surface compositions approach bulk two phase co-existing compositions as predicted theoretically.

Outputs

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Phase Behavior of Polyolefin Blends

K. Migler, A. Nakatani, C. Jackson, A. Karim and E. Amis

Objective

The objective is to characterize phase behavior of polyolefin blends and the effects of shear, pressure and copolymer additives.

Technical Description

- Utilize the NIST neutron scattering shear cell and the NIST pressure cell to measure the effects of external fields on polyolefin blend interactions and miscibility.
- Examine the miscibility of metallocene copolymers as a function of copolymer architecture and content.
- Measure pressure induced shifts of the spinodal curve in critical polymer blends via optical cloud point technique.
- Explore the origins of the composition dependence of the interaction parameter of polyolefin blends by probing the response of these systems to pressure.

External Collaborations

- Exxon Research and Engineering- CRADA developed to measure the pressure and shear rate dependence of the phase behavior of metallocene catalyzed polyolefin blends by SANS and optical techniques.
- Polytechnic University - Special synthesis of model polyolefins and study of the effects of external fields.

Accomplishments

- In collaboration with Exxon, large pressure induced demixing in metallocene polyolefin blends was demonstrated through optical cloud point measurements. The observed linear dependence of the demixing temperature on pressure is 0.24 °C/MPa. High pressures are typical in most polymer processing, including polyolefins, and the strong dependence on pressure will greatly shift phase boundaries.
- Measured the interaction parameter as a function of pressure and temperature for a series of blends consisting of a model deuterated copolymer and various commercial EXACT™ copolymers, differing by copolymer content and type.
- Determined scaling of interaction parameter for several UCST polyolefin blends as a function of density.
- Examined the shear behavior of two polyolefin blend types (UCST and LCST) by *in-situ* shear SANS. Observed behavior similar to shear induced suppression of concentration fluctuations found in prior studies on model blends systems.
- Developed a “smart optical cloudpoint” software algorithm for pressure cell to increase data acquisition by an order of magnitude.

Outputs

Publications

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Polymer-Filler Interactions

A. I. Nakatani, A. Karim, B. Lee, J. F. Douglas, S. Glotzer, E. K. Hobbie¹ and E. J. Amis

¹University of Pennsylvania, Philadelphia, Pennsylvania

Objective

The objective is to initiate project to characterize interactions between polymers and fillers in dispersions, in blends and under the effect of shear.

Technical Description

- Develop plan for characterizing interactions between polymers and fillers and initiate feasibility studies for conducting planned research.
- Determine whether particle inclusions can stimulate the development of concentration waves similar to those found for planar interfaces and, if the phenomenon exists, determine the influence of particle size on this behavior.
- Combine numerical and analytical techniques based on Cahn-Hilliard theory to examine the influence of spherical inclusions on mixture phase separation.
- Characterize the polymer molecular dimensions, domain sizes and interaction parameters of poly(dimethyl siloxane) (PDMS) blended with silica fillers.
- Develop measurement methods appropriate for characterization of instabilities, demixing, nucleation and cluster growth in model hard sphere colloids.
- Characterize the role of preferential polymer interactions and the size of the inclusions relative to the correlation length of concentration fluctuations in the two-phase region.
- Contrast numerical results with experimental studies of phase separation with inclusions in thin films.

External Collaborators

- Dow Corning Corporation - CRADA developed to examine poly(dimethyl siloxane) (PDMS) blended with filler materials by SANS.

- Building and Fire Research Laboratory, NIST - Provided test samples of silica gel-filled polypropylenes for SANS feasibility studies.

- Goodyear Tire and Rubber Company - Provided test samples of carbon black and fumed silica filled polybutadienes and styrene-butadiene rubbers for SANS feasibility studies.

Accomplishments

- Developed and initiated research plans to characterize interactions between polymers and fillers in the following areas: Viscosity and modulus of filled polymer systems; Kinetics and morphology of phase separation and ordering in filled systems; Hydrodynamic behavior and diffusion in filled polymer samples; Interfacial interactions between polymers and filler surfaces.
- Contacts made with potential collaborators: Cabot; Goodyear; Dow Corning; Dow Chemical; Building and Fire Research Laboratory (BFRL) at NIST.
- SANS experiments on polypropylene filled with silica gel particles performed to assess the feasibility of characterizing filled polymers by SANS. Differences in scattering due to pore volume and surface treatment were easily noted. Differences in scattering due to mechanical preparation and primary particle size were not apparent.
- SANS feasibility experiments were performed on carbon black filled and fumed silica filled polybutadiene and styrene-butadiene random copolymer (SBR) (provided by Goodyear). Data analysis in progress.
- Conducted simulations of blend phase ordering in the presence of a spherical impurity in two and three spatial dimensions. Demonstrated, within our model, the existence of resulting spherical spinodal waves and quantified the extent of the pattern as a function of quench depth and molecular mass.
- SANS measurements on solutions of the individual PDMS and filler components were performed in a collaboration by a Dow Corning scientist.
- Obtained radius of gyration of protonated PDMS samples in deuterated toluene which compare well with GPC preliminary to studies on polymer-filler systems. Deuterated polymer synthesis completed by Dow Corning.
- Sample cell and experimental method using real time video microscopy was developed for quantitative measurements of kinetics of aggregation of hard spheres.
- Demonstrated cluster-size distribution function dynamic scaling in agreement with simulations of two-dimensional evaporation/condensation phenomena.

Outputs

Publications

E.K. Hobbie, *Kinetics of Size Segregation in Quasi-Two-Dimensional Nearly-Hard- Sphere Mixtures*, Physical Review E, 55, 6281 (1997).

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Characterization and Applications of Dendrimer-Polymer Blends

B. Bauer, E. Amis, A. Topp¹, T. Prosa, D. Valachovic², C. Jackson, D. Liu, A. Karim and J. Douglas

¹University of Koln, Koln, Germany

²University of Southern California, Los Angeles, California

Objective

The objective is to characterize the size, shape and density distribution of dendrimers and the pair interactions between dendrimer pairs and between polymers and dendritic polymers.

Technical Description

- Characterize the average radius of gyration and segment density distribution of various dendrimers, dendrigrafts and hyperbranched polymers.
- Develop a method of locating the end groups and molecules associated with the end groups of dendrimers.
- Develop methods of quantifying the interpenetration of dendritically branched polymers in solution and in blends.
- Characterize by TEM dendrimers in solution and on grids as to size, size distribution and interpenetration.
- Produce molecularly dispersed dendritic molecules in a polymeric matrix by use of blending and interpenetrating polymer networks.
- Prepare monolayer films of dendrimers and measure film thickness by reflectivity.

- Measure interfacial thickness between linear polymers and dendrigrafts of differing graft density.

External Collaborations

- Michigan Molecular Institute - CRADA developed for supply of materials, custom synthesis and joint research.
- DSM - collaboration has been established for supply of materials and a guest researcher has been sent to work at NIST on joint research.
- Army Research Office - grant (35109-CH) for work on dendrimer blends; collaboration with Army scientists.
- Mario Gautier, U. Waterloo - collaboration has been established for supply of materials for joint research.

Accomplishments

- Dendrimer molecules of divergent types have been characterized with a combination of small angle neutron scattering, small angle x-ray scattering, and transmission electron microscopy. Four critical observations arise from the solution characterization which contrast dendrimers with other classes of polymers: Dendrimers are spherical in shape and have a narrow size distribution even at relatively low molecular mass; the segment density distribution profile is nearly uniform within the dendrimer; the terminal units of the dendrimer are located within a relatively narrow shell toward the periphery of the molecule; and with increasing concentration the dendrimers appear to collapse and pack in a random close packing arrangement with little interpenetration. These characteristics suggest possible applications as size and molecular mass calibration standards for SANS, SAXS, TEM, AFM, MALDI, SEC, and filtration.
- Sample preparation techniques have been developed to measure the size and interpenetration of dendrimers in solution and on a surface by TEM.
- Molecularly dispersed dendrimers in a polymeric matrix have been prepared by use of blending and IPN techniques.
- Monolayers of dendrimers have been placed on a solid substrate and the thickness has been measured as a function of generation showing dimensions in agreement with measurements made by scattering and microscopy.
- The interfacial thickness of linear polystyrene and dendritic polyethyloxazoline has been measured and has been found to vary only slightly with generation.

Outputs

Publications

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E.J. Amis, *Structural Characterization of Dendrimers by Light, Neutron and X-Ray Scattering*, American Physical Society March Meeting, Kansas City, MO, March 1997.

B.J. Bauer, *Dendrimers and Dendrimer/Polymer Blends*, Center for Interfacial Engineering, Spring Workshops, Minneapolis, MN, May 1997.

B.J. Bauer, *Dendrimer Solutions and Blends*, NIST-ERATO Joint Meeting on "Multicomponent Polymers and Polyelectrolytes", NIST, Gaithersburg, MD, June 1997.

E.J. Amis, *Light, Neutron and X-Ray Scattering of Dendrimers and Dendrimer/Polymer Blends*, American Chemical Society Central Region, 100 Years of Dow Chemical Co., Midland, MI, May 1997.

E.J. Amis, *Scattering Methods and Dendrimer Materials*, American Crystallographic Association, Session on Small Angle Scattering, St. Louis, MO, July 1997.

B.J. Bauer and A. Topp, *SANS Study of Labeled PAMAM Dendrimer*, NIST-ERATO Joint Meeting on "Multicomponent Polymers and Polyelectrolytes," NIST, Gaithersburg, MD, June 1997.

A. Topp, *Small Angle Neutron Scattering from Dilute and Concentrated DAB(PA)_x Dendrimer Solutions*, NIST-ERATO Joint Meeting on "Multicomponent Polymers and Polyelectrolytes," NIST, Gaithersburg, MD, June 1997.

T.J. Prosa, *A SAXS Study of the Internal Structure of Dendritic Polymer Systems*, NIST- ERATO Joint Meeting on "Multicomponent Polymers and Polyelectrolytes", NIST, Gaithersburg, MD, June 1997.

A. Topp, *Small Angle Neutron Scattering from Dilute and Concentrated DAB(PA)_x Dendrimer Solutions*, American Chemical Society National Meeting, Las Vegas, September 1997.

B.J. Bauer, *SANS and SAXS Investigations of the Internal Structure of Dendritic Molecules*, American Chemical Society National Meeting, Las Vegas, September 1997.

A. Karim, *Influence of Generation Number on the Formation of Dendrimer Monolayers*, American Chemical Society National Meeting, Las Vegas, September 1997.

A. Topp, *SANS Study of Labeled PAMAM Dendrimer*, American Chemical Society National Meeting, Las Vegas, September 1997.

C.L. Jackson, *Characterization of Dendrimer Molecules by Staining and Cryoelectron Microscopy Techniques*, American Chemical Society National Meeting, Las Vegas, September 1997.

D.E. Valachovic, *Dendrimer End Group Localization Determined by Counterion Mirroring*, American Chemical Society National Meeting, Las Vegas, September 1997.

Polymer Solutions

E. Amis, R. Ivkov, Y. Zhang¹, B. Ermi², F. Ikkai³, D. Valachovic², B. Bauer and D.-W. Liu

¹The Chinese University of Hong Kong, China

²University of Southern California, Los Angeles, California

³Kyoto Institute of Technology, Kyoto, Japan

Objective

The objective is to characterize molecular interactions and phase behavior of polymers, polymer gels and polyelectrolytes in water and other solvents.

Technical Description

- Static light scattering, SLS, and small angle neutron scattering are used to characterize interactions in polyelectrolyte solutions under control of charge density, backbone solvation and counterion concentration.
- Dynamic light scattering is combined with SLS and SANS to provide molecular interpretation of coupling of dynamics to structure in polyelectrolyte solutions.
- Developed methods using scattering in combination with rheology for characterization of associative polymers and transient gels.
- Characterize thermoreversible polyolefin physical gels of ethylene/propylene copolymers in organic solvents and in motor oil.
- Investigate the influence of cross-link density, temperature and degree of ionization on the structural inhomogeneities in a weakly charged gel of (N- isopropylacrylamide-co-acrylic acid) copolymers by SANS and compare with recent theoretical treatments.
- Develop scattering contrast methods to measure the distribution of counterions in the vicinity of polyelectrolyte spheres and chains.

External Collaborations

- Dendritech and Michigan Molecular Institute - supplied dendrimers for use as model polyelectrolyte spheres.
- Ethyl Petroleum Additives - Collaboration has been established for supply of materials, custom synthesis and joint research. Guest research arrangements for Christophe Daniel and Tse-Chi Jao of Ethyl have been established.
- University of Southern California - two Ph.D. students from the chemistry department completed their thesis research at NIST.
- NIH Biophysics Research Group - initiated interactions in areas of polyelectrolytes, dendrimers and dense media scattering.

Accomplishments

- Model for multi-chain domains formed by presence of attractive interaction within polyelectrolyte solutions has been proposed to explain observations of fast and slow diffusive modes in dynamic light scattering and low q upturn in SANS.
- Scattering experiments from polyelectrolyte solutions using solvents which are good for both neutral and charged polymers have demonstrated that the so-called "polyelectrolyte effect" cannot be explained adequately by current models based on the influence of residual hydrophobic interactions. Electrostatic interactions dominate the experimental observations.
- Polyelectrolyte dendrimers were shown to have dilute solution SLS, DLS and SANS features consistent with observations on linear polyelectrolytes. However, dendrimers cannot be modelled with the electrostatic blobs, extended persistence lengths, or intermolecular entanglements which are often invoked in theories of polyelectrolytes. These observations therefore challenge current models.
- The technique of counterion mirroring demonstrates that terminal units of dendrimers in aqueous solution are located predominately at the periphery of the molecule.
- Matched deuterium labeled ethylene/propylene copolymers have been synthesized at Ethyl Corporation for initial SANS and neutron diffraction experiments on solutions and thermoreversible gels. Single chain scattering has been measured in both solution and gel states and it has been shown that in the gel state crystalline diffraction peaks appear. Characterization the gelation mechanism is essential for applications of these polymers as additives to control the rheology of industrial lubricants.
- Established that microstructural inhomogeneities in weak polyelectrolyte gels have an anomalous dependence on cross-linking by a series of experiments as a function of preparation and experimental conditions. Recent theory for inhomogeneity in gels provides reasonable fitting of the scattering data.

Outputs

Publications

F. Ikkai, M. Shibayama, S. Nomura and C.C. Han, *Effect of Degree of Cross-linking on Spatial Inhomogeneity in Charged Gels*. 2. Small-Angle Neutron Scattering Study, *Macromolecules*, submitted.

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

B.D. Ermi and E.J. Amis, *Influence of Backbone Solvation on Small Angle Neutron Scattering from Polyelectrolyte Solutions*, *Macromolecules*, in press.

D.E. Valachovic, B.J. Bauer, E.J. Amis and D.A. Tomalia, *Dendrimer End Group Localization Determined by Counterion Mirroring*, American Chemical Society-PMSE Preprints, 77, 230 (1997).

Presentations

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

E.J. Amis, *Structure and Dynamics in Polyelectrolyte Solutions*, Princeton University, Chemical Engineering Department, Princeton, NJ, November 1996.

E.J. Amis, *Structure and Dynamics in Polyelectrolyte Solutions*, University of Delaware, Chemical Engineering Department, Newark, DE, December 1996.

E.J. Amis, *Structure and Dynamics in Polyelectrolyte Solutions*, University of Nebraska, Chemistry Department Colloquium, Lincoln, NB, January 1997.

E.J. Amis, *Probing Polyelectrolyte Solutions by Light and Neutron Scattering*, Rohm and Haas Co. Spring House, PA, March 1997.

E.J. Amis, *Polyelectrolyte Solutions: Structure and Dynamics from Strong Interactions*, International Conference on Strongly Coupled Coulomb Systems, Boston, MA, August 1997.

F. Ikkai, *Effect of Degree of Cross-linking on Spatial Inhomogeneity in Polymer Gels*, NIST-ERATO Joint Meeting on "Multicomponent Polymers and Polyelectrolytes", NIST, Gaithersburg, MD, June 1997.

B.D. Ermi, *Probing Polyelectrolyte Solutions by Light and Neutron Scattering*, American Chemical Society Colloid and Surface Science Meeting, Symposium on Scattering Methods in Colloid Science, Newark, Delaware, July 1997.

D.E. Valachovic, *Dendrimer End Group Localization Determined by Counterion Mirroring*, American Chemical Society National Meeting, Las Vegas, September, 1997.

Polymer Blends and Processing Center

E. Amis, A. Bur, C. Han, A. Nakatani, B. Bauer and T. Prosa

Objectives

The objectives are to stimulate adoption of measurement advances and to obtain feedback from industry on successes making use of NIST research and identify areas not yet addressed concerning polymer blends and processing, by facilitating workshops, improved communications

and to develop protocols for user access to measurement facilities for polymer blends and processing.

Technical Description

- In collaboration with the NIST Center for Neutron Research and the Applied Mathematics Division of the Information Technology Laboratory, protocols for analysis of small angle neutron scattering are being developed and documented with instructions and examples of standard methods of analysis.
- Joined the Participating Research Team for the Advanced Polymer X-ray scattering beamline (X27C) at NSLS-Brookhaven National Laboratory. This provides state-of-the-art small and wide angle measurement capabilities, specifically tailored for use in the characterization of polymer structure.
- Electronic mechanisms for communication with industrial collaborators are being prepared including a web site with descriptions of program objectives, highlights of recent work and on-line reprint distribution.
- Staff continue to build collaborative relationships and disseminate results of NIST research within the scientific and technical community by organizing meetings, symposia and working groups.

Accomplishments

- NIST hosted a three day joint scientific workshop with the Hashimoto Phasing Project of the Exploratory Research and Technology Organization (ERATO) of Japan, which was attended by over 65 representatives of U.S. industry, ERATO, and NIST. In addition to further developing the scientific interactions between these two research groups, the workshop provided U.S. industrial researchers a direct view of the ERATO-supported project.
- Contributed to a Dow Corning Corporation resin characterization workshop, with focus on identification of measurement methods to characterize resin fillers.
- Held several meetings with Dow Chemical, including visits by their nanocomposites team, resulted in two new cooperative efforts; first, a theoretical modeling project on rheology of filled polymers and second, characterization of polymer-clay interactions by SANS.
- NIST hosted an organizational meeting for an Industry-NIST-University-Army Research Consortium on filled polymers. If successful this would be the first ARC and could result in merging Army research interests, industrial participation and strong university involvement for this research area.
- Quality of image plate detector data from AP-PRT Brookhaven beamline was compared favorably with data acquired using two-dimensional multi-wire proportional detector at NIST.

- Industrial visits and visitors this year: Amoco, Aristech, Cabot, Dow Chemical, Dendritech, Dow Corning, DSM Research, DuPont, Exxon, Ethyl, GE, Goodyear, Packard Electric, Rohm and Haas and 3M.
- New collaborations on NIST problems have been established with academic researchers at Polytechnic University (polyolefins), Utah (sensors), Connecticut (ionomer blends), Pennsylvania (multiphase materials), Penn. State (blend rheology).
- Symposia were organized at national meetings of Materials Research Society, American Chemical Society and American Physical Society.

has already been developed for testing and
Industrial visits and visitors this year. Major studies in China, Korea,
Dow Corning, IBM Research, Ford, Boeing, GE, etc.
Kohn and Hark and IM
Industrial visits and visitors this year. Major studies in China, Korea,
Dow Corning, IBM Research, Ford, Boeing, GE, etc.
Kohn and Hark and IM
Industrial visits and visitors this year. Major studies in China, Korea,
Dow Corning, IBM Research, Ford, Boeing, GE, etc.
Kohn and Hark and IM

POLYMER COMPOSITES PROGRAM

The Polymer Composites Program seeks to facilitate the introduction of lightweight, 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 lead to products that are superior and competitive in international markets. Industries as diverse as transportation, construction, marine, offshore oil, medical devices, and sporting goods have recognized those benefits and are making 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 offshore 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, and then to use those tests to identify the chemical and physical mechanisms of degradation, and finally 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.

Significant Accomplishments

- A database of permeability and other reinforcement properties was released in collaboration with the NIST Standard Reference Data Program. These data will aid the composites industry in designing liquid molding processes by providing critical input to mold filling simulation software.
- An industry/NIST workshop on interfacial micromechanics in May, 1997 brought together leading researchers in the field and important industrial users of composites. The important problems in interface testing were identified and routes to solving some of them agreed upon. For example, an international program on interface test standardization under the auspices of VAMAS was announced to solve the problem of poor intercomparison.
- A Lattice-Boltzmann microflow simulation was successfully compared to experimental data for flow in a model of the porous tows of composite reinforcements. The formation of voids and their subsequent size reduction was successfully recreated, and the permeability of the model porous medium was accurately predicted. The Lattice-Boltzmann method is much more computationally efficient than conventional finite element methods for multiphase flows in complex geometries. This will enable the rapid assessment of fiber architecture effects on composite processing and void formation.
- The reduction in permeability due to fabric curvature was demonstrated for flow around corners by building specialized flow molds with 90° curves of several radii of curvature. Material deformation in curves and at the corners of molds is responsible for modeling difficulties, and characterization data for such deformed material is very sparse.
- Demonstrated ability of Optical Coherence Tomography to image internal fabric architecture and residual porosity distribution for refractive index matched glass reinforced epoxy and vinylester composites. This new technology uses visible and near infrared light, is fast, and may be a low cost alternative to X-ray imaging in a number of commercially important composite systems.

- Demonstrated utility of optical fiber sensor system using existing thermocouple ports in structural reaction injection molding equipment used by the automotive industry. The ability to collect data without disrupting production equipment is an important step towards more widespread use of sensors in industry.
- Automated the single fiber fragmentation test by designing and building a specialized instrument that collects high resolution images under precisely controlled loading conditions. This will permit the development of standardized test procedures for assessing interfacial properties of polymer composites.

Liquid Composite Molding: Development of Permeability Measurement Techniques and Data

R.S. Parnas, K.M. Flynn, R. Peterson and M. DalFavero¹

¹ NIST Standard Reference Data Program

Objectives

The objectives are to establish a data base of permeability values for use in the design tools used by the composites industry, and to develop new permeability measurement techniques for assessing flow behavior in deformed materials.

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

Industrial: Dr. Henry Friedman, Textile Research Institute, flow behavior in deformed fabrics.

Academic: Prof. Raymond Gauvin, University of Montreal, permeability Data.

Prof. Christopher Rudd, University of Nottingham, permeability Data.

Planned Outcomes

The database released in 1997 is expected to be used by molders to help design their processes and parts. Version 2 of the database is planned for release in 1999 with an expanded data set and enhanced graphics display.

Accomplishments

- A database of permeability and other reinforcement properties was released in collaboration with the NIST Standard Reference Data Program. These data will aid the composites industry in designing liquid molding processes by providing critical input to mold filling simulation software.
- The reduction in permeability due to fabric curvature was demonstrated for flow around corners by building specialized flow molds with 90° curves of several radii of curvature. Material deformation in curves and at the corners of molds is responsible for modeling difficulties, and characterization data for such deformed material is very sparse.

Impact

NIST permeability data are being used in flow simulations at several companies, including ATP recipients, in the automotive and aerospace industries. 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. Preform 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, November 1995.

R.S. Parnas, K.M. Flynn and M. DalFavero, *A Permeability Database for Composites Manufacturing by Liquid Molding*, Polymer Composites, in press.

Liquid Composite Molding: Development and Verification of Process Simulation Models

F. R. Phelan Jr.

Objectives

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

Technical Description

In the past, LCM 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 being 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 the tool is closed enough to partially compress the preform. In the “open mold” process 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. In open mold I/C, there is some penetration of resin into the preform during the injection phase, so that during the compression step there is a combination of in-plane and through-thickness flow. 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.

External Collaborations

Industrial:

Dave Pinella, Structural Dynamics Research Corp., I-DEAS/CRIMSON interface development.

Doug Denton, Automotive Composites Consortium, I/CLCM flow simulation.

Gilbert Carpenter, Northrup/Grumman, RTM flow simulation.

Chuck Stuart, The Budd Co., RTM flow simulation.

Chihdar Yang, Specialty Plastics, Inc., RTM flow simulation.

Academic:

Prof. John Collier, Louisiana State University, RTM flow simulation.

Prof. Chuck Tucker, University of Illinois at Urbana-Champaign, preform deformation modeling.

Planned Outcome

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

Accomplishments

This year, work has begun in cooperation with the University of Illinois at Urbana-Champaign (UIUC) to develop a numerical simulation of the open mold I/C process. In the first phase of this collaboration, UIUC has developed a preprocessor which can generate a three-dimensional finite element mesh from a given two-dimensional shell mesh for flow computations. The preprocessor step is an important component of the open mold I/C simulation strategy. In this step, a 3-D flow mesh which functions as input for the CRIMSON program is constructed. Two inputs are needed in the pre-processing step: a 2.5-D mesh of the final molded geometry and all information on the preform “layup” in this geometry. This information is normally known by a part designer after a preliminary stress analysis stage has been completed. From this information, a 3-D mesh of the uncompressed preform geometry and “spines” are constructed. “Spines” are lines that run through groups of co-linear nodes from the lower surface to the upper surface of the 3-D FE mesh and are used in the mechanical analysis of the preform as discussed below. Included in the 3-D mesh are elements which account for all the different layers in the preform layup, and the gap spacing present during injection. The development of the preprocessor has been completed at this time and tested for a variety of 2.5-D shell meshes, and preform layups.

The second phase of the UIUC collaboration is to develop a module which models the non-linear deformation of the fibrous preform during compression of three-dimensional geometries. This module contains mechanical analysis routines for linking with CRIMSON. This module will enable CRIMSON to compute the volume change that occurs in the elements during compression of the preform which is a necessary calculation in order to track the movement of the flow front during this stage of the fill operation. At the time of this writing, the mechanical deformation module is not fully complete. In the mechanical theory being used to model the preform, local 1-D mechanics with no shear deformation are assumed for the sake of robustness. In response to compression, the preform deforms along the "spines" constructed in the preprocessing step. The nodes remain along the spines as the spines rotate in response to the imposed deformation. For each increment of deformation, new nodal locations are computed. The nodal locations satisfy the equilibrium condition of constant stress in all layers of the preform layup.

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. Phase II of this effort has now been initiated in which the interface will be modified to include I/C properties.

Impact

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

Outputs

Publications

F.R. Phelan Jr., *Simulation of the injection process in resin transfer molding*, Polymer Composites, 18, 460 (1997).

F.R. Phelan Jr., *Analysis of Injection/Compression Liquid Composite Molding*, Proceedings of the 5th International Conference on Automated Composites ICAC97, Glasgow Moat House, Glasgow, Scotland, UK, September 1997.

F.R. Phelan Jr., *Analysis of In-Plane Injection/Compression Liquid Composite Molding*, Composites A, submitted.

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F.R. Phelan Jr., *Simulation of Injection/Compression Liquid Composite Molding*, The First Joint Topical Conference on Processing, Structure, and Properties of Polymeric Materials, Chicago, IL, November, 1996.

F.R. Phelan Jr., *Analysis of Injection/Compression Liquid Composite Molding Process Variants*, Symposium on Multi-Disciplinary Issues in Manufacturing of Composites, 1996 ASME International Mechanical Engineering Conference and Exhibition, Atlanta, GA, November 1996.

F.R. Phelan Jr., *Simulation of Injection/Compression Liquid Composite Molding*, Gordon Conference on Computer Aided Engineering (CAE) in Polymer Processing, Harbortown Marina Resort, Ventura, CA, February 1997.

F.R. Phelan Jr., *Analysis of Injection/Compression Liquid Composite Molding*, 5th International Conference on Automated Composites ICAC97, Glasgow Moat House, Glasgow, Scotland, UK, September 1997.

Liquid Composite Molding: Development and Verification of Permeability Prediction Models

F.R. Phelan Jr., Richard Peterson and Michael A. A. Spaid

Objective

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

Technical Description

In previous work, a Lattice Boltzmann (LB) simulation for computing the flow behavior in real preform reinforcement materials was developed. LB methods involve the solution of the discrete Boltzmann equation on a lattice. Traditional flow quantities such as density and velocity are recovered by taking moments of the particle distribution function. The basic LB formulation found throughout the literature has been modified in this study to model flow in heterogeneous media such that the momentum transport is governed by Stokes flow in open media, and by the Brinkman equation in porous media. This enables us to model flow in the heterogeneous preform microstructure and is crucial for modeling void formation.

Planned Outcome

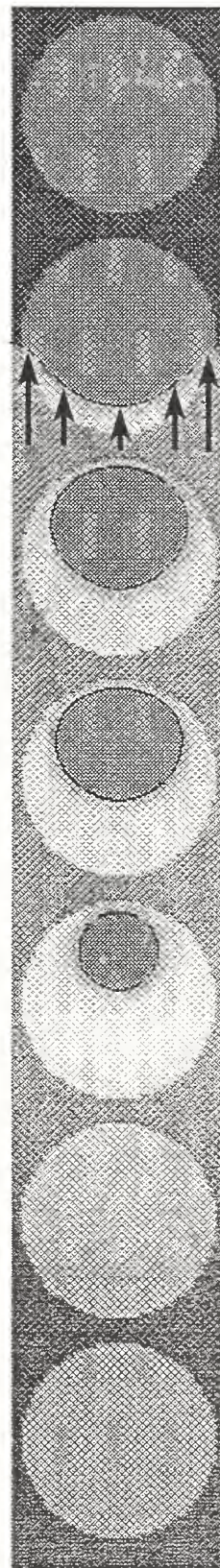
Simulation tools which can be used to determine the steady and unsteady permeability of fiber preforms used in LCM operations.

Accomplishments

In the past year, the existing LB formulation was modified to enable modeling of multi-component flow in heterogeneous media in order to study the mechanisms of void formation which occur primarily due to the heterogeneous nature of the preform microstructure in LCM applications.

The Figure shows the filling patterns obtained from a numerical simulation with a constant pressure injection for flow over a single column of circular tows, where the nominal porosity, or the percentage of the unit cell unoccupied by the porous tows, is 39 %. The simulation predicts that the flow front advances more rapidly in the gaps between fiber tows, resulting in air entrapment within the fiber tow. The trapped air is initially elliptical in shape with the major axis perpendicular to the flow direction, while at later times surface tension forces cause the voids to assume a more circular shape. The simulation predicts that the trapped air volume shrinks as a function of time and eventually dissipates. That is the reason why in the Figure there is no air trapped in the first two tows. This is not due to compressibility effects, but due to trapped air being slowly carried away and escaping with the bulk flow. This effect is currently being investigated experimentally and preliminary results indicate the simulation is correctly modeling the physics of the process.

Using the LB simulation it is possible to calculate the unsaturated permeability by tracking the location of the fluid front as a function of time. A plot of front position raised to the second power vs. time yields a straight line for simulations at both 39 % and 50 % nominal porosity, indicating a constant permeability. By comparing with previously computed saturated flow results the ratio of the unsaturated and saturated permeability was obtained. These results are given in the Table. The results show that in both cases the unsaturated permeability is lower than the saturated permeability and this effect increases with increasing volume fraction. These results are consistent with experimental observation in which the unsaturated permeability is reduced relative to the saturated permeability.



Nominal Porosity	K_s	K_{us}	K_{us}/K_s
0.39	2.90	0.68	0.23
0.50	7.77	3.82	0.49

Table 1 -- Comparison of the saturated and unsaturated permeabilities (in lattice units) for the simulations depicted the Figure.

Outputs

Publications

M.A.A. Spaid and F.R. Phelan, Jr., *Lattice Boltzmann methods for modeling microscale flow in heterogeneous porous media*, Phys. Fluids, **9**, 2468 (1997).

M.A.A. Spaid and F.R. Phelan Jr., *Modeling of Void Formation Dynamics in Fibrous Porous Media using the Lattice Boltzmann Method*, Proceedings of the 12th Annual Advanced Composites Conference and Exposition ACCE97, 213, April 1997.

F.R. Phelan Jr. and M.A.A. Spaid, *Modeling of Unsaturated Flow Dynamics in Composites Processing*, Proceedings of the 5th International Conference on Automated Composites, Glasgow Moat House ICAC97, Glasgow, Scotland, UK, September 1997.

M.A.A. Spaid and F.R. Phelan Jr., *Modeling of Void Formation Dynamics in Fibrous Porous Media using the Lattice Boltzmann Method*, Composites A, submitted.

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F.R. Phelan Jr., *Micro-Scale Flow Modeling Issues in Composites Processing*, Gordon Conference on Computer Aided Engineering (CAE) in Polymer Processing, Harbortown Marina Resort, Ventura, CA, February 1997.

Phelan Jr., F.R., *Modeling of Unsaturated Flow Dynamics in Composites Processing*, General Electric Corporate Research Center, Schenectady, NY, August 1997.

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

J. P. Dunkers, R. S. Parnas, K. M. Flynn, R. E. Neff and D. D. Sourlas

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, and flow inconsistencies are major

contributors to composite non-uniformity. The cure monitoring work focuses on fluorescence and near infrared spectroscopies, using an optical fiber drawn from commercially available high refractive index glass as the sensing element. Optical systems are designed and built to provide high speed spectral acquisition and chemometric methods are explored to provide equally high speed spectral analysis. The interfacial sensitivity of the evanescent wave sensors is determined with optical theory that quantifies the coupling between the excitation radiation and the fluorescence radiation.

The same optical fiber sensors used for cure monitoring are also being explored for flow monitoring by taking advantage of the change in signal strength that occurs as a fiber is covered by fluid when operated in evanescent wave mode. The effects of fiber bending and local environment around the fiber are being explored. In this work, flow simulation is being used to optimize the fiber trajectory in the mold to provide flow data most indicative of proper mold filling.

Planned Outcome

Demonstrate usefulness of process monitoring to the composites industry and indicate a potential low cost route with optical fiber sensors.

External Collaborations

Industrial: Carl Johnson, Automotive Composites Consortium and Ford, test sensor system in industrial processing environment.

Tom Donnell, Northrup/Grumman (DARPA), develop control structure for processing ceramic matrix composites.

Rob Bannerjee, EDX, develop quality control methods for sandwich panel products.

Academic: Dennis Sourlas, University of Missouri, develop process control algorithms.

Suresh Advani, University of Delaware, apply sensors to flow monitoring.

Accomplishments

Optical theory was used to model the sensitivity of the evanescent wave sensor geometry to the region around the optical fiber. An expression was derived for the fluorescence power transmitted by the optical fiber when the same fiber is used to provide the excitation. The model was solved for the fluorescence power in the fiber as a function of radial position around the fiber to determine the radial sensitivity of the evanescent sensing geometry. It was found that the current optical system, which uses all available modes of excitation and fluorescence, collects approximately 2/3 of the fluorescence signal from within 1000 Å of the fiber surface at the beginning of resin cure. At the end of resin cure, 2/3 of the signal is collected from a radius of approximately 3000 Å. The expansion of the signal collection region is due to the increase of refractive index of the resin, which causes the evanescent field to expand radially around the fiber. These observations are consistent with experiments where no difference was observed between evanescent wave and bulk resin measurements, indicating that sensing regions of 1000 Å and larger do not resolve the interfacial region of amorphous polymer networks. Such a

conclusion is also consistent with scaling theory which indicates a length scale of approximately 100 Å for the interfacial region of the polymer systems explored here. Thus, the current optical fiber sensor measures bulk cure. The development of an optical fiber sensor to measure the 100 Å interphase is described in the next project.

To demonstrate the convenience of optical fiber fluorescence spectroscopy, a portable high speed optical fiber fluorometer constructed earlier in this project was shipped to Ford Motor Co. and installed in the structural reaction injection molding development laboratory for testing. The optical fiber sensor was interfaced seamlessly with the Ford molds through existing thermocouple ports by encasing the optical fiber in a steel jacket. The sensor system was able to acquire data in real time and the sensor proved reusable for at least five sequential mold shots.

After shipment back to NIST, the fluorescence sensor system was incorporated into an experimental apparatus for evaluating the sensitivity of an evanescent wave optical fiber to fluid flow behavior. Preliminary work indicates that large signal changes occur as the fiber is covered with fluid, and that fiber quality, fiber bending and nonlinear optical effects all play a role in determining signal strength.

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*, **18**, 518 (1997).

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*, **18**, 133 (1997).

J.P. Dunkers, K.M. Flynn, R.S. Parnas and D.D. Sourlas, *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, November 1996.

D. Sourlas, S. Maha, G. Peterson and R. Parnas, *On-Line Control of Liquid Composite Molding*, Proceedings of ISA Control Conference, New Orleans, LA, June 1997.

Richard S. Parnas, Joy P. Dunkers, Raymond A. Neff, *Optical Fiber Based Sensors for Monitoring and Control of Composites Manufacturing*, Proceedings of International Conf. On Automated Composites, Glasgow, Scotland, U.K., September 1997.

Presentations

J.P. Dunkers, *Real-Time Process Control and Mid-Infrared Cure Sensing of Liquid Molding*, American Institute of Chemical Engineers, Chicago, IL, November 1996.

R.S. Parnas, *Measurement and Control of Liquid Composite Molding*, American Institute of Chemical Engineers, Chicago, IL, November 1996.

R.A. Neff, *Real-Time Cure Monitoring of Liquid Molding by Optical Fiber Evanescent Wave Techniques*, American Institute of Chemical Engineers, Chicago, IL, November 1996..

Joy P. Dunkers; Kathleen M. Flynn; Mitchell T. Huang, *Near Infrared Cure Monitoring and Control of a Resin Transfer Molded Epoxy Composite Using an Evanescent Wave High Index Fiber Optic Sensor*, Society of Plastics Engineers Annual Technical Conference, Toronto, Canada, April 1997.

Richard S. Parnas, *Evanescent Wave Fiber Optic Spectroscopy in Polymer Composites*, College de France, Paris, France, September 1997 and Corning, S.A., Fountainbleau, France, September 1997.

Liquid Composite Molding: Interphase Sensitive Sensors for Process Monitoring

R.S. Parnas, Joseph Lenhart¹ and John VanZanten¹

¹Department of Chemical Engineering, Johns Hopkins University, Baltimore, MD

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. Previously, a stilbene dye was synthesized with a chemical tail containing a surface reactive silane coupling group. After completing the synthesis, surface grafting was conducted on a flat glass substrate. The fluorescence of the surface bound material was measured in the presence of various solvents and resins to assess the ability of the surface bound fluorophore to respond to the environment. However, reproducibility problems were encountered associated with the limited hydrolytic stability of the Robello siloxane dye. More stable fluorophores are needed to make this approach feasible. Additional analytical methods such as contact angle, atomic force microscopy and IR spectroscopy are used to characterize the surface layer, and calibrate the surface bound fluorophore. Alternative methods of grafting are also explored to determine if low temperature aqueous methods are sufficient to deposit stable surface films.

Planned Outcome

Develop an integrated optical fiber fluorescence sensor sensitive to the interfacial region of fiber and polymer matrix.

External Collaborations

Academic: Steve Pollack, Howard University, synthesis of Robello Siloxane compounds.
John vanZanten, The Johns Hopkins University, characterization of mixed silane layers.

Accomplishments

- Advanced precursors of the Robello siloxane fluorophore were obtained that are very stable to moisture, and final synthesis procedures were developed at NIST to prepare the dye on an as needed basis.
- Ambient temperature silane deposition procedures were also investigated as a possible alternative to the 134 °C deposition procedure currently performed in xylene. A solvent mixture of 80 % acetone / 20 % water appears to produce a stable silane layer. The characteristics of that layer must still be assessed. Preliminary measurements using UV/Visible spectroscopy indicate that the layer is stable to brief immersions in water and acetone.

Microstructure Studies: Performance Relationships

D.L. Hunston, C.R. Schulthiesz, W.G. McDonough, G.A. Holmes, C. L. Schutte, K. Liao¹, Z. Miyagi², D. Raghavan³ and J. He³

¹Northwestern University, Evanston, Illinois

²National Research Laboratory for Metrology, Tsukuba, Japan

³Howard University, Department of Chemistry, Washington, DC

Objectives

The objectives are to develop and apply measurement tools that establish relationships between the microstructural features generated during processing and the performance properties of polymer composite systems. The focus is durability and the role of the polymer-polymer and the polymer-fiber interfaces in composite performance.

Technical Description

The work in this project involves three areas: resins, interfaces, and full composites. With resins, the focus is toughened thermosets. In these two phase material systems, the fracture resistance or toughness depends on the morphology of second phase (the toughener). Since the morphology in most such systems develops by phase separation during cure, the microstructure is difficult or impossible to control and vary systematically. The work here uses materials made from suspensions of preformed toughener particles to minimize morphological change during cure. Consequently, features like particle size, size distribution, and concentration can be systematically varied by changing the starting suspension and the dilution prior to cure. The work on interfaces uses simplified geometries that isolate the interface behavior so it can be studied independently. This information can then be combined with results on full composite to determine the role of the interface in the total performance. Two such studies are underway. One is developing an ultrasonic technique to characterize non-destructively the interface between

a flat surface and a polymer. Once developed, the technique will be used to monitor the interface region during polymer cure or attack of the cured polymer by water. The second interface study uses the single fiber fragmentation test to obtain information about the fiber-matrix interface itself and how that interface is affected by water. The interface region is varied through the use of coupling agents and surface treatments. For some systems, full composites are fabricated and tested to examine the relationship between the fragmentation results and composite behavior. The final study in this project examines the fatigue behavior of pultruded composites to develop test methods for durability and generate data to improve the understanding of degradation mechanisms.

External Collaboration

Industry: Dr. Dwight Hoffman, Dow Chemical, structure-property relationships in rubber-toughened epoxy systems.

Dr. David Dwight, Owens Corning, interface studies examining the relationship between fragmentation test results and the behavior of full composites.

Mr. Glenn Barefoot and Dr. Daniel Witcher, Strongwell (formerly Morrison Molded Fiber Glass), durability of studies on pultruded composites used in infrastructure applications.

Academic: Dr. John Fildes, and Prof. Catherine Brinson, Northwestern University, durability studies for pultruded composites used in infrastructure applications.

Prof. D. Raghavan, Howard University, structure-property relationships in rubber-toughened epoxy systems.

Planned Outcome

The work on toughening will generate structure-property relationships that provide generic guidelines to help industry develop more fracture resistant materials.

The ultrasonic studies will produce a fully automated instrument for characterizing and monitoring changes in the shear mechanical properties of thin films.

The durability studies will provide guidelines and methodologies for testing the resistance of composite materials to attack by long term exposure to moisture.

Accomplishments

The work on toughened resins has provided the first definitive experiments that show the effects of changing toughener concentration at a fixed morphology (size and size distribution of toughener particles in the matrix resin). The results shown in the figure indicate that fracture resistance goes through a maximum at 15 phr (parts toughener per hundred parts epoxy by mass). This contradicts previous ideas which asserted that the decrease in toughness seen at high concentrations was the result of changes in the morphology from a dispersed particle-matrix microstructure at higher concentrations.

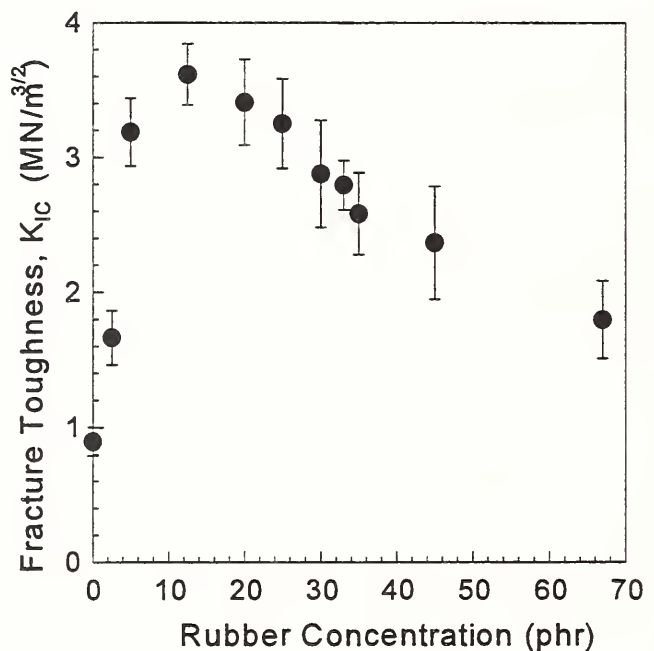
Work on the ultrasonic test for characterizing the dynamic shear storage and loss moduli of coatings and interface regions has now succeeded in totally automating the measurement and data analysis processes. A new temperature chamber was also built which will make it possible to use the technique to study moisture attack on the interface between quartz and a polymer resin.

Interface studies have compared results from the single fiber fragmentation test with data from experiments on full composites where both sample types are immersed in water for times up to 4500 hours. All samples were prepared at NIST to minimize variations. The moisture-induced fiber degradation patterns seen in the fragmentation tests are quite similar to those seen in the composite data although quantitative prediction of one result from the other is not presently possible. Moisture-induced degradation of the interface measured in the fragmentation tests is also reflected in the composite results, but the comparison is complicated by the fact that the composite tests are dependent on a number of factors in addition to the interface behavior. The conclusion was that qualitative correlations can be made but to go beyond that will require advances in both the tests methods and our ability to analyze the results.

Studies of environmental fatigue for pultruded composites were conducted by testing samples in water and in air. The results show that water had a significant detrimental effect on fatigue life only at loads below 45% of the static strength. Consequently, using higher loads to accelerate studies on moisture effects will be very misleading. Pre-exposure to water before testing in water had no effect so both water and load are needed for reductions in fatigue life. Pre-exposure to water at elevated temperatures did increase degradation rates but there were indications that the mechanisms changed so temperature is also a poor way to accelerate this type of environmental testing.

Outputs

Publications



The error bars indicate the standard uncertainty in the data.

K. Liao, R. Altkorn, S.M. Milkovich, J. Gomez, C.R. Schultheisz, L.C. Brinson, J.M. Fildes, and D.L. Hunston, *Long-Term Durability of Glass Fiber Reinforced Composites in Infrastructure Applications*, Journal of Advanced Materials, 28, 54 (1997).

D.L. Hunston, *Liquid Composite Molding--Processing Methods for the Future*, Composite Fabrication, in press.

K. Liao, C.R. Schultheisz, D.L. Hunston and L.C. Brinson, *Environmental Fatigue of Pultruded Glass Fiber-Reinforced Composites*, ASTM Seventh Symposium on Composites: Fatigue and Fracture, in press.

K. Liao, C.R. Schultheisz, D.L. Hunston, R. Altkorn, S.M. Milkovich, J.M. Fildes and J. Gomez, *Long-Term Durability of Composites in Infrastructure Applications*, Proceedings, The National Seminar on Advanced, Composite Material Bridges, in press.

Presentations

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*, EURAD'96, European Adhesion Conf., Cambridge, England, September 1996.

D.L. Hunston, *Failure Behavior of Polymers Used in Structural Applications like Adhesives and Composites*, Chemistry Department Seminar, Howard University, Washington, DC, October, 4, 1996.

D.L. Hunston, *Toughening of Thermoset Resins*, Symposium on Polymers for Electronics, Photonics, and Communications: Science & Technology for New Leading Industries, Tokyo, Japan, January 8, 1997.

D.L. Hunston, *Fiber-Matrix Interface Bonding in Composites*, Symposium on Polymers for Electronics, Photonics, and Communications: Science & Technology for New Leading Industries, Tokyo, Japan, January 11, 1997.

D.L. Hunston, *Comments on the Role of Viscoelasticity in Adhesion*, Plenary Lecture at Society of Rheology Meeting, Hilton Head, SC, February 24, 1997.

D.L. Hunston, J. He, D. Raghavan, and D. Hoffman, *The Effects of Particle Morphology on Toughness for a Rubber Modified Epoxy*, Polymer Stabilizers and Modifiers '97, Conference and Exhibition, Hilton Head, SC, March 5, 1997.

D.L. Hunston, and C.L. Schutte, *Opportunities and Research Challenges for Commercial Applications of Composites*, CMMC Technical Forum, Composites: New challenges - New Opportunities, Center for Micro- and Molecular Composites, Akron, OH, April 18, 1997.

K. Liao, C.R. Schultheisz, D.L. Hunston, R. Altkorn, S.M. Milkovich, J.M. Fildes, and J. Gomez, *Long-Term Durability of Composites in Infrastructure Applications*, The National Seminar on Advanced, Composite Material Bridges, Arlington, VA, May 1997.

K. Liao, C.R. Schultheisz, D.L. Hunston, and L.C. Brinson, *Environmental Fatigue of Pultruded Glass-Fiber Reinforced Composites*, ASTM Seventh Symposium on Composites: Fatigue and Fracture, St. Louis, MO, May 1997.

D.L. Hunston, *Performance Relationships*, Industry Workshop on Micro-Mechanics Measurement Technologies, NIST, Gaithersburg, MD, May 29, 1997.

Gale A. Holmes, Donald L. Hunston, Richard C. Peterson, Walter G. McDonough, and Carol L. Schutte, *Influence of Model Interfaces on Composite Durability*, Symposium on Application of Fiber Composites in Offshore and Marine Technologies, 1997 International Mechanical Engineering Conference and Exposition, ASME, Dallas, TX, November 16, 1997.

Microstructure Studies: Improve the Utility of the Single Fiber Fragmentation Test

G.A. Holmes, R.C. Peterson, W.G. McDonough, D.L. Hunston, R.S. Parnas and J.F. Cheng¹
¹Massachusetts Institute of Technology, Cambridge, MA

Objectives

The objectives in this project are to investigate the effects of resin viscoelasticity and assess the influence of moisture absorption on the interpretation of single fiber fragmentation test data.

Technical Description

The interfacial shear strength (or shear stress transfer coefficient) is typically calculated from experimental test data using models that assume the matrix material is linear elastic or elastic-perfectly plastic. Because the matrix material must have a high extension to failure relative to the failure strain of the embedded fiber, the linear elastic and elastic-perfectly plastic matrix condition is rarely met in experimental conditions where the matrix material is polymeric. This project seeks to quantify the impact of non-ideal matrix behavior on the interfacial shear strength determined by the single fiber fragmentation test. This will be accomplished by: (1) monitoring the change in load in single fiber fragmentation test (SFFT) specimens with increasing strain, (2) monitoring the evolution of the fragmentation process with increasing strain, (3) investigating the impact of loading rate on the matrix modulus and fragmentation of the embedded fiber, (4) development of shear stress transfer models to account for the impact of matrix property changes with increasing strain and strain rate, and (5) comparing results from the new models with values predicted by traditional linear elastic and elastic-plastic based shear stress transfer models.

Research designed to obtain reliable values of the strength of the fiber-matrix interface has been pursued in an effort to assess the durability of E-glass coatings made from silane coupling agents.

These coupling agents are designed to promote adhesion of the matrix to the embedded fiber and provide a protective barrier against moisture absorption. Because moisture absorption alters the properties of the matrix material, a significant portion of the change in interfacial shear strength determined from moisture exposed SFFT specimens is due to stiffness changes in the matrix. Hence, assessing the durability of an E-glass coating requires the decoupling of changes in interfacial shear strength resulting from changes in matrix properties from changes in interfacial shear strength due to degradation of the chemical bonds formed between the silane coupling agent and the E-glass fiber. To accomplish this aspect of the project, model systems will be prepared in which the impact of resin stiffness on the calculated interfacial shear strength can be determined independently of fiber-matrix interface degradation and fiber strength degradation. The matrix behavior from these model systems will be compared with resin systems plasticized by moisture to assess the applicability of this approach. Analytical models will be developed to predict theoretically the change in interfacial shear strength arising from changes in matrix properties. These values will be compared with values derived from experimental data to determine the durability of E-glass coatings.

External Collaborations

Industry: David Dwight, Owens Corning, develop model composite systems.
Eric Pohl, OSI, durability of industry coatings.

Academia: John Nairn, University of Utah, dynamics of debond region formation.
Larry Drzal, Michigan State University, data analysis procedures.

International: Graham Sims, Versailles Advanced Materials and Standards Program (VAMAS), establish standardized test for interfacial shear strength.

Planned Outcome

Establish international protocol for single fiber fragmentation test.

Accomplishments

- *VAMAS Program*

During the recent Workshop on Micro-Mechanical Measurement Technologies for Fiber-Matrix Interfaces, NIST announced the official initiation of an international round robin testing program for interfacial shear strength measurements. The effort is co-organized by Michigan State University and is under the auspices of the Composites Technical Working Group of VAMAS, the Versailles Project on Advanced Materials and Standards. This is an international organization that promotes pre-standards research. Currently, 17 laboratories representing 8 countries have agreed to participate. The program has three tasks. The first is to develop a consensus procedure for preparing the samples and conducting the tests. The second is to complete a round robin using the recommended test procedure and samples prepared in a single batch. The final task is to use the program as a forum for identifying critical research issues, exchanging results, and encouraging cooperation among researchers active in the area. The initial focus is the fragmentation test, but the work will expand to other methods if successful. In

addition to officially initiating the program during the past year, the first draft of a test procedure for fragmentation was developed.

- *Research on Fragmentation Test and Viscoelastic Characterization*

Model composites with and without a single bare E-glass fiber embedded in a diglycidyl ether of bisphenol-A / m-phenylene diamine (DGEBA/m-PDA) epoxy resin were prepared.

Fragmentation of the bare E-glass fibers was found to initiate in the stress-strain region where the DGEBA/m-PDA epoxy matrix exhibits nonlinear viscoelastic behavior. To account for this nonlinear viscoelastic behavior in the analysis procedure, the Cox model was extended to the nonlinear viscoelastic regime by replacing the linear elastic modulus with a strain-dependent secant modulus. Interfacial shear strength calculations using the experimental data from one particular sample and the assumption that the strength in the fiber at the critical length is approximately 2.5 GPa are shown in the Table below. These results show that assuming linear elastic or elastic perfectly plastic behavior for the DGEBA/m-PDA epoxy resin stress-strain behavior yields drastically different answers for the calculated interfacial shear strength.

Calculations using the strain-dependent secant modulus gave relative results approximately 15 % lower than the linear elastic modulus results. These results show clearly that the calculated interfacial shear strength is dependent on the matrix properties.

Tabulated values of interfacial shear strength using different models for data analysis.

Model	Interfacial Shear Strength
Linear Elastic Cox (Modulus = 3.06 GPa, typical value)	(129-144) MPa
nonlinear Cox (Secant Modulus = 1.71 GPa)	(105-117) MPa
Kelly-Tyson Model	(34-38) MPa

- *Model Interface Research*

The hydrophilic nature of model interfaces were characterized by coating fibers and glass plates with various molar compositions of γ -aminopropyl triethoxysilane (γ -APTES) and propyl trimethoxysilane (PTMS). An aqueous coating procedure, analogous to the procedure used in industry, was developed. Dynamic contact angle data from the model interfaces obtained by using equal chain length bonding (γ -APTES) and non-bonding (PTMS) silane coupling agents indicate that significant damage to the fibers can occur during their separation from the fiber tow. In addition, data on the E-glass plate specimens indicate that the hydrophilic character of a surface coated with PTMS is sensitive to the pH of the depositing solution. In addition, the hydrophilic character did not increase monotonically with increasing γ -APTES proportion of

total silane concentration. This suggests that at these higher proportions appreciable amounts of the amino head group on the γ -APTES may be oriented towards the glass surface, resulting in a more hydrophobic surface than expected based on the hydrophilic character at lower proportions. More research is being conducted to confirm these results. To resolve the issue of fiber damage during sample preparation a single fiber coater was designed and built. Fibers coated by this method should minimize damage during the sample preparation procedure.

- *Instrumentation Development*

Automated the single fiber fragmentation test by designing and building a specialized instrument that collects high resolution images under precisely controlled loading conditions. This will permit the development of standardized test procedures for assessing interfacial properties of polymer composites.

Outputs

Publications

G.A. Holmes, R.S. Parnas and D.L. Hunston, *Report on the Industry Workshop for On-line Composite Process Monitoring*, NISTIR 6044, (1997).

Presentations

Gale A. Holmes, Richard C. Peterson, Donald L. Hunston, Walter G. McDonough, *Refinement of the Single Fiber Fragmentation Procedure*, 24th Annual Conference of the National Organization for the Professional Advancement of Black Chemist and Chemical Engineers, Orlando, FL, March 24-29, 1997.

Gale A. Holmes, Richard C. Peterson, Donald L. Hunston, Walter G. McDonough, *Impact of Nonlinear Viscoelasticity on Single Fiber Fragmentation Measurements*, General Electric Corporate Research Center, Schenectady, NY, August 1997.

Optical Coherence Tomography of Polymer Composites

J.P. Dunkers, F.R. Phalen Jr., C.G. Zimba, R.S. Parnas, B. Bouma¹ and J. Fujimoto¹

¹Electrical Engineering Department, Massachusetts Institute of Technology, Cambridge, MA

Objective

The objective is to evaluate nondestructively glass reinforced polymer composites using optical coherence tomography (OCT) and optical coherence microscopy (OCM). Of particular interest is the determination of residual porosity and the three-dimensional structure of the glass preform within the polymer matrix.

Technical Description

The development of technologies, such as ultrasound, computed x-ray tomography and magnetic resonance imaging has had an impact in a wide range of industries, including steel, ceramics, composites, polymers, and semiconductors, as well as medicine. The recent invention of OCT at MIT offers a new, cost-effective NDE tool. Preliminary work indicates that OCT can likely provide information on the microstructural properties of polymeric materials leading to improved designs and manufacturing techniques. In the context of polymer composites, rapid evaluation of fiber orientation and voids is a pressing need to support process and product design. Most of the techniques now used in industry involve labor-intensive and time-consuming evaluation of the material after the processing is complete.

The OCT technology is nondestructive, can be used to probe structure well beneath the surface, and can be used in real-time. OCT is essentially a light scattering technique that rejects multiple light scattering events by interferometrically combining a probe beam with a reference beam. Currently, a 25 fs, diode laser pumped, optical fiber cavity pulse laser is used. The laser can generate radiation at either 800 nm or 1300 nm wavelengths, and both wavelengths have been used successfully. The instrument focuses the light into the sample such that an interior focal plane is imaged at up to 5 μm resolution, thereby providing cross-sectional images of the sample. A computer controlled, piezoelectric actuated, optical fiber interferometer provides precise control of the focal plane, allowing cross-sectional images to be collected at spatial increments as small as 10 nm and at speeds as high as 8 frames/s. Limitations in image collection are primarily determined by optical density of the sample. Either highly absorbing or highly scattering material is difficult to image since single light scattering events do not occur deeply in such materials.

Planned Outcome

To provide the composites community a tool for predicting permeability in complex materials and in complex geometries not readily accessible with standard permeability measurement techniques.

External Collaborations

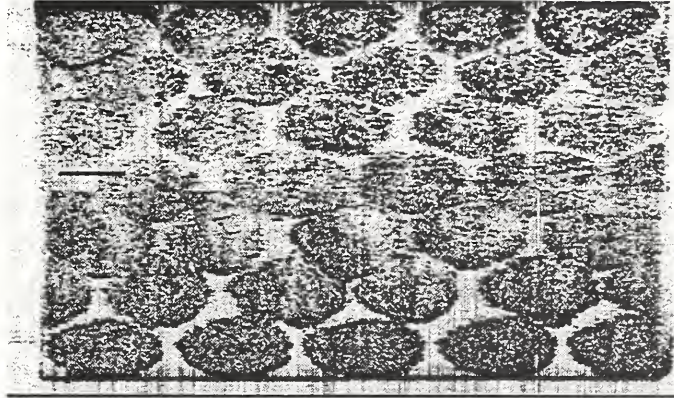
Academic: James Fujimoto, MIT, OCT imaging.

Accomplishments

A high degree of correlation between the residual porosity observed in OCT images and that observed by optical microscopy has been demonstrated in unidirectional glass / vinyl ester composites. The OCT images were obtained from within a block of material with dimensions of several millimeters on a side. Each image represents a transverse slice of the sample in a plane perpendicular to the upper surface. The presence of the fiberglass bundles, both tows and crossing threads, as well as voids, are clearly indicated in the OCT images. Optical microscopy of cross-sections of the same sample confirmed the presence of these features, albeit with considerable more effort required to prepare the sample.

The quality of OCT imaging is shown in the Figure for a sample in which the refractive indices of the unidirectional glass fibers and an epoxy polymer matrix are well matched. In this low

magnification image, two separate images taken from opposite sides of the sample were combined to show the entire 4 mm x 6 mm sample. The variety of pore shapes clearly demonstrates the difference between model structures and this real structure. In higher magnification images, individual fibers within each bundle can clearly be observed. The clarity of this image when combined with others obtained at different imaging planes provides a volumetric representation of the sample that can be used for the predictive modeling of permeability. Combination of the individual OCT images to form a three-dimensional digital representation of the sample is currently underway.



Outputs

B. Bouma, J. Dunkers, R. Parnas, J. Fujimoto, *Non-destructive Imaging of Biological and Synthetic Materials with Optical Coherence Tomography*, presented at the Workshop on Intelligent Processing and Inspection of Composite Materials, Baltimore, MD, August 1997.

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

W.G. McDonough, Y.-H. Kim, K.M. Flynn 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 single fiber fragmentation test (SFFT) are typically prepared by pouring premixed resin into an open rubber mold, and then curing the resin in an autoclave. This 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 dog bone samples thus prepared will be tested by SFFT to determine if the interface strength is degraded under rapid processing conditions. Another goal of the program is to use the technology described in the Liquid Composite Molding: Bulk Resin Measurements for Process Monitoring and Control project to monitor a fast curing polyurethane system. Whereas resin

transfer molded epoxy resins may take hours to cure, the rapid reaction of polyurethanes can result in gel formation in less than a minute. The Fourier Transform Infrared Sensor shall be used to monitor and control the curing of the much faster reacting polyurethane resin. An extension of this part of the project will be to assess the effect of processing changes on the interfacial shear properties.

External Collaborations

Industrial: Thomas Dearlove, Automotive Composites Consortium, processing effects on the interface.

James Entringer, The Dow Chemical Co., tailored resin supply.

Charles Seagrave, Bayer Corporation, tailored resin supply.

Accomplishments

An existing mold 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 and the Bayer system were very encouraging.

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

The Fourier Transform Infrared sensor has been used successfully to follow the cure of the polyisocyanurate system from Dow Chemical.

Impact

The ACC makes void free polyurethane composites in an SRIM process using a NIST developed procedure involving the controlled application of back pressure to the mold during and after injection.

Outputs

Workshop on Micro-Mechanics Measurement Technologies for Fiber-Polymer Interfaces, NIST, Gaithersburg, MD, May 28-30, 1997.

Publications:

R. Clough and W. McDonough, *The Measurement of Fiber Strength Parameters in Fragmentation Tests by Using Acoustic Emission*, Composite Science and Technology, 56, May 2, 1996.

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, rheological and mechanical properties, and performance. Molecular mass and its distribution have significant effects on the processibility of polymers through dramatic effects on their rheological properties. Mechanical properties and performance are significantly affected by the solid state structure formed during processing. Importantly, unlike many other common engineering materials, polymers exhibit mechanical properties that exhibit time dependent viscoelastic and aging behaviors, even at low temperatures. As a result, the focus of the program is on techniques that measure molecular mass and its distribution, solid state structure, mechanical properties, and rheological behavior of polymeric materials.

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

Adequate characterization of the time-dependent viscoelastic and aging behaviors of polymers requires large amounts of testing. For this reason, methods are developed that reduce the number of tests required to describe the nonlinear thermo-viscoelastic properties of polymers. The approach applies the frameworks of solid and fluid continuum mechanics to interrelate mechanical responses under different geometries of deformation and in varied deformation histories. Phenomenological models and underlying physical theories are tested using the NIST torsional dilatometer, conventional rotational rheometry, and servo-hydraulic mechanical testing machines.

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 mass and molecular mass distributions. Melt flow standards are used in the calibration of instruments used to determine processing conditions for thermoplastics. Rheological standards are developed for secondary calibrations of rheological instruments in industry and academia.

Significant Accomplishments

- Recertification of SRM 1482, a polyethylene narrow molecular mass standard, was completed and a report issued. The standard is intended for use in calibration and performance evaluation of instruments used to determine molecular mass and its distribution by size exclusion chromatography.
- Nearly 100 different procedures for preparing samples of synthetic polymers for analysis by matrix assisted laser desorption ionization mass spectrometry (MALDI-MS) were taken from the literature and placed on the World Wide Web for use by practitioners of MALDI-MS.
- Quantified the influence of the static magnetic field on spectral resolution in ^{13}C NMR under magic angle spinning conditions and reported findings to NMR user community to facilitate design of experiments that optimize resolution.
- A spatial ordering of the micelles consisting of graft copolymer of polystyrene (PS) and poly(methacrylic acid)(PMAA) was observed in TEM images of vitrified aqueous solutions using cryo-electron microscopy. Furthermore, the micelles appear to be connected by "arms" hypothesized to consist of the PMAA corona. The observed structure differs from disordered morphology seen using conventional drying and staining methods, suggesting that the latter perturbs the structure.
- A statistical procedure was developed to characterize uncontrolled systematic errors and noise effects on Small Angle Scattering (SAS) data. Modeling studies and real data demonstrate that adequate characterization of the precision of SAS data is not possible unless both noise and systematic error are presented to the end user. This finding will provide important input into the development of standardized data reduction and data transport tools for the SAS community.
- NIST has joined four industrial laboratories in the Participating Research Team (PRT) for the Advanced Polymer Beamline at Brookhaven National Laboratory. Data taken during the commissioning phase demonstrated wavevector range and resolution much superior to laboratory based facilities. When fully implemented, this beamline will provide real-time simultaneous small and wide angle x-ray scattering with high incident flux and multiple area detectors for dynamic measurements. Beam time available through PRT membership will complement our in-house SAXS facilities and significantly enhance capabilities available for internal research and industrial collaborations.
- The first ever comparison between time-strain and time-temperature superposition master curves was made. The stress relaxation master curves obtained from time-strain superposition are not the same as those obtained from time-temperature superposition. This severely limits the use of the material clock class of nonlinear constitutive equations based on time-strain superposition in materials modeling.

- The results from aging experiments on polycarbonate demonstrate that the conventional expectation of a singularity in the viscosity at approximately 50 °C below T_g is not observed. This result is in agreement with recent theoretical developments in these laboratories and dramatically alters the conventional view of molecular mobility as the glass transition is traversed.
- An isochoric glass transition was observed in dilatometric experiments on polycarbonate. This discovery strongly brings into question the validity of free volume models of the glass transition that are commonly used to describe thermal behavior of solid polymers during processing.
- Demonstrated by model calculations that structural recovery in polymeric glasses can dramatically affect the heat flow signal in modulated DSC measurements. This finding is important to users of modulated DSC instruments as it helps them to avoid misinterpretation of data due to structural recovery induced artifacts.
- Demonstrated by model calculations of structural recovery that dynamic heat spectroscopy results are a simple manifestation of structural recovery in high fictive temperature glasses. This leads to a different interpretation of dynamic heat capacity from that previously used to interpret such experiments. This could have profound implications for the relationship between structural recovery and fluctuations in complex fluids.
- An international round robin was initiated to study the thermoviscoelastic behavior of a research grade polycarbonate. The co-leader on the project is Prof. J.M. Hutchinson of the Aberdeen University in Scotland with eight confirmed participants and five tentative participants. This round robin will help to resolve the fundamental issues involved in the reports from various laboratories of different (or not) fictive temperatures for different processes in glass forming liquids.
- Established that the distribution of the shear strain along the interface near the crack tip in mode II fracture conforms to a power law singularity under small as well as large scale yielding conditions. This changes the paradigm by which researchers model large deformation crack tip singularities. There was no prior solution to the large scale yielding problem in mode II fracture conditions.
- Discovered a transition in craze growth rate in stress relaxation conditions for a styrene-acrylonitrile copolymer. The logarithmic craze growth rate decreases by approximately a factor of five in going from below to above the transition aging time. If this is a universal behavior for all polymers it implies that the long term performance may be enhanced due to the aging process stabilizing the material against craze growth.
- Demonstrated that a hybrid viscoelastic constitutive model can predict multi-step stress relaxation and creep results for polyurethane elastomers to within approximately 10% when

the history is primarily one of increasing deformation or stress. This approach to nonlinear viscoelasticity will lead to simple test methods for characterizing the non-linear material parameters needed in computer simulations of, for example, blow molding processes.

Standard Reference Materials

Charles Guttman, William Blair, Bruno Fanconi and John Maurey

Objective

The objective is to 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 mass 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 Mass 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 mass of these polymers. Yet, few SEC calibration standards are available on the market for the calibration of high temperature SEC. Molecular mass fractions with M_w/M_n of less than 1.2 are the most useful materials for calibrating SEC. The NIST polyethylene standard reference materials are the only available narrow fractions of polyethylene. These SRM's will soon be out of stock.

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

The original fractionation of a broad distribution polyethylene that provided the fractions previously certified also yielded other fractions including ones with molecular masses around (5,000, 75,000 and 160,000) g/mole in sufficient quantity to produce three additional narrow fraction polyethylene SRM's.

These new materials along with current SRM 1482 and 1483 would provide a set of polyethylene fractions covering the molecular mass range from 5,000 g/mol to 160,000 g/mol. This will provide the polymer industry with an adequate set of molecular mass 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 SRM's measurements are conducted leading to recertification of SRM's that are out of stock, exceeded normal shelf life, or were repackaged for market reasons. If the SRM is out of stock then a complete certification must be carried out on a new batch of material, preferably one with molecular mass characteristics similar to 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 mass such as SEC or viscometry and compare results with those obtained during the original certification.

Planned Outcomes

The three new 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 5,000 g/mol to 160,000 g/mol.

Accomplishments

New Polyethylene Molecular Mass Standards

All three polyethylene fractions have been purified by recrystallisation and bottled by SRMP. Preliminary SEC analysis was conducted to check for homogeneity. The dynamic light scattering apparatus was modified to conduct static light scattering measurements at elevated temperatures. A glass rod has been calibrated against benzene as a Rayleigh scattering standard. It will be used to determine the effective Rayleigh ratio of the solvent, trichlorobenzene, at 130 °C. The calibrated trichlorobenzene will be used to calibrate the apparatus at regular intervals during measurements on the polymer solutions.

Polyethylene SRM 1482, a narrow molecular mass fraction

Recertification of SRM 1482, a polyethylene narrow molecular mass standard, was completed and a report issued. The standard is intended for use in calibration and performance evaluation of instruments used to determine molecular mass and its distribution by size exclusion chromatography.

Polystyrene SRM 706

Recertification of SRM 706 was completed and a report issued. No differences between the new standard and the previously certified material were detected in either the molecular mass, as determined by light scattering, or in the molecular mass distribution as determined by gel permeation chromatography.

Outputs

Standard Reference Materials

SRM 1482, Polyethylene Narrow Fraction Molecular Mass Standard

SRM 706a, Polystyrene Molecular Mass Standard

Publications

C.M. Guttman, W.R. Blair and J.R. Maurey, *Recertification of SRM 1482a, a Polyethylene*, NISTIR 6054.

C.M. Guttman, W.R. Blair and J.R. Maurey, *Recertification of SRM 706a, a Polystyrene*, NISTIR, in press.

Mass Spectrometry of Polymers

Charles Guttman, William Blair and William Wallace

Objectives

The objective is improved calibration standards for size exclusion chromatography (SEC) to make this technique, widely used by the polymer industry, more reliable for characterizing the molecular mass distribution (MMD) and the moments of the MMD of synthetic polymers. Explore mass spectrometry as a method to measure the MMD and the moments of the MMD of 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 Spectroscopy (MS) allows the detection of the mass spectrum of whole undegraded polymer molecules with molecular masses up to 300,000 g/mol. A MALDI TOF MS was purchased and installed in April, 1997. The instrument is part of an effort to explore the usefulness of this technique as a method to determine the absolute molecular mass of a polymer molecule for the production of molecular mass SRM's.

External Collaborations

In collaboration with S. Samat of Ravenshaw College, Cuttack, India, matrix materials are developed which will be compatible with synthetic polymers.

In collaboration with Professor J. Girard at American University methodology is developed to compare SEC and MALDI-TOF-MS.

Accomplishments

Initial work has focused on the repeatability of the spectra obtained as a function of various sample preparation methods, and also studies on instrument operation fundamentals and new matrix materials.

In collaboration with NIST staff in the Statistical Engineering Division methodology is developed to analyze mass spectral data of synthetic polymers. Other absolute methods (light scattering or membrane osmometry) yield only one moment of the molecular mass distribution (MMD) of synthetic polymers. Obtaining the MMD from the SEC is fraught with broadening problems and interpretation problems. MALDI-TOF-MS of the whole synthetic polymer can, in principle, yield the overall MMD in which (in the best case) at least 20 different oligomer peaks can be analyzed.

Recently some researchers have reported limited success in comparing the molecular mass distribution (MMD) of synthetic polymers obtained from Size Exclusion Chromatography (SEC) with the MMD obtained from time of flight mass spectrometry (TOF-MS). As part of the NIST effort to develop the applicability of MALDI-MS to the determination of the absolute molecular masses and molecular mass distributions of synthetic polymers, a general methodology is under development to compare the MMD obtained from MALDI TOF MS using a number detector

with the MMD obtained from SEC using a variety of SEC detectors. The effects of SEC broadening are included in this comparison.

Nearly 100 different procedures for preparing samples of synthetic polymers for analysis by matrix assisted laser desorption ionization mass spectrometry (MALDI-MS) were taken from the literature and placed on the World Wide Web for use by practitioners of MALDI-MS.

Outputs

Publications

C.M. Guttman, W.R. Blair, P.O. Danis, *Mass Spectroscopy and SEC of SRM 1487, a Low Molecular Weight Poly(methyl methacrylate) Standard*, J. Polym. Sci., Polym. Phys., 35, 2409 (1997).

C.M. Guttman, W.R. Blair, P.O. Danis, *Comparison of Copolymer Distribution Using SEC and MALDI TOF MS of SRM 1487, A Low Molecular Weight poly(methyl methacrylate)*, Proceeding of the American Chemical Society Division of Polymeric Materials: Science and Engineering, 77, 28, (1997).

Presentations

C.M. Guttman, W.R. Blair, P.O. Danis, *Mass Spectroscopy and SEC of a Poly(methyl methacrylate) NIST Standard*, The 45th ASMS Conference on Mass Spectrometry and Allied Topics, Palm Springs, CA, June 1997.

W. Wallace, C.M. Guttman, W.R. Blair, *Comparison of MALDI-TOF with Other Absolute Methods to Determine Synthetic Polymer Molecular Weight*, The 45th ASMS Conference on Mass Spectrometry and Allied Topics, Palm Springs, CA, June 1997.

C.M. Guttman, W.R. Blair, P.O. Danis, *Comparison of Copolymer Distribution Using SEC and MALDI TOF MS of SRM 1487, a low molecular weight poly(methyl methacrylate)*, American Chemical Society Fall Meeting, Las Vegas, NV, September 1997.

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

The NMR work is aimed at both development of new NMR techniques for characterizing polymers and application of these and other methods to uncover new insights into polymer structure. Activities in both facets were undertaken in FY 97. The following techniques have been drawn upon in the NMR 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, which cause large fluctuations in the local magnetic fields at the protons, a process which along with spin diffusion is the mechanism for perturbing the proton relaxation.

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

External Collaborations

- Yi Feng, Goodyear Tire and Rubber Co., Akron, OH, (ionomer blends)
- Professor Robert Weiss of Univ. of Connecticut, Storrs, CT (ionomer blends)
- Professor Norritsu Terashima of Nagoya, Japan (lignin synthesis)
- Satish Kumar of Georgia Institute of Technology, Atlanta, Ga. (modified PBZT)
- R. Alamo and L. Mandelkern of Florida State University, Tallahassee, FL (isotactic poly(propylene), iPP's)
- J.A. Randall of Exxon Research, Baytown, TX (iPP's)
- E. Pérez of the Institute for Polymer Science in Madrid, Spain (iPP's, EVOH copolymers)
- R. Tycko of National Institutes of Health, Bethesda, MD (¹³C resolution)

Planned Outcomes

-Determination of mechanism(s) whereby different defect structures in isotactic polypropylene (iPP) dictate properties. The presently available variety of catalyst structures (particularly metallocene) and polymerization conditions now offers a great variation in the nature, amount, and distribution of defect structures in iPP products; hence, it is technologically important to reach a better understanding of the extent to which each kind of defect is incorporated into the crystalline phase (or partitioned between the crystalline and non-crystalline phases). ¹³C spectra offer the possibility to make such assessments.

- A better understanding of chemical changes and their uniformity in high-temperature chars when additives are added 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. Certain characteristics of chars render spectroscopic characterization more difficult than for other organic materials. For example, there is the question of whether the unpaired electrons generated in the charring process obscure a sufficient number of spins so as to make the NMR measurements non-quantitative or non-representative of the whole sample. Also important is the question whether ^{13}C signals, generated via cross-polarization from the protons, are seriously distorted as a result of the proton-poor character of chars. Cross-polarization is very important for generating better sensitivity for ^{13}C signals; so the latter is a question motivated mainly by sensitivity considerations.

- A better understanding of what controls spectral resolution in the ^{13}C MAS spectra of strongly-dipolar-coupled, crystalline polymers. This will have a wide-ranging impact on everyone who is trying to improve spectral resolution in organic solids.

- An assessment of the effectiveness of strategies whereby high-strength, high-temperature-stable fibers like Poly(benzo-bis-thiazole), PBZT, are chemically modified so that their compressive strengths can be improved via lateral crosslinking. Weak compressive strength greatly limits applications for lightweight fiber-reinforced composite materials. ^{13}C spectra are useful for assaying the level of crosslinking.

Accomplishments

Characterization of isotactic polypropylene- With assistance from external collaborators, a suite of iPP's was obtained. The iPP's have different types of chemical defects whose identity and concentration have been characterized via solution-state high-resolution NMR. These samples are examined to elucidate the influence of chain defects on crystal morphology. Defect structures which are accepted into the crystal lattice are expected to adopt one (or two) well defined conformations in order to impose the least perturbation on the 3_1 helix of the iPP chain. A corollary expectation, then, is that ^{13}C resonances for defects in well-defined geometries will have linewidths comparable to the backbone resonances. A full treatment of this problem involves completing four tasks: a) demonstration that ^{13}C signals from the crystalline and the non-crystalline regions can be separately identified. b) demonstration that defect resonances are visible and have measurable relative intensities in either the spectrum of the crystalline or the non-crystalline carbons. c) assignment of the defect resonances, or groups of resonances, to particular kinds of defects. d) assignment of the defect resonance positions to particular conformations of the chain in the vicinity of the defect. Item d) also provides the critical information about the number of carbons, per defect site, that these resonances represent.

Solid state spectra were obtained and separated into features arising from either 'crystalline' or 'non-crystalline' regions. Approximately five resonance positions were identified for the 'mmrrmm' stereo defect and at least two for the 2,1 defect. {The nomenclature for stereo-sequencing usually defines a 'meso' or 'm' **dyad** as two consecutive monomers that polymerize with their methyl groups on the same side of the all-trans zigzag plane (defined by the positions of the carbon backbone atoms); a 'racemic' or 'r' **dyad** has methyl groups on opposite sides of this plane. The 2,1 defect refers to a head-to-head monomer sequence.} The assignments are based on the 'crystal' spectra of different samples with known chemical defect structures.

Another defect, termed 1,3 in which an n-propylene repeat unit replaces the usual isopropyl unit, offers no sharp resonances in the 'crystal' spectra, only a shoulder of broad additional intensity appears. Moreover, a mobility greater than that of the crystalline backbone carbons is associated with carbons of the 1,3 defect. These results are consistent with the hypothesis that the 1,3 defects are concentrated at the interfaces. The intensities of approximately $\frac{1}{2}$ of the defect structure resonances may be treated quantitatively, the remaining resonances overlap the main peaks too strongly for quantitative treatment. If it is hypothesized that each of the most easily quantified defect resonances represents **all** of the carbons at **one particular** site at or near a defect, then it is concluded that the 'mmrrmm' stereo defect has a concentration in the crystal which is about 35 % to 50 % of its overall concentration and the 2,1 defect has a similar concentration in the range from 25 % to 55 %. At this stage, it looks like the partitioning of 'mmrrmm' stereo defects is comparable to 2,1 defects and that these defects indeed take on very well defined configurations in the crystalline lattice.

Characterization of polymer chars - This work is carried out with Dr. Jeff Gilman of the Fire Science Division at NIST. Our emphasis this year has been on the quantitative aspects of the ^{13}C spectra of chars. One aspect is the role of unpaired electrons in masking certain portions of the signal. It is found that these electrons do indeed reduce the ^{13}C signal strength. A second aspect involved the observation that lineshapes observed using cross-polarization from protons, are different from ^{13}C lineshapes obtained by tediously waiting for the recovery of Boltzmann spin populations. Therefore, the representative character of ^{13}C spectra seems better using Boltzmann populations. Whether the latter spectra are truly representative also depends on the larger scale compositional inhomogeneity of the chars and this is being further investigated using proton spin diffusion techniques.

Spectral Resolution in ^{13}C spectra with magic angle spinning - One of the main activities was to gather good linewidth data for LPE at high field (9.4 T at NIH). These data enabled quantitation of the non-linear influence of the static magnetic field on resolution. Extensive computations on other data were performed in order to estimate the correlation time for proton spin fluctuations for protons attached to ^{13}C nuclei. This correlation time dictates the timescale over which certain "second-averaging" schemes must apply in connection with the implementing of 'improved' proton decoupling schemes.

Modified Poly(benzo-bis-thiazole) - Methyl-modified, heat-treated samples were analyzed for the extent of crosslinking during heat treatment. It was concluded that the strategy of crosslinking during heat treatment appears to be a rather inefficient process. In the most favorable case a fraction (0.1 to 0.2) of methyl groups are transformed into methylene crosslinks; however, there is also a substantial loss of the other methyls, mostly in the form of methane, and a serious embrittlement which accompanies this crosslinking.

Characterization of ethylene/vinyl alcohol copolymer - It was shown that good estimates of long spacing, co-monomer composition and crystallinity in an ethylene/vinyl alcohol copolymer

can be made based on solid-state proton NMR data which takes only about 20 minutes to acquire. Normally one would need two or three techniques to estimate these parameters.

Outputs

Publications

J.W. Gilman, S. Lomakin, T. Kashiwagi, D.L. VanderHart, and V. Nagy, *Characterization of Flame Retarded Polymer Combustion Chars by Solid-State ^{13}C and ^{29}Si NMR and EPR*, American Chemical Society Polymer Preprints, 38, 802 (1997).

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

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N. Terashima, J. Hafrén, U. Westermark and D.L. VanderHart, *Structure of Lignin in Ginkgo Wood Determined by a Combination of Specific ^{13}C -Enrichment Technique and Solid State NMR Spectroscopy*, *Proceedings of the 9th International Symposium on Wood and Pulping Chemistry*, in press.

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X. Hu, S. Kumar, M.B. Polk and D.L. VanderHart, *Tetramethylbiphenyl Substituted Poly(benzobisthiazole) 2. Synthesis and Characterization of Polymers*, *J. Polym. Sci. Polym. Chem.*, submitted.

X. Hu, S. Kumar, M.B. Polk and D.L. VanderHart, *Poly(Benzobisthiazole) with Tetramethylbiphenyl Moiety in the Main Chain*, *American Chemical Society Polymer Preprints*, submitted.

Presentations

D.L. VanderHart, *Aspects of ^{13}C NMR of Solid Polymers: Crystallinity of Cellulose and its Derivatives, Partitioning of Defects in Semicrystalline Polymers; and Spectral Resolution in Strongly-Coupled Systems*, Institute for Chemical Research, University of Kyoto, Japan (Uji campus), October 1996.

D.L. VanderHart, *Comments on the Interpretation of Proton Spin Diffusion Data in Polymers and on ^{13}C Resolution in CPMAS Spectra of Strongly Coupled Carbons*, Chemistry Department, University of Kyoto, Japan, October 1996.

D.L. VanderHart, *Characterization of Heterogeneities in Solid Polymers and Polymer Blends Using Proton Spin Diffusion*, 10th Symposium of the Society of Solid State NMR for Materials, Kyoto, Japan, October 1996.

D.L. VanderHart, *Characterization of Heterogeneities in Solid Polymers by Solid State NMR*, Department of Polymer Chemistry, Tokyo Institute of Technology, Japan, November 1996.

D.L. VanderHart, *Characterization of a Decorated Polymer Blend by Solid State NMR*, Department of Polymer Science and Technology, Superior Counsel for Scientific Investigation, Madrid, Spain, November 1996.

D.L. VanderHart, *Contributions to CPMAS Linewidths in Hydrocarbons for Strongly-Coupled Carbons Using CW Proton Irradiation: Polyethylene*, 38th Experimental NMR Conference, Orlando, FL, March 1997.

D.L. VanderHart, *Contributions to CPMAS Linewidths in Hydrocarbons for Strongly-Coupled Carbons Using CW Proton Irradiation: Polyethylene*, Gordon Conference on Magnetic Resonance, Henniker, NH, June 1997.

Characterization of Polymer Morphology by Microscopy Techniques

C. L. Jackson

Objectives

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

Technical Description

The characterization of 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), as well as 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, dendrimers and organic-inorganic hybrid materials.

External Collaborations

Dr. Henri Chanzy of CERMAV and CNRS in Grenoble, France.

Dr. Frank Booy of the Laboratory of Structural Biology, NIAMS, NIH, Bethesda, MD.

Dr. Kennecorwin Gardner, DuPont Company, Wilmington, DE

Dr. Jonathan Coddington, National Museum of Natural History, Smithsonian, Washington D. C.

Professor Reimund Stadler, University of Bayreuth, Bayreuth, Germany

Dr. Donald Tomalia, Michigan Molecular Institute, Midland, MI

Accomplishments

- The characterization of dendrimer molecules of poly(amidoamine) (PAMAM) was achieved for generations ten (G-10) down to G-5, ranging in size from 14.7 nm to 4.5 nm, respectively, using biological-type TEM staining methods. For G-10 dendrimer, cryoelectron microscopy was also possible, where the molecules were imaged in vitrified solvent at very low temperature. This technique avoids both drying and staining of the particles and may give a more accurate representation of the size and shape of dendrimers in solution. For G-10, the sizes measured for both methods were similar, but the shapes observed by the cryo technique were more polyhedral than strictly spherical, as seen for the positively stained specimens. This work was done in collaboration with Dr. Frank Booy (NIH) and the samples were obtained from Dr. Donald Tomalia (MMI).
- A spatial ordering of the micelles consisting of graft copolymer of polystyrene (PS) and poly(methacrylic acid)(PMAA) was observed in TEM images of vitrified aqueous solutions using cryo-electron microscopy. Furthermore, the micelles appear to be connected by "arms" hypothesized to consist of the PMAA corona. The observed structure differs from disordered morphology seen using conventional drying and staining methods, suggesting that the latter perturbs the structure. This work was done in collaboration with C. C. Han (NIST) and C. L. Gettinger (3M, previously at NIST).
- Semi-crystalline block copolymers of polystyrene (PS), polycaprolactone (PCL), and polybutadiene (PB) were crystallized from solution to form single crystals of PCL with the amorphous block forming a thin layer on the crystal surfaces. The morphology and electron diffraction patterns were obtained by TEM and the shape and thickness of the crystals were measured by atomic force microscopy (AFM) in the non-contact mode. This work was done in collaboration with Prof. R. Stadler (University of Bayreuth) and future studies of the relative block lengths of the amorphous and crystalline blocks and a comparison with the morphology in bulk specimens will be made to better understand the unique properties of semi-crystalline block copolymers of this type.
- In collaboration with K. Gardner (DuPont) and J. Coddington (Smithsonian), the morphology of spider silk from the brown recluse family, which produces a ribbon-like morphology because of a unique slit-die spinneret, has been characterized. TEM and electron diffraction data in combination with SEM and X-ray diffraction data from DuPont has been obtained to characterize the crystal structure. In addition, AFM was used to

measure the thickness of the silk ribbons. This work is stimulated by DuPont's interest in artificial silk produced by genetic engineering.

- TEM was used to help characterize the morphology in polymer/clay nanocomposite materials and associated char materials being studied in the Fire Science Division at NIST (with Jeff Gilman, BFRL) for their revolutionary flame retardant behavior. A comparison of the original delaminated nylon-6/clay (5%) nanocomposite to the char of the material suggested that the delaminated structure subsequently collapses during combustion and returns to a layered clay structure that resembles the original material.

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., 37, 1 (1997).

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C.L. Jackson, H.D. Chanzy, C.C. Han, V. Balsamo, R. von Gyldenfeldt and R. Stadler, *Surface Topology and Organization of Single Crystals from Polystyrene-Polycaprolactone (PS-*b*-PCL) and PS-Polybutadiene-PCL (PS-*b*-PB-*b*-PCL) Block Copolymers*, American Chemical Society PMSE Preprints, 77, 650 (1997).

C.L. Jackson and B.J. Bauer, *Synthesis and Characterization of Organic-Inorganic Interpenetrating Polymer Networks*, Society of Plastics Engineers ANTEC '97, 1908 (1997).

C.L. Jackson and G.B. McKenna, *Vitrification and Crystallization of Organic Liquids Confined to Nanoscale Pores*, Chem. Mater., 8, 2128 (1996).

Presentations

C.L. Jackson, *Characterization of Dendrimer Molecules by Staining and Cryoelectron Microscopy Techniques*, American Chemical Society, Las Vegas, NV, September 1997.

C.L. Jackson, *Surface Topology and Organization of Single Crystals from Polystyrene-Polycaprolactone (PS-*b*-PCL) and PS-Polybutadiene-PCL (PS-*b*-PB-*b*-PCL) Block Copolymers*, American Chemical Society, Las Vegas, NV, September 1997.

C.L. Jackson, *Characterization of Polymer Micellar Suspensions and Dendrimer Solutions by Cryo-electron Microscopy* (poster) and *Morphology Evolution and Phase Separation Kinetics in a Polymer Blend with Diblock Copolymer Additive*, NIST-ERATO Joint Meeting on "Multicomponent Polymers and Polyelectrolytes", Gaithersburg, MD, June 1997.

C.L. Jackson, *Synthesis and Characterization of Organic-Inorganic Interpenetrating Polymer Networks*, Society of Plastics Engineers, Toronto, Canada, April 1997.

C.L. Jackson, *Morphology and Phase Separation Kinetics in a Ternary Polymer Blend*, Lehigh University, Bethlehem, PA, November 1996.

Structural Characterization of Polymers by Small Angle X-Ray Scattering

J.D. Barnes and T.J. Prosa

Objectives

The objectives are to maintain a state-of-the-art Small Angle X-ray Scattering (SAXS) Facility that incorporates improvements in analysis methods and instrumentation to expand the use of SAXS as a technique for characterizing materials and processes. The SAXS Facility is promoted as a user facility for outside industrial clients and to support research within the Polymers Division.

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. The facility has a two-dimensional area detector capability and flexible sample handling for oblique incidence scattering, elevated temperature measurements, liquid samples, and uniaxial deformation. Test and analysis capabilities are constantly upgraded and implemented as the need or opportunity arise.

External Collaborations

The SAXS facility was used during the year for projects with outside users that fall into three categories. Collaborative research that is expected to lead to technical publications are currently underway with Mobil Chemical Co R&D Laboratory (SAXS and Wide Angle X-ray Diffraction, WAXD, orientation texture in HDPE films) and with Air Products Company (microstructure of high performance polyurethanes). Proprietary measurements in which the industrial client is interested in protecting sensitive data were performed by W. R. Grace and Mobil Chemical Co. Finally, the facility attracts collaborators from the academic community; staff from the University of Maryland study processing methods for producing oriented block copolymers as starting materials for nano-engineered polymer products.

NIST Internal Collaborations

Extensive measurements on dendrimers were carried out with the Polymer Blends and Processing Group. Studies on SAXS from several glassy polymers and, particularly semicrystalline polymers below their T_g , demonstrated that the scattering at low q differs from that which is to be expected from a liquid. Although the appearance of scattering from inclusions on the micrometer distance scale is not surprising, the observation of an additional component exhibiting a $q^{-2.5}$ power law dependence is, however, anomalous. A new study pursuing an understanding of such results is in its early stages. The Polymers Divisions 4-circle wide-angle x-ray diffractometer is aiding this work by its ability to characterize orientation in the amorphous component of these materials.

NIST has joined four industrial laboratories in the Participating Research Team (PRT) for the Advanced Polymer Beamline at Brookhaven National Laboratory. Data taken during the commissioning phase demonstrated wavevector range and resolution much superior to laboratory based facilities. When fully implemented, this beamline will provide real-time simultaneous small and wide angle x-ray scattering with high incident flux and multiple area detectors for dynamic measurements. Beam time available through PRT membership will complement our in-house SAXS facilities and significantly enhance capabilities available for internal research and industrial collaborations. In addition, the complementarity of SAXS and SANS has played an important role in the dendrimer work and in work on metal uptake by bacteria carried out with the NIST Center for Neutron Research.

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

- Provided Proprietary usage beam time to Mobil Chemical Co. R&D Laboratories and W. R Grace Co.
- Upgraded SAXS area detector to provide improved electronic stability and to gain better resolution.
- Demonstrated, in collaboration with University of Maryland researchers, that shear using a channel die when crystallizing EtP/Et/EtP triblock copolymers (EtP = ethylene - propylene copolymer, E = ethylene) produces two distinct kinds of orientation that depend on cooling history.
- Provided support to dendrimers project within Polymer Blends and Processing Group.

Outputs

Publications

B.J. Bauer, D-W Liu, C.L. Jackson, and J.D. Barnes, *Epoxy/SiO₂ Interpenetrating Networks*, Chapter 17 in *IPN's Around the World: Science and Engineering*, S. C. Kim and G. L. Sperling, Eds, John Wiley and Sons, Ltd., p. 279 (1997).

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*, *Polymer Science and Engineering*, 37, 1480 (1997).

R. Hu, W.S. Lambert, and J.D. Barnes, *Structure-Property Correlation in Stretched LLDPE Film Using Oblique Incidence Small Angle X-ray Scattering*, *Polymer Science and Engineering*, 37, 1475 (1997).

Presentation

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*, Materials Research Society, Boston, MA, December 1996.

Descriptive Measures for Small-Angle Scattering (SAS)

J. D. Barnes and T. J. Prosa

Objective

The objective is to improve the usability, precision and accuracy of SAS data. The development of software tools for reducing SAS data and for characterizing the performance of SAS measuring systems are the primary focus.

Technical Description

Experience with the user community for the NIST Digital SAXS Camera demonstrated that a lack of straightforward techniques for interpreting data from SAS patterns in "real space" terms is a barrier to the wider acceptance of this methodology, particularly in industry. This project seeks to devise software tools that will make this translation easier for inexperienced users of SAS methods.

Computer simulations and studies on model scattering systems are used in combination to develop and validate appropriate analytical tools. The simulations generate "virtual" SAS experiments whose results can be used as test cases for the development of improved algorithms for data reduction. The virtual SAS experiments also help to assess the importance of instrumental factors, interfering scattering sources, and noise. Scattering experiments on the model systems provide the relevant experimental data.

During FY 1997 three principal lines of investigation were pursued: (1) a careful study of the precision of SAS data from both real and virtual experiments, (2) methods for modeling data

from isolated spherical polymer molecules in dilute solution, and (3) characterization of the scattering from oriented dispersed particulate scatterers in the form of pores in commercial track-etched membranes (rod-like particles).

External Collaborations

This project is closely linked to the worldwide SAS community through the Commission on Small-Angle Scattering of the International Union of Crystallography and the Small Angle Scattering Special Interest Group of the American Crystallographic Association.

Accomplishments

- A statistical procedure was developed to characterize uncontrolled systematic errors and noise effects on Small Angle Scattering (SAS) data. Modeling studies and real data demonstrate that adequate characterization of the precision of SAS data is not possible unless both noise and systematic error are presented to the end user. This finding will provide important input into the development of standardized data reduction and data transport tools for the SAS community.
- Monte Carlo methods have been shown to be an effective means of generating “virtual” SAS experiments for testing data reduction and model fitting procedures as well as for characterizing instrumental effects and counting noise.
- The SAS Worldwide web site (<http://www.nist.gov/sas>) has grown to include over 300 subscribers from the international SAS community as reflected in the subscriber list of its associated list server.

Outputs

Publications

J.D. Barnes and T.J. Prosa, *Statistics in Area Detector Data Reduction*, Advances in X-Ray Analysis, submitted.

Presentations

T.J. Prosa and J.D. Barnes, *Parameterization of Morphology in Small-Angle Scattering*, Fall Meeting of the Materials Research Society, Boston, MA, December 1996.

J.D. Barnes and T.J. Prosa, *Statistics in Area Detector Data Reduction*, Amer. Crystallographic Assn, St. Louis, MO, July 1997.

T.J. Prosa and J.D. Barnes, *Descriptive Measures for Small Angle Scattering: Track-etched Membranes*, St. Louis, MO, July 1997.

J.D. Barnes and T.J. Prosa, *Statistics in Area Detector Data Reduction*, Denver X-Ray Conference, Steamboat Springs, CO, August 1997.

Other

Dr. J.D. Barnes organized three sessions on Small-Angle Scattering at the annual meeting of the Amer. Crystallographic Assn. held July 20-24 in St. Louis, Mo.

Nonlinear Viscoelasticity of Solid Polymers

G.B. McKenna, D.M. Colucci and P.A. O'Connell¹

¹University of Leeds, U.K.

Objectives

The objectives are to develop measurement methods, to characterize the nonlinear viscoelastic response of solid polymers and to evaluate the range of validity of material clock models for the prediction of the behavior of solid polymers.

Planned Outcomes

- A comprehensive materials data base for the nonlinear viscoelastic properties of a single glassy polymer in multiple deformation geometries (tension, torsion, compression) in stress relaxation conditions is to be created. The data are to be available for researchers to evaluate different constitutive models of polymer glasses.
- Establish the range of validity of reduced time based nonlinear viscoelastic constitutive laws to the behavior of solid, glassy polymers.
- Provide fundamental knowledge of the nonlinear viscoelastic response of glassy polymers.

Task 1. Time-Temperature, Time-Aging Time and Time-Strain Superposition below the Glass Transition

G.B. McKenna, P.A. O'Connell

Technical Description

Reduced time or material clock models of polymer behavior have been proposed as potentially powerful methods of introducing nonlinear behavior into the constitutive description of polymeric solids. Such models are a conceptual extension of the time-temperature and time-aging time superposition principles to the mechanical domain. However, there are few systematic studies that evaluate the validity of such concepts. Torsional stress relaxation measurements are used to characterize and compare time-temperature, time-aging time and time-strain superposition responses of a polycarbonate glass in the temperature range from 30 °C to 135 °C; that is, below the glass transition temperature.

External Collaborations

This work is being performed using the polycarbonate grade that is being used in the GM/GE ATP project and the results of this study are reported periodically to the appropriate technical team members at GM and GE.

Accomplishments

- Showed that time-temperature superposition is a valid descriptor for the viscoelastic response below the glass transition temperature in polycarbonate. The KWW (Kohlrausch-Williams-Watts) stretched exponential function often used in liquid and glassy state relaxation, however, does not successfully describe the master curve.
- The first ever comparison between time-strain and time-temperature superposition master curves was made. The stress relaxation master curves obtained from time-strain superposition are not the same as those obtained from time-temperature superposition. This severely limits the use of the material clock class of nonlinear constitutive equations based on time-strain superposition in materials modeling.
- The results from aging experiments on polycarbonate demonstrate that the conventional expectation of a singularity in the viscosity at approximately 50 °C below T_g is not observed. This result is in agreement with recent theoretical developments in these laboratories and dramatically alters the conventional view of molecular mobility as the glass transition is traversed.

Outputs

Publications

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

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, in press.

P.A. O'Connell and G.B. McKenna, *Large Deformation Response of Polycarbonate: Time-Temperature, Time-Aging Time and Time-Strain Superposition*, Polymer Engineering and Science, in press.

P.A. O'Connell, C.R. Schultheisz and G.B. McKenna, *The Physics of Glassy Polycarbonate: Superposability and Volume Recovery*, The Physics of Glassy Polymers, ed. By A. Hill and M. Tant, American Chemical Society books, 1998, in press.

G.B. McKenna, *Torque and Normal Force Measurements in Viscoelastic Solids*, Proceedings, 10th International Conference on Deformation, Yield and Fracture of Polymers, Institute of Materials, Chameleon Press, London, 79-82, 1997.

P.A. O'Connell and G.B. McKenna, *Reduced Time Concepts and the Sub- T_g Response of A Polycarbonate Glass*, Proceedings, 10th International Conference on Deformation, Yield and Fracture of Polymers, Institute of Materials, Chameleon Press, London, 415-418, 1997.

P.A. O'Connell and G.B. McKenna, *Time-Temperature Superposition at Equilibrium in Polycarbonate below T_g* , Proc. NATAS 25th Annual Conference, September 1997, in press.

Presentations

G.B. McKenna, *Solid Mechanics in Glasses: Time, Temperature and Deformation Effects*, Institute of Materials Industries, Conference on 'Oriented Polymers and Composites,' Boucherville, Canada, October 1996.

G.B. McKenna, *Torque and Normal Force Measurements in the Study of the Nonlinear Response of Solid Polymers*, Society of Engineering Sciences Annual Meeting, Tempe, AZ, October 1996.

P.A. O'Connell and **G.B. McKenna**, *Time-Strain Superposition in Polymer Glasses*, American Physical Society March Meeting, Kansas City, MO, March 1997.

G.B. McKenna, *Torque and Normal Force Measurements in Viscoelastic Solids*, Churchill Conference on Deformation, Yield and Fracture of Polymers, Cambridge, England, April 1997.

P.A. O'Connell and **G.B. McKenna**, *Reduced Time Concepts and the Sub- T_g Response of a Polycarbonate Glass*, Churchill Conference on Deformation, Yield and Fracture of Polymers, Cambridge, England, April 1997.

G.B. McKenna, *Viscoelastic Behavior of Glass Forming Systems: Mechanical, Volumetric and Enthalpic Responses*, Institut Charles Sadron, Strasbourg, France, April 1997.

G.B. McKenna, *Time Dependent Properties of Polymers: Physical Aging, Viscoelasticity and their Implications for Long Term Use*, EMPA (Swiss Federal Materials Testing Laboratory), Dübendorf, Switzerland, April 1997.

G.B. McKenna, *Viscoelastic Behavior of Glass Forming Systems: Mechanical, Volumetric and Enthalpic Responses*, Polymers Division, NIST, Gaithersburg, MD, May 1997.

G.B. McKenna, *Time Dependent Processes in Polymeric Materials: Viscoelasticity, Aging and Failure*, Institute for Mechanics and Materials, Summer School, The Mechanics-Materials Linkage, Catholic University of America, Washington, DC, August 1997.

Task 2. Volumetric Behavior for Stress Relaxation Experiments in Tension and Compression of Polycarbonate below the Glass Transition Temperature

Technical Description

Few experiments are performed in stress relaxation conditions in which the volumetric response is measured. And while there is increasing evidence that the nonlinear viscoelastic response of polymeric glasses is not a simple function of the volume, it is essential that the volumetric response in such conditions be determined in order to separate the relative contributions of dilatational and deviatoric stresses to molecular mobility--i.e., nonlinear viscoelasticity. The technical approach is measurement of stress and volumetric responses during stress relaxation conditions in polycarbonate in tension and compression in the nonlinear viscoelastic, sub-yield regime. Biaxial extensometry is performed, using a modified lateral extensometer, on cylindrical samples to measure the lateral strain during uniaxial stress relaxation experiments. Experiments were performed in both tension and compression on samples that had been quenched from above the glass transition temperature to below it and aged for 24 hours at the testing temperature (22 °C) prior to testing. Stress and lateral strain measurements at constant axial strains were made for times to 3000 s. Two grades of polycarbonate were tested to investigate the possibility that the volumetric responses might be different because one sample yielded and the other fractured during tensile loading.

Accomplishments

- Discovered an apparent "implosion" event in glassy polycarbonate subjected to tensile and compressive deformations. Implosion means that upon tensile deformations, while the sample increases in volume initially, after long relaxation times at strains in the order of 0.03 to 0.04 the sample density becomes greater than that of the original, undeformed, polymer. In compression, implosion is manifested by a decrease in volume followed by a continuing densification. The two polycarbonates showed some implosion upon compression. However, the polycarbonate with the greatest propensity to implode in tension yielded while that which showed negligible tensile implosion fractured at strain of about 0.035. The results suggest that the factors leading to implosion may be related to the propensity of a material to yield or to fracture.

Outputs

Publications

D.M. Colucci, P.A. O'Connell and G.B. McKenna, *Stress Relaxation Experiments in Polycarbonate: A Comparison of Volume Changes for Two Commercial Grades*, Polymer Engineering and Science, in press.

Presentations

G.B. McKenna, *Mechanical Measurements in Viscoelastic Solids: Time-scale and Volume Phenomena*, Chalmers Institute of Technology, Gothenburg, Sweden, April 1997.

G.B. McKenna, *Stress and Strain Induced Mobility Changes in Glassy Polymers: Some Thoughts about Reduced Time in Constitutive Modeling*, International Discussion Meeting on Relaxations in Complex Systems, Vigo, Spain, July 1997.

Physical Aging and Structural Recovery in Polymers

G.B. McKenna, C.R. Schultheisz, J.J. Filliben¹, D.M. Colucci, P.A. O'Connell², M.L. Cerrada³, S.L. Simon, A. Lee⁵, D.B. Curliss⁶, K.B. Bowman⁶, J.D. Russell⁶

¹Statistical Engineering Division, NIST

²University of Leeds, U.K.

³Instituto de Ciencia Y Tecnologia de Polimeros, Madrid, Spain

⁴University of Pittsburgh, Pittsburgh, PA

⁵Michigan State University, East Lansing, MI

⁶U.S. Air Force, Wright Laboratory Materials Directorate, Dayton, OH

Objective

The objective is to use existing methods and develop, where appropriate, new methods to measure kinetics of glass formation. The kinetics are related to the underlying microstructure of the glass through appropriate physical models.

Planned Outcomes

- Establish whether or not there exists an isochoric glass transition through experimentation with a glassy polycarbonate.
- Determine the material parameters in the Tool-Narayanaswamy-Moynihan-Kovacs-Aklonis-Hutchinson (TNM-KAHR) model of structural recovery for the polycarbonate being used in the GM/GE ATP project on thermoplastic engineering design.
- Determine the physical aging response of poly(ethylene naphthalate) in both semi-crystalline and amorphous states and provide results to Eastman Kodak Company.
- Establish a research material for the purpose of a round robin investigation on the relative time-scales required for glassy properties, such as relaxation response and volume or enthalpy recovery, to attain equilibrium.
- Provide a new analysis of the Kovacs enhanced set of structural recovery data for poly(vinyl acetate) and establish whether or not the data support the controversial τ -effective paradox and expansion gap which are often used as bench marks for structural recovery models.

Task 1. Isobaric and Isochoric Responses of Polymers

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

Technical Description

The technical approach is to perform pressure, volume, temperature (PVT) experiments in which both the isobaric and isochoric paths into the glassy state are followed. The fragility of glass forming liquids along both isochoric and isobaric paths is analyzed and compared to the experimental results. PVT experiments can be performed in two ways. First, in the classical manner, the sample is brought to the liquid state, pressurized and then cooled under constant pressure. The volume is measured as a function of temperature and an isobaric glass transition is obtained. Conversely, the material can be brought into the liquid state, pressurized to a given volume and then cooled while the pressure is changed to maintain constant sample volume. The pressure is then recorded as a function of temperature and a break in the P-T curve is interpreted as an isochoric glass transition. Polycarbonate was used and studied over a range of pressures from 10 MPa to 200 MPa and temperatures from 50 °C to 250 °C. Experiments at six constant specific volume conditions from (0.8275 to 0.8550) cc/g were also performed. The results were analyzed in the context of the Fox-Flory free volume model.

The temperature dependence of the viscosity of glass forming liquids is often analyzed in terms of the Angell plot. Here, the logarithm of the viscosity (or of the shift factor) is plotted vs T_g/T to yield an Arrhenius plot that is reduced by the distance one is above the glass transition temperature T_g . Strong deviations of the response (Vogel or WLF-type behavior) are interpreted as a fragile liquid behavior, while Arrhenius behavior is interpreted as strong liquid response. To bring new insight into the meaning of fragility an examination was made of the dynamic (mechanical or dielectric) data from the literature for 14 polymers for which there existed both the dynamic (mechanical or dielectric) and PVT data above the glass transition. Cross-plotting the response both isobarically and isochorically yielded a comparison of the fragility of the materials as a function of path.

Accomplishments

- An isochoric glass transition was observed in dilatometric experiments on polycarbonate. This discovery strongly brings into question the validity of free volume models of the glass transition that are commonly used to describe thermal behavior of solid polymers during processing.
- Thermodynamic analysis of the PVT surfaces of isochoric vs isobaric glass forming systems showed that the glass formation pressure, temperature and volume points are independent of the path. However, the isochoric glass has a lower specific volume than does the isobaric glass.
- Showed that the strength of the isochoric glass transition as measured by, e.g., the change in the coefficient of thermal expansion or bulk modulus at T_g , is weaker for the isochoric glass than for the isobaric glass.

- Showed that the isochoric liquid is less fragile than is the isobaric liquid.

Outputs

Publications

D.M. Colucci, G.B. McKenna, J.J. Filliben, A. Lee, D.B. Curliss, K.B. Bowman and J.D. Russell, *Isochoric and Isobaric Glass Formation: Similarities and Differences*, J. Polym. Sci., Polym. Phys. Ed., 35, 1561 (1997).

D.M. Colucci and G.B. McKenna, *Fragility of Polymeric Liquids: Correlations between Thermodynamic and Dynamic Properties*, in Structure and Dynamics of Glasses and Glass Formers, ed. by C.A. Angell, T. Egami, J. Kieffer, K.L. Ngai and U. Nienhaus, MRS Symposium Proceedings, Vol. 455, 1997.

D.M. Colucci and G.B. McKenna, *Measurement of an Isochoric Glass Transition*, Proceedings, 10th International Conference on Deformation, Yield and Fracture of Polymers, Institute of Materials, Chameleon Press, London, 411-414, 1997.

Presentations

D.M. Colucci and **G.B. McKenna**, *Path Dependence of the Fragility of Polymeric Glass Formers*, American Physical Society March Meeting, Kansas City, MO, March 1997.

D.M. Colucci and **G.B. McKenna**, *Measurement of an Isochoric Glass Transition*, Churchill Conference on Deformation, Yield and Fracture of Polymers, Cambridge, England, April 1997.

Task 2. Dilatometric Investigation of the Structural Recovery of Polymer Glasses

G.B. McKenna, C.R. Schultheisz, M. Vangel¹, S.D. Leigh¹, A. Rushkin¹, C. Straupe² and B. Lotz²

¹Statistical Engineering Division, NIST

²Institute Charles Sadron, Strasbourg, France

Objectives

The objectives are: *i.* Determine the Tool-Narayanaswamy-Moynihan-Kovacs-Aklonis-Hutchinson (TNM-KAHR) parameters for the polycarbonate glass used by the GM/GE Thermoplastic Engineering Design project supported by the ATP. *ii.* Create an international round robin with the same polycarbonate to investigate the glassy and approach to glassy behavior using multiple measurement techniques for glassy dynamics. *iii.* Determine the time-scales for mechanical and volume responses in the model epoxy being studied in the NIST torsional dilatometer at temperatures further below the glass transition than obtained previously. *iv.* Analyze the Kovacs volume recovery data for poly(vinyl acetate) using both his published and

unpublished data to establish whether or not the Struik criticisms of the data as insufficiently accurate to support the existence of the τ -effective paradox and expansion gap.

Technical Description

Up and down temperature jump experiments are performed in both classical dilatometers and the NIST torsional dilatometer for measurement of the structural (volume) recovery response in asymmetry of approach conditions. In the case of classical dilatometers, experiments are performed at temperatures as high as 150 °C on polycarbonate. The data are analyzed using the TNM-KAHR model of glassy kinetics. Material parameters for the models are obtained and compared with those in the literature for enthalpy recovery. The parameters are also to be provided to the technical contacts in the GM/GE ATP project. In the case of the torsional dilatometry, mechanical measurements are also made and the time-scales for the structural recovery as determined by volume and the evolution of the mechanical properties (physical aging) are compared. This work extends work performed previously on the same type of epoxy, but at temperatures nearer to the glass transition. Here, because the temperatures are farther below the glass transition temperature experimental times can be in excess of two months simply to equilibrate the samples volumetrically.

In 1964 Kovacs published a paper in which he analyzed structural recovery data in asymmetry of approach experiments using a parameter that he referred to as τ -effective (τ_{eff}) defined in terms of the volume departure from equilibrium δ as $\tau_{\text{eff}} = -1/\delta \, d\delta/dt$. In plots of the $\log(1/\tau_{\text{eff}})$ vs δ Kovacs observed an apparent paradox in that the values of τ_{eff} did not converge to the same point as δ approached zero, i.e., equilibrium--hence the equilibrium mobility of the structural recovery seemed path dependent. Also, the apparent paradox was accompanied by a spreading of the curves for τ_{eff} in the up-jump experiments which has come to be known as the expansion gap. While it is currently accepted that the paradox itself does not exist because the curves will converge if the measurements are made closer to $\delta=0$ (Kovacs' measurements went to $\delta \approx 2 \times 10^{-5}$), the existence of the expansion gap is still a subject of dispute. In particular, Struik in 1997 published an article claiming that the experimental uncertainties were too great to support the existence of the expansion gap. It is particularly important to resolve the issue now because recent models of structural recovery have claimed 'success' specifically because the expansion gap is obtained. The original Kovacs 1964 data as well as unpublished data from his note books and more recent data obtained at the Institut Charles Sadron under his tutelage were subjected to a rigorous statistical analysis. The following hypothesis was tested: the value of τ_{eff} as $\delta \rightarrow 10^{-4}$ for a temperature jump from T_i to T_0 is significantly different from the value obtained for the temperature jump from T_j to T_0 . The T_i 's can be either greater or less than T_0 . If the hypothesis is rejected, the τ_{eff} -paradox and expansion gap need to be rethought. If the hypothesis is accepted, then the argument that reproduction of the expansion gap is an important test of structural recovery models is strongly supported. The hypothesis is also being examined with new data from the polycarbonate dilatometry.

Accomplishments

- The TNM-KAHR parameters for polycarbonate used in the GM/GE ATP project have been obtained.
- An international round robin was initiated to study the thermoviscoelastic behavior of a research grade polycarbonate. The co-leader on the project is Prof. J.M. Hutchinson of the Aberdeen University in Scotland with eight confirmed participants and five tentative participants. This round robin will help to resolve the fundamental issues involved in the reports from various laboratories of different (or not) fictive temperatures for different processes in glass forming liquids.
- Torsional dilatometry experiments have been performed at temperatures as much as 15 °C below the nominal glass transition. Replicate experiments are underway.
- A new statistical analysis shows that, by accounting for the correlation of the errors in the Kovacs 1964 data, the expansion gap exists and is statistically significant at the 2σ level for values of $\delta \geq 1 \times 10^{-4}$. This is well within the range of the observed expansion gap and makes the Kovacs observations valid for testing the behavior of structural recovery data.
- The volume dilatometry from polycarbonate also shows an expansion gap, though not as strongly as that observed in poly(vinyl acetate) by Kovacs.

Outputs

Publications

C.R. Schultheisz and G.B. McKenna, *Volume Recovery and Physical Aging in Polycarbonate Following Temperature Jumps*, Proceedings, 10th International Conference on Deformation, Yield and Fracture of Polymers, Institute of Materials, Chameleon Press, London, 419-422, 1997.

C.R. Schultheisz and G.B. McKenna, *Volume Recovery and Physical Aging in Glassy Polycarbonate Following Temperature Jumps*, Proc. NATAS 25th Annual Conference, September 1997, in press.

Presentations

C.R. Schultheisz and G.B. McKenna, *Volume Recovery and Physical Aging in Glassy Polycarbonate Following Temperature Jumps*, Society for Experimental Mechanics Spring Conference on Experimental and Applied Mechanics, Bellevue, WA, June 2-4, 1997.

C.R. Schultheisz and G.B. McKenna, *Volume Recovery, Physical Aging and the Tau-Effective Paradox in Glassy Polycarbonate Following Temperature Jumps*, Joint ASME/ASCE/SES Summer Meeting, McNU 97, Northwestern University, Evanston, IL, June 29 - July 2, 1997.

C.R. Schultheisz and G.B. McKenna, *Volume Recovery, Physical Aging and the Tau-Effective Paradox in Glassy Polycarbonate Following Temperature Jumps*, North American Thermal Analysis Society 25th Annual Conference, McLean, VA, September 1997.

C.R. Schultheisz and G.B. McKenna, *Volume Recovery and Physical Aging in Polycarbonate and Epoxy*, Society of Rheology Meeting, Galveston, TX, February 1997.

C.R. Schultheisz and G.B. McKenna, *Volume Recovery and Physical Aging in Polycarbonate Following Temperature Jumps*, 213th American Chemical Society National Meeting and Exposition, San Francisco, CA, April 1997.

C.R. Schultheisz and G.B. McKenna, *Volume Recovery and Physical Aging in Polycarbonate*, GE/GM ATP Semiannual Meeting, Buffalo, NY, October 1996.

C.R. Schultheisz and **G.B. McKenna**, *Volume Recovery and Physical Aging in Glassy Polycarbonate Following Temperature Jumps*, Churchill Conference on Deformation, Yield and Fracture of Polymers, Cambridge, England, April 1997.

B. Lotz, C. Straupe, **G.B. McKenna**, M. Vangel, A.L. Rushkin, and S.D. Leigh, *The τ -effective Paradox Revisited: An Extended Analysis of Kovacs' Original and Unpublished Volume Recovery Data on Poly(vinyl Acetate)*, International Discussion Meeting on Relaxations in Complex Systems, Vigo, Spain, July 1997.

G.B. McKenna, *Physical Aging, Viscoelasticity, and Their Effects on the Performance of Polymers and Composites*, Society of Plastics Engineers, Regional Technical Conference, Akron, OH, October 1996.

Task 3. The Physical Aging Response of Industrial Materials

G.B. McKenna, C.R. Schultheisz, J.M. O'Reilly¹, J. Greener¹, J.R. Gilmore¹ and M. Cerrada²

¹Eastman Kodak, Rochester, NY

²Instituto de Ciencia Y Tecnologia de Polimeros, Madrid, Spain

Technical Description

Classical time-aging time experiments are being performed to characterize the evolution of material properties at temperatures typical of industrial processing and annealing and subsequent use. The properties are important in determining the dimensional stability of the materials: e.g., amorphous and semi-crystalline films of poly(ethylene naphthalate) (PEN). While in many instances one has the option of choosing materials so that classical time-aging time and time temperature superposition principles apply, many industrial materials do not fall into this range of behaviors. Hence, semi-crystalline materials or amorphous glasses with large " β " relaxations may not obey the classical time-aging time or time-temperature reduction principles. Currently amorphous and semi-crystalline PEN are studied. Classical analysis of the data cannot always be

performed due to the presence of two large and overlapping transitions in PEN in the temperature and aging time ranges. Means are being sought to separate the mechanisms through both appropriate data analysis and by the use of new experimental tests sequences.

External Interactions

This work is being performed in collaboration with researchers at Eastman Kodak Company.

Accomplishments

- Demonstrated that for amorphous and semi-crystalline PEN there are two ranges of behavior: at low temperatures and short aging times, the creep and relaxation behaviors follow a power law behavior. Here the time-aging time and time-temperature superpositions appear to work. At long aging times and at low temperatures there appears a second mechanism which looks typically non-exponential, but is not a power law. Hence, time-aging time superposition is no longer valid. At intermediate temperatures, both mechanisms are present at all aging times. At high temperatures one only observes the non-exponential behavior and one finds again the time-aging time superposition. Detailed analysis of the data shows that, strictly speaking, simple temperature and aging time superposition principles do not apply to PEN and deconvolution of the two viscoelastic mechanisms needs to be performed.

Outputs

Publications

J. Beckmann, G.B. McKenna, B.G. Landes, D.H. Bank, and R.A. Bubeck, *Physical Aging Kinetics of Syndiotactic Polystyrene as Determined from Creep Behavior*, Polymer Engineering and Science, 37, 1459 (1997).

A. Lee and G.B. McKenna, *Anomalous Aging in Two Phase Systems: Creep and Stress Relaxation Differences in Rubber-Toughened Epoxies*, J. Polym. Sci., Polym. Phys. Ed., 35, 1167 (1997).

M.L. Cerrada and G.B. McKenna, *Viscoelastic and Physical Aging Behavior in Semi-Crystalline PEN*, Proc. NATAS 25th Annual Conference, September 1997, 404-410.

Presentations

G.B. McKenna, *Physical Effects in the Aging of Amorphous Resins*, McNU '97, Northwestern University, July 1997.

M.L. Cerrada and G.B. McKenna, *Viscoelastic and Physical Aging Behavior in Semi-Crystalline PEN*, NATAS 25th Annual Conference, September 1997.

Task 4. Effects of Structural Recovery on Modulated and Dynamic Thermal Measurements

Technical Description

The technical approach consists of: i. Analyze the impact of structural recovery and thermal lag within a sample on the heat flow signal obtained in modulated differential scanning calorimetry experiments. ii. Compare predictions from the structural recovery model of Tool-Narayanaswamy-Moynihan with literature results showing an apparent dynamic heat capacity. The Tool-Narayanaswamy-Moynihan (TNM) model of structural recovery under oscillatory thermal histories is solved to address two problems in the thermal analysis of glass forming materials. The first problem is the effect of structural recovery on the thermal signal obtained in modulated DSC experiments. This question is important because increasing numbers of laboratories are purchasing modulated DSC calorimeters for thermal analysis and one needs to fully understand this new technique. Hence, the TNM model is solved using material parameters for polystyrene (PS) and poly(vinyl chloride) (PVC) for typical thermal histories encountered in the thermal analysis laboratory. Using a Lissajous loop analysis in which heat flow is plotted vs the time derivative of temperature (HF vs dT/dt) it is shown that the response can be tremendously influenced by structural recovery and that a linear analysis will give erroneous results in these cases. Hence it is recommended that users of the modulated DSC avoid thermal histories in which there is a great deal of structural recovery (enthalpy overshoot). It was further shown, by performing an analysis that included sample geometry, that thermal lag in the samples due to simple thermal conductivity effects can cause anomalous phase lags in the thermal signals even for relatively small samples (thickness ≈ 0.2 cm).

For the dynamic heat spectroscopy analysis, it was shown that the apparent dynamic heat capacity obtained by Birge and Nagel for glycerol and by Donth and co-workers for poly(vinyl acetate) could be quantitatively predicted from the TNM model using material parameters obtained in the glass transition region. These calculations show that structural recovery in high fictive temperature glasses can explain the dynamic heat capacity of glass forming liquids. It also suggests, strongly, that dynamic heat spectroscopy measurements may be a powerful method to determine the structural recovery retardation function used in the TNM model in a way that is independent of the other material parameters. This is important because the model is highly nonlinear and the parameters are normally obtained by curve fitting results to, e.g., DSC measurements. Because the parameters in the model are not statistically independent having a means to determine by independent experiments one of the parameters removes some of the uncertainties in the model.

Accomplishments

- Demonstrated by model calculations that structural recovery in polymeric glasses can dramatically affect the heat flow signal in modulated DSC measurements. This finding is important to users of modulated DSC instruments as it helps them to avoid misinterpretation of data due to structural recovery induced artifacts.

- Demonstrated by model calculations of structural recovery that dynamic heat spectroscopy results are a simple manifestation of structural recovery in high fictive temperature glasses. This leads to a different interpretation of dynamic heat capacity from that previously used to interpret such experiments. This could have profound implications for the relationship between structural recovery and fluctuations in complex fluids.

Outputs

Publications

S.L. Simon and G.B. McKenna, *Interpretation of the Dynamic Heat Capacity Observed in Glass-Forming Liquids*, J. Chem. Phys., in press.

S.L. Simon and G.B. McKenna, *The Effects of Structural Recovery and Thermal Lag in MDSC*, Thermochemica Acta, in press.

S.L. Simon and G.B. McKenna, *The Effects of Structural Recovery in Modulated DSC*, Society Plastics Engineers, ANTEC, II, 2232 (1997).

S.L. Simon and G.B. McKenna, *The Effects of Structural Recovery and Thermal Lag in Modulated DSC Measurements*, Proc. NATAS 25th Annual Conference, September 1997, 358-365.

G.B. McKenna and S.L. Simon, *Interpretation of the Dynamic Heat Capacity Observed in Glass-Forming Liquids*, Proc. NATAS 25th Annual Conference, September 1997, 677-684

Presentations

G.B. McKenna and S.L. Simon, *Dynamic Heat Capacity: Myth or Reality*, Max Planck Institut für Polymerforschung, Mainz, Germany, April 1997.

S.L. Simon and **G.B. McKenna**, *The Effects of Structural Recovery in Modulated DSC*, Society Plastics Engineers, ANTEC, Toronto, CN, May 1997.

S.L. Simon and G.B. McKenna, *The Effects of Structural Recovery and Thermal Lag in Modulated DSC Measurements*, NATAS 25th Annual Conference, McLean, VA, September 1997.

G.B. McKenna and S.L. Simon, *Interpretation of the Dynamic Heat Capacity Observed in Glass-Forming Liquids*, NATAS 25th Annual Conference, McLean, VA, September 1997.

G.B. McKenna, *The Glass Transition as a Kinetic Phenomenon: Implications for Thermal Analysis*, NATAS 25th Annual Conference, McLean, VA, September 1997.

Task 5. Physical Aging and Structural Recovery in Polymeric Glasses in Plasticizing Environments

G.B. McKenna and W.H. Han¹

¹Korean Government Fellowship for Overseas Doctoral Studies

Technical Description

The technical approach is to investigate the hypothesis that the chemical activity (or solvent concentration) can be treated in the same way as temperature as a means of treating structural recovery and physical aging in polymeric glasses. It is well known that small molecules such as H₂O and CO₂ act to depress the glass transition in polymers: hence they act as plasticizers. Furthermore, there is some evidence that concepts such as time-concentration superposition can account for much of the change in viscoelastic properties in plasticized polymers. However, there have been few works to explore how changes in concentration (as induced by a change in the activity of the surrounding environment) impact the structure of the glass. This is an issue of fundamental importance for both processing and long term performance in materials because the volume changes induced by changes in plasticizer content can easily be equivalent to hundreds of degrees of temperature change.

An investigation is made of the hypothesis that changes in glassy structure induced by changes in plasticizer concentration are equivalent to similar changes in temperature. In order to test the hypothesis an apparatus is under construction that permits the rapid change of relative humidity or supercritical carbon dioxide pressure over thin polymer films simultaneously tested for creep response, volume change and mass uptake. Because the measurement of volume change and mass uptake are the most difficult to automate, the focus is on the physical aging response in a model epoxy system subjected to isothermal relative humidity (RH) jumps and iso-RH temperature-jumps. Investigations have also begun using isothermal carbon dioxide pressure-jumps and iso-CO₂ pressure, temperature-jumps.

Accomplishments

- Made the first measurements demonstrating that RH-jump experiments manifest the 'memory' effect typically seen in volume recovery experiments.
- Preliminary results show that RH-jump and T-jump experiments lead to the same response for the epoxy system considered. This may be because the moisture uptake is less than 2% by mass.
- Preliminary results show that jumps in the CO₂ pressure induce a different structure in a glassy polycarbonate than do temperature jumps to the same final condition. The creep response in the CO₂ pressure jump experiments exhibits a narrower distribution of retardation times than the same response in the temperature-jump experiments.

Outputs

Publications

W.H. Han and G.B. McKenna, *The Physical Aging Response of Epoxy in Relative Humidity Jump Experiments*, Proceedings NIST/Rome Laboratories Workshop on Moisture Effects in Microelectronics, NIST, Gaithersburg, MD, October 1996, in press.

W.H. Han and G.B. McKenna, *Plasticizer Effects on Physical Aging of Epoxy*, (1997) Society Plastics Engineers ANTEC, II, 1539.

W.H. Han and G.B. McKenna, *Polymers and Small Molecules: Glass Transition and Aging Effects*, Proc. NATAS 25th Annual Conference, September 1997, 382-389.

Presentations

W.H. Han and **G.B. McKenna**, *Physical Aging of Polycarbonate Films under High Pressure Gases*, McNU '97, Northwestern University, July 1997.

W.H. Han and **G.B. McKenna**, *Plasticizer Effects on Physical Aging of Epoxy*, Society Plastics Engineers ANTEC, Toronto, Canada, May 1997.

W.H. Han and **G.B. McKenna**, *Structural Recovery and Physical Aging after Relative Humidity Jumps: First Evidence of a Memory Effect*, American Physical Society March Meeting, Kansas City, MO, March 1997.

W.H. Han and **G.B. McKenna**, *The Physical Aging Response of Epoxy in Relative Humidity Jump Experiments*, Rome Laboratories/NIST Workshop on Moisture in Electronic Packaging, NIST, Gaithersburg, MD, October 1996.

W.H. Han and G.B. McKenna, *Polymers and Small Molecules: Glass Transition and Aging Effects*, NATAS 25th Annual Conference, McLean, VA, September 1997.

W.H. Han and G.B. McKenna, *Physical Aging of Plasticized Polymer Glass*, the 4th Sigma-Xi Postdoctoral Presentation, NIST, February 1997.

W.H. Han and G.B. McKenna, *Plasticization Effects in Polymer Glasses: Concentration Jump Experiments*, 68th Annual Meeting of the Society of Rheology, Galveston, Texas, February 1997.

Failure in Polymers and Adhesives

M.Y.M. Chiang, G.B. McKenna, M. Delin¹, H. Chai² and M. Fernandez-Garcia³

¹Chalmers University of Technology, Goteborg, Sweden

²Tel Aviv University, Israel

³Instituto de Ciencia Y Tecnologia de Polimeros, Madrid, Spain

Objectives

The objectives are to develop numerical models of adhesive behavior and validate these with experimental observation. The effect of aging and environment on the failure and pre-failure behavior of polymers and adhesives is investigated.

Planned Outcomes

- Demonstration by experiment and finite element analysis that mode II fracture can be described by a criterion in which the local strain at the crack tip determines failure.
- Development of test methods that impact on long term performance evaluation and predictability in polymers, composites and adhesives.
- Establish correlations between long term moisture exposure and the mechanical response of commercial adhesives to support ATP focus program on Composites.
- Validation of theoretical models of craze initiation and growth through use of structural recovery (physical aging) to vary the material's viscoelastic response.

Task 1. Finite Element Analysis of Interfacial Crack Propagation Criterion Based on Local Shear (Near Tip Deformation and Fracture)

M.Y.M. Chiang and H. Chai

Technical Description

The majority of early strength analysis of lap shear joints either neglected stress variations across the bond or employ LEFM (linear elastic fracture mechanics) based approaches. More recently, small scale yielding solutions were produced for bi-material interface crack problems. Such solutions, however, are still insufficient to account for the very large deformations that occur in tough adhesives. Recent experiments from this laboratory show that the fracture process in shear loaded adhesive bonds is characterized by a stable crack propagation followed by catastrophic growth. During the stable growth, a variety of failure process may be activated at or ahead of the crack tip, the most predominant one being interfacial cracking. One of the more interesting aspects of this failure mode is that even though the deformation in the majority of the bond remains in the elastic range, very large shear strains (i.e over unity) may develop over a considerable distance ahead of the crack tip. The plastic zone in this case may be several orders of magnitude greater than the bond thickness while the relative shearing displacement across the bond is of the same size as the bond thickness. Therefore, the present study is carried out using a large strain, incremental plasticity finite element analysis. The analysis focuses on the interface straight ahead of the crack tip, where the fracture occurred.

Accomplishments

- Showed that the distribution of the engineering shear strain, γ , along the interface conforms to the following relationship: $\gamma = A \bar{x}^{-\delta}$, $\bar{x} = x/h$ where x is a horizontal coordinate axis originating from the crack tip, h is the bond thickness, $\bar{\gamma}$ is the average shear strain in the bond ("load") and A and δ are known numerical functions of $\bar{\gamma}$.
- Established that the distribution of the shear strain along the interface near the crack tip in mode II fracture conforms to a power law singularity under small as well as large scale yielding conditions. This changes the paradigm by which researchers model large deformation crack tip singularities. There was no prior solution to the large scale yielding problem in mode II fracture conditions.

Outputs

Publications

M.Y.M. Chiang, and H. Chai, *Finite Element Analysis of Constrained Interfacial Crack Propagation Based on Local Shear, Part I - Near Tip Solution*, Intl. J. Solids and Structures, in press.

H. Chai and M.Y.M. Chiang, *Finite Element Analysis of Constrained Interfacial Crack Propagation Based on Local Shear Deformation, Part II - Fracture*, Intl. J. Solids and Structures, in press.

S. Yang, M.Y.M. Chiang and F.G. Yuan, *Analytical Forms of Higher-order Asymptotic Elastic-plastic Crack-tip Fields in a Linear Hardening Material under Antiplane Shear*, Intl. J. of Fracture, 80, 59 (1996).

M.Y.M. Chiang and H. Chai, *A Fracture Criterion Based on Local Shear Strain for Adhesive Bonds*, Proceedings 20th Anniversary Meeting of the Adhesion Society, Hilton Head, SC, February 1997.

M.Y.M. Chiang, *Finite Element Analysis and Experimental Monitoring of Strain Localization and Failure Process of Thin Adhesive Bonds*, 42nd Intl. SAMPE Symposium, 1997.

A. Kuo, D. Newport, W. Yin, and M.Y.M. Chiang, *Generalized Stress Intensity Factor Concept for Fatigue and Fracture Evaluations*, ASME EEP-Vol.19, Advances in Electronic Packaging 1997, pp.1451-1460.

Presentations

M.Y.M. Chiang, *An Intrinsic Fracture Criterion Based on Local Strain for Highly Constrained Interfacial Cracking*, Society of Engineering Science, 33rd Annual Technical Meeting, Tempe, AZ, October 1996.

M.Y.M. Chiang, *Finite Element Analysis and Experimental Monitoring of Strain Localization and Failure Processing of Thin Adhesive Bonds*, Intl. Conferences on Polymer Characterization (POLYCHAR-5), Denton, TX, January 1997.

M.Y.M. Chiang, *A Fracture Criterion Based on Local Shear Strain for Adhesive Bonds*, 20th Anniversary Meeting of the Adhesion Society, Hilton Head, SC, February 1997.

M.Y.M. Chiang, *Finite Element Analysis and Experimental Monitoring of Strain Localization and Failure Process of Thin Adhesive Bonds*, 42nd Intl. SAMPE Symposium/Exhibition, Anaheim, CA, May 1997.

M.Y.M. Chiang, *Finite Element Analysis and Experimental Monitoring of Strain Localization and Failure Process of Thin Adhesive Bonds*, Intel Corp., San Jose, CA, May 1997.

M.Y.M. Chiang, *Finite Element Analysis and Experimental Monitoring of Strain Localization and Failure Process of Thin Adhesive Bonds*, Hexcel Composites, Dublin, CA, May 1997.

M.Y.M. Chiang, *Finite Element Analysis and Experimental Monitoring of Strain Localization and Failure Process of Thin Adhesive Bonds*, AlliedSignal, Morristown, NJ, June 1997.

Task 2. Hygrothermal Aging of Commercial Adhesives

M.Y.M. Chiang and M. Fernandez-Garcia¹

¹Instituto de Ciencia Y Tecnologia de Polimeros, Madrid, Spain

Technical Description

The implementation and use of adhesive materials in structural and engineering designs require understanding of material performance under environmental conditions during long-term use. Also, increased use of adhesive bonding in structural components has renewed interest in the analysis of adhesive joints. A particular problem is effects of the diffusion of environmental agents into the adhesive layer. Diffusion of moisture or solvent into the adhesive can significantly change the state of stress field and hence the reliability of the bond joints. In this project, hygrothermal aging of commercial adhesives is studied in terms of effects on mechanical properties and failure behavior of highly constrained thin adhesive layers.

Most engineering analyses of adhesive materials either neglect the effect of the interlayer or assume that it behaves like the bulk material. However, recent experimental observations and finite element analyses show that the mechanical mass of the interlayer are greatly affected by its thickness. For example, it was found that the ultimate shear strain of a brittle epoxy increases from a bulk value (about 6%) to between 15% and 300% upon decreasing the bond thickness from 0.1 mm to 25 μ m. In this work, the interaction of environmental conditions (dry and wet) and bond thickness on the stress-strain relation of the adhesive will also be studied in order to

enhance our understanding of their effects. Experimental tests under simple shear conditions will be studied using the napkin ring specimen. The bond thickness is a primary variable which will be varied from several micrometers up to values large enough to expose the bulk behavior.

Accomplishments

- Developed method to make void free thin films appropriate to the commercial adhesives used in this study.

Task 3. Measurement of Craze Initiation and Growth in Polymers

G.B. McKenna and M. Delin¹

¹Chalmers University of Technology, Goteborg, Sweden

Technical Approach

This project examines the crazing process as one that depends very strongly on the viscoelastic response of the glassy polymer under study. It is known that temperature can have large effects on craze initiation and growth. In the current work the viscoelastic response is altered by changing both temperature and aging time, the aging time permitting isothermal changes in the 'glassy structure'. Craze initiation and growth is studied using special fixtures to provide equibiaxial and uniaxial loading in creep conditions and uniaxial loading in stress relaxation conditions.

Accomplishments

- Modified existing equipment to make visual measurements of craze growth under uniaxial stress relaxation conditions.
- Discovered a transition in craze growth rate in stress relaxation conditions for a styrene-acrylonitrile copolymer. The logarithmic craze growth rate decreases by approximately a factor of five in going from below to above the transition aging time. If this is a universal behavior for all polymers it implies that the long term performance may be enhanced due to the aging process stabilizing the material against craze growth.

Outputs

Publications

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, in press.

M. Delin and G.B. McKenna, *Impact of Physical Aging on Craze Growth in a Styrene-Acrylonitrile Co-Polymer*, Proc. NATAS 25th Annual Conference, September 1997, in press.

Presentations

M. Delin, and G.B. McKenna, *Impact of Physical Aging on the Craze Initiation and Propagation in Styrene Acrylonitrile Co-polymer*, Fourth Annual SigmaXi Post-Doctoral Associate Poster Presentation, National Institute of Standards and Technology (NIST), Gaithersburg, MD, February 1997.

G.B. McKenna and M. Delin, *Craze Propagation in Stress-relaxation Conditions for a Styrene-acrylonitrile Copolymer*, Poster Session of the Polymers Division, National Institute of Standards and Technology (NIST), Gaithersburg, MD, May 1997.

R.W. Rychwalski, J. Vernel, M. Delin, J. Kubát, C. Klason, J.M. Hutchinson, A.V. Vannikov and V. Pelíék, *Effect of Physical Aging on The Dynamic - Mechanical, Enthalpic And Non-linear Optical Mass of PVAc*, 3rd International Discussion Meeting on Relaxations in Complex Systems, Vigo, Spain, June 30 -July 11, 1997.

M. Delin and G.B. McKenna, *Impact of physical aging on craze growth in a styrene-acrylonitrile co-polymer*, 25th Annual Conference of North American Thermal Analysis Society, McLean, VA, September 7-9, 1997.

Other

C.R. Schultheisz, W.G. McDonough, S. Kondagunta, C.L. Schutte, K.S. Macturk, M. McAuliffe, G.A. Holmes, D.L. Hunston, *Durability of E-Glass/Epoxy Composites Immersed in Water*, Society of Plastics Engineers Regional Technical Conference (SPE RETEC), Cuyahoga Falls, Ohio, October 28-29, 1996.

C.R. Schultheisz, W.G. McDonough, S. Kondagunta, C.L. Schutte, K.S. Macturk, M. McAuliffe, G.A. Holmes, D.L. Hunston, *Durability of E-Glass/Epoxy Composites Immersed in Water*, University of Delaware, Wilmington, DE, November 15, 1996.

C.R. Schultheisz, K. Liao, D.L. Hunston, *Long-Term Durability of Composites in Infrastructure Applications*, National Seminar on Advanced Composite Material Bridges, Arlington, Virginia, May 5-6, 1997.

C.R. Schultheisz, W.G. McDonough, S. Kondagunta, C.L. Schutte, K.S. Macturk, M. McAuliffe, G.A. Holmes and D.L. Hunston, *Effect of Moisture on E-Glass/Epoxy Interfacial and Fiber Strengths*, NIST Polymers Division Workshop on Micro-Mechanics Measurement Technologies for Fiber-Polymer Interfaces, NIST, Gaithersburg, MD, May 28-30, 1997.

Rheological Characterization of Polymer Dynamics

G.B. McKenna, C.R. Schultheisz, V. Rouiller¹ and R. Zorn²

¹NIST Guest Research from Houdemont, France

²KFA, Julich, Germany

Objective

The objective is to develop rheological descriptions for polymeric materials that provide standard reference materials, produce critical data and provide defining tests of existing physical and phenomenological models for polymer dynamics.

Planned Outcomes

- Produce a new nonlinear fluid as a Standard Reference Material.
- Provide a good representation of the viscoelastic response of polyurethane based on a hybrid Valanis-Landel-BKZ model.
- Extension of hybrid viscoelastic model to foams in hydrostatic creep.

Task 1. Develop a Nonlinear Fluid Standard

G.B. McKenna and C.R. Schultheisz

Technical Description

Polymeric fluids, such as polymer melts and solutions, often do not follow the simple, Newtonian ideal in their flow behavior. Such fluids see wide application in everyday life (injection molding, paints and coatings, food products, etc.), and the ability to measure accurately and characterize their behavior is very important to optimizing their processing conditions. Since there are a number of commonly used methods to measure the flow behavior of polymers, the new Standard Reference Material will provide a means for comparing the performance of different instruments. The new fluid will be certified for the shear rate dependence of viscosity and first normal force difference over a temperature range of approximately 50 °C. The linear viscoelastic responses will also be certified along with the temperature dependence of the shift factors and the zero shear viscosity.

The new fluid supersedes the previous Standard Reference Material 1490 Nonlinear Fluid Standard, which was composed of a high molecular mass polyisobutylene, PIB, dissolved in n-hexadecane. This fluid was found to have two problems: first, it showed evidence of a loss of homogeneity on storage, and second, the working range of the fluid was limited by the crystallization of the n-hexadecane, which has a melting point of 18 °C. The approach taken to overcome these difficulties focuses on using a solution of high molecular mass polyisobutylene dissolved in low molecular mass (oligomeric) polyisobutylene. The material is produced by dissolving the two components in a third, highly volatile solvent, such as n-pentane or cyclohexane. By driving off the solvent, one thus obtains a homogeneous solution of the desired concentration of PIB in its oligomer. Initial experimentation shows that the approach leads to a solution with the appropriate range of viscosity and normal force response. However, the material produced shows some excessive tackiness which makes it difficult to handle. Further, there is some evidence that the oligomer itself may contain low molecular mass species that also evaporate, albeit more slowly than the solvent used to prepare the solution. This leads to

somewhat less control over the final product than desired. Therefore, several alternatives are investigated including a different processing method for the current solution, the use of a higher molecular mass solvent that can be retained in a stable manner in the solution, and the use of a long-chain branched alkane (similar to the n-hexadecane but with a lower melting temperature) in place of the low molecular mass PIB.

The project goals also include a round robin test of the candidate Standard Reference Material involving instrument manufacturers and users in industry and at universities. The round robin will ensure that the chosen material mass are acceptable to the community, and will provide information regarding the lab-to-lab variability in the measurements. The Statistical Engineering Division at NIST will be involved in evaluating the results of the round robin.

External Collaborations

The following have agreed, in principle, to participate in the round robin.

Instrument Manufacturers

ATS RheoSystems	Paar Physica
Bohlin Instruments	Rheometric Scientific
Brookfield Engineering Laboratories	TA Instruments
Capillary Rheometer	TherMold Partners
Goettfert	Vilastic Scientific
Haake	

Industrial Users

DuPont	National Starch and Chemical
Fluid Dynamics	Procter and Gamble

University

David Boger	University of Melbourne
Ralph Colby	Pennsylvania State University
Francis Gadala-Maria	University of South Carolina
William Graessley	Princeton University
Chris Macosko	University of Minnesota
Jaye Magda	University of Utah
Gareth McKinley	Harvard University
Skip Rochefort	Oregon State University

Accomplishments

- A candidate material has been successfully produced, and preliminary measurements indicate that it has appropriate shear thinning and normal stress difference behavior.

- A new rheometer, redesigned in collaboration with NIST staff to improve normal force measurement capability, has been acquired.
- Industry and academic partners have been contacted for the purpose of running the round robin and interest in the new fluid and promise of participation in the round robin has been high.

Outputs

Presentation

C. R. Schultheisz and G.B. McKenna, *A Nonlinear Fluid Standard Reference Material: Progress Report*, 69th Annual Meeting of the Society of Rheology, Columbus, Ohio, October 23, 1997.

Task 2. Viscoelastic Constitutive Model for the Creep Behavior of Polyurethane Foams

G.B. McKenna and V. Rouiller

Technical Approach

The applicability of using a hybrid Valanis-Landel-BKZ type of constitutive equation as a robust means of describing the nonlinear viscoelastic response of polymers above the glass transition is explored. In the past this worked reasonably well for modeling the response of a poly(vinyl chloride) film material. Under sponsorship of the NSWC Carderock of the U.S. Navy, the same approach is applied to characterization of polyurethane rubber. In addition, the project aims to use the time and temperature dependent parts of the model to obtain an accurate description of the behavior of polyurethane foams used by the Navy. Experimentation requires tension and compression characterization of the neat resin over a range of deformations and temperatures. Comparison of the hybrid model predictions with both creep response of the rubber and the response in multi-step creep and stress relaxation experiments are being made. Experiments in hydrostatic compression of foams are planned and a foam model extension of the hybrid viscoelastic model will be used to predict the long term performance of the foams.

Accomplishments

- Built temperature and humidity control chamber for uniaxial test apparatus.
- Developed new software to drive the uniaxial test apparatus in multi-step creep and stress relaxation experiments.
- Demonstrated that a hybrid viscoelastic constitutive model can predict multi-step stress relaxation and creep results for polyurethane elastomers to within approximately 10% when the history is primarily one of increasing deformation or stress. This approach to nonlinear

viscoelasticity will lead to simple test methods for characterizing the non-linear material parameters needed in computer simulations of, for example, blow molding processes.

- Showed limits of the hybrid Valanis-Landel-BKZ model in unloading deformations or stresses is not a very good predictor of material response.

General Outputs in Rheology

Publications

G.B. McKenna and J.M. Crissman, *Temperature and Crosslinking Effects on the Swelling of Poly(isoprene) in Isopiestic Conditions*, J. Polym. Sci., Polym. Phys. Ed., 35, 817 (1997).

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.

R. Zorn, F.I. Mopsik, G.B. McKenna, L. Willner, D. Richter, *Dynamics of Polybutadienes with Different Microstructures: 2. Dielectric Response and Comparisons with Rheological Behavior*, J. Chem. Phys., in press.

G.B. McKenna, F.I. Mopsik, R. Zorn, L. Willner, and D. Richter, *Mechanical and Dielectric Measurements in Polymers: Differences in Time-temperature Superposition Behavior*, Society Plastics Engineers ANTEC, II, 1027 (1997).

Presentations

G.B. McKenna, *Alternate Representations to Reptation to Describe the Behavior of Polymer Melts*, Exxon Chemical Company, Baytown, TX, November 1996.

R. Zorn, **G.B. McKenna**, F.I. Mopsik, L. Willner, D. Richter, *Dielectric and Rheological Measurements in Different Microstructure Polybutadienes: Comparison of Time-Temperature Superposition Behaviors*, Society of Rheology 1996 Annual Meeting, Galveston, TX, February 1997.

R. Zorn, **G.B. McKenna**, F.I. Mopsik, L. Willner and D. Richter, *Time-Temperature Superposition in Polymer Melts: Rheological and Dielectric Measurements on Polybutadienes*, American Physical Society March Meeting, Kansas City, MO, March 1997.

G.B. McKenna, F.I. Mopsik, R. Zorn, L. Willner and D. Richter, *Mechanical and Dielectric Measurements in Polymers: Differences in Time-Temperature Superposition*, Society Plastics Engineers ANTEC, Toronto, Canada, May 1997.

viscoelasticity will lead to simple test methods for linear viscoelasticity. The non-linear viscoelasticity of polymer solutions will be discussed in a separate paper.

- * Showed limits of the Hybrid Volume-Linear-Non-Linear model for the prediction of the linear viscoelasticity of polymer solutions.

General Outputs in Rheology

Publications

O.P. McKenna and M. D. Graham, *Journal of Rheology*, 41(5), 1071-1085 (1997)

F. denbroek & M. D. Graham, *Journal of Rheology*, 41(5), 1087-1105 (1997)

R. I. Tanner, *Journal of Rheology*, 41(5), 1061-1070 (1997)

O.P. McKenna, *Journal of Rheology*, 41(5), 1061-1070 (1997)

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 mass 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 mass 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. 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 (NIDR), 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

- A variety of new fluorinated monomeric and oligomeric urethane methacrylates were synthesized and examined in photopolymerizable resins. The identification of several moderately to highly fluorinated resins that combine excellent mechanical strength and hydrophobicity may offer new dental composites with enhanced durability.
- Demonstrated the ability of photo-differential calorimetry to characterize the influence of monomer structure on the photopolymerization kinetics and efficiencies of dental resins based on conventional dimethacrylate monomers and experimental multimethacrylate oligomers. This technique provides a convenient method for optimization of resin compositions to ensure the high reactivity and the adequate degrees of conversion that are essential in dental resins as well as in other photopolymer applications.
- Demonstrated that acid catalysts bring about not only the desired ring-opening polymerization of spiro orthocarbonate (SOC) monomers but also the rapid hydrolytic degradation of the monomers. The efficient competition between these two processes will affect how the SOC resins can be used as potential dental materials with minimal polymerization shrinkage.
- N-phenyliminodiacetic acid (PIDAA) was shown to be a multi-functional dental primer with the ability to etch dentin and at the same time stabilize collagen in demineralized dentin, thereby facilitating adhesive resin infiltration. In addition, PIDAA has the ability to initiate interfacial polymerization. This unique combination of mass in one adhesive agent permits the development of simplified, highly effective dental adhesive systems.
- Developed facile syntheses for acrylic organosilsesquioxanes from readily available silane coupling agents. These reactive oligomers are readily polymerized and have potential for use in dental composites, sealants and adhesives. Other applications, e.g. in electronic packaging, that require fast-curing resins yielding polymers with high thermal stabilities and low dielectric mass also may be feasible.
- Demonstrated that the microbond test could be successfully adapted to probe adhesion to a variety of flat substrates, e.g., quartz, dentin, enamel. This new technique facilitates the evaluation of a variety of adhesive agents with diverse substrates.

- A Memorandum of Understanding (MOU) was signed by three government agencies--- NIST (Polymers Division and Standard Reference Materials Program), the Food and Drug Administration, and the National Institute of Health---for the development of reference materials for biomaterials. The MOU may facilitate the cooperative efforts of these agencies to produce reference materials that are intended for use in quality assurance of biomaterials for medical devices.

Dental Resins Based on Fluorinated Monomers and Oligomers

Jeffrey W. Stansbury

Objective

The objective is the development of new resins and coupling agents that will provide dental composite restoratives with significantly improved durability and reduced polymerization shrinkage compared with current dental materials.

Technical Description

Through appropriate monomer design, the resin phase of dental composites can undergo efficient photopolymerization with minimal shrinkage. The use of oligomeric multimethacrylates, cyclopolymerizable methacrylate monomers or spiro orthocarbonate monomers that undergo double ring-opening polymerization all provide routes to low shrinkage polymerization processes. 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. Thus, there is need for more hydrophobic and 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 mass. 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 silane coupling agent used to fuse the resin matrix with the reinforcing filler particles can also serve to improve the strength and stability of dental composites.

External Collaborations

Dr. Kyung Choi, a Guest Scientist from the University of California, Irvine, is actively advancing the work with fluorinated resins and modified coupling agents under an NIDR-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 (by mass) of conventional materials. Expect more durable composites that retain their excellent initial mass 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 mass and better retention of these mass upon long-term storage in water.

Accomplishments

Fluorinated resins and composites: New fluorinated urethane monomers and oligomers have been prepared and several have been identified that produce polymerized resins with acceptably high flexural strengths as well as high water contact angles and very low levels of water uptake that are indicative of improved long-term stability. Studies with composites have shown that the introduction of a more hydrophobic silane coupling agent improves compatibility between the fluorinated resins and fillers while allowing for significantly higher filler loading levels. Photo-DSC studies have been used to compare the polymerization inhibition effects of oxygen on fluorinated and conventional resins. Air inhibition effects were demonstrated in the bulk rather than just at the surface of both fluorocarbon and hydrocarbon polymers. A separate study showed a modest polymerization inhibition effect associated with low to moderate levels of filler, while high filler levels resulted in more significant reductions in monomer conversion.

Dimethacrylate comonomers for fluorinated resins: An evaluation of homopolymers of commercially available hydrocarbon dimethacrylate diluent monomers was made to select an appropriate comonomer for use in fluorinated resin formulations. While ether-containing dimethacrylates produce high strength polymers, water uptake was judged to be excessive for these polymers and previous experience has indicated problems with phase separation in fluorinated resins. Based on photopolymerization rate, water contact angle, water uptake and flexural strength results, 1,12-dodecanediol dimethacrylate was chosen as an acceptable, compatible comonomer for use with a wide variety of fluorinated monomers and reactive oligomers.

Photopolymerization kinetics of methacrylate resins: A photo-differential calorimetry-based investigation was undertaken with the following conventional dental resins: 1) Bis-GMA/triethylene glycol dimethacrylate (TEGDMA); 2) ethoxylated bisphenol A dimethacrylate/TEGDMA; and 3) urethane dimethacrylate (UDMA)/TEGDMA. A broad range of comonomer compositions were evaluated for each resin. In each resin system, the more mobile TEGDMA monomer tended to increase the overall conversion but the more viscous monomers were responsible for enhanced resin reactivity. Resin viscosities were measured and correlated with the photopolymerization reactivities. In addition, hydrogen bonding interactions in the Bis-GMA and UDMA resin systems were determined by FT-IR. For Bis-GMA/TEGDMA resins in particular, the compositions with the highest photopolymerization rates cured much more rapidly than either of the individual comonomers alone. Bis-GMA/TEGDMA resins were most reactive at an approximately equimolar composition while the other resins were most reactive when only a small amount of TEGDMA was included. The UDMA/TEGDMA resin

system had the highest overall optimized resin reactivity. The photopolymerization reaction rate is clearly related to resin viscosity. Optimum reactivity occurs when resin viscosity allows sufficient mobility of small monomer molecules but limits termination reactions between macromolecular radicals. The result is an essentially instant onset of the autoacceleration effect.

Expanding polymers: Water sensitivity problems were demonstrated during the homopolymerizations of spiro orthocarbonate (SOC) monomers and oligomers. While the ring-opened polymers are relatively hydrophobic, the bicyclic monomers are hydrophilic and absorb water. With appropriate SOC structures, the water does not degrade the monomer; however, during cationic polymerization with strong acid catalysts, hydrolysis of the SOC linkage to diol and cyclic carbonate competes quite effectively with the desired ring-opening polymerization process. Under dry conditions, the new oligomeric SOC's produce glassy, cross-linked polymers with little if any soluble fraction. Dual cure (radical/cationic) copolymerization studies with methacrylate and SOC monomers gave primarily interpenetrating network structures with minor amounts of crossover due to hydrogen abstraction.

Outputs

Publications

K.M. Choi and J.W. Stansbury, *New Families of Photocurable Oligomeric Fluoromonomers for Use in Dental Composites*, Chem. Mater. 8, 2704 (1997).

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B.B. Reed, K.M. Choi, S.H. Dickens and J.W. Stansbury, *Effect of Resin Composition on Kinetics of Dimethacrylate Photopolymerization*, Amer. Chem. Soc., Div. Polym. Chem., Polym. Prepr. 38, 108 (1997).

H. Takahashi, J.M. Antonucci, J.W. Stansbury, F.W. Wang, *Relationship Between the Tensile and Flexural Strength of Composite Resins*, Amer. Chem. Soc., Div. Polym. Chem., Polym. Prepr. 38, 163 (1997).

Presentations

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J.W. Stansbury, *Designing monomers to minimize polymerization shrinkage*, AT&T Bell Labs, Lucent, Murray Hill, NJ, February 3, 1997.

J.W. Stansbury, *Alternative polymers for use in dental materials*, Institute of Materials Science, University of Connecticut, Storrs, CT, March 28, 1997.

J.W. Stansbury, K.M. Choi and J.M. Antonucci, *Considerations in the Development of Semifluorinated Methacrylate Dental Resins and Composites*, Symposium on Dental Materials and Composites, American Chemical Society Meeting, Las Vegas, NV, September 8, 1997.

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B.B. Reed, K.M. Choi, S.H. Dickens and J.W. Stansbury, *Effect of Resin Composition on Kinetics of Dimethacrylate Photopolymerization*, Symposium on Dental Materials and Composites, American Chemical Society Meeting, Las Vegas, NV, September 9, 1997.

J.W. Stansbury and M.H. Dermann, *Radical/cationic Photopolymerization of SOC-modified Methacrylate Resins*, International Association for Dental Research Meeting, Orlando, FL, March 20, 1997.

Patents

A provisional patent was filed on November 14, 1996 (NIST #96-042PA): High strength polymeric networks derived from (meth)acrylate resins with organofluorine content and process for preparing same. Full patent filing is currently in progress. A dental materials manufacturer, has expressed interest in licensing due to potential problems with bisphenol-A based monomers, among other reasons.

Dental Composites With Improved Interfaces

Joseph M. Antonucci, W. G. McDonough, J. P. Dunkers and B.O. Fowler¹

¹National Institute of Dental Research, Bethesda, MD

Objective

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

Technical Description

It is anticipated that improvements in the quality of the interfacial phase along with similar improvements in the polymer matrix and fiber 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 microbond test and the single fiber fragmentation test, have also been used to assess interfacial behavior. The microbond test has proved to be a useful method for assessing polymer-fiber shear bond strengths and for exploring the interaction of silane coupling agents with silica surfaces and dental polymers. The microbond test also has been used successfully in durability studies and, most recently, has been modified to assess the interfacial shear strength between dental polymers and primed dentin and enamel substrates. Thus far, attempts to use the single-fiber fragmentation test to determine the strength and durability of the interface derived from dental polymers and variously treated glass fibers have met with limited success due to the premature fracture of the brittle polymer matrices. Preliminary experiments with more flexible resin systems suggests that this approach may obviate this problem.

There has been increasing interest in the development of reactive organosilsesquioxanes for composite, coating, adhesive and other applications. The feasibility of synthesizing reactive organosilsesquioxanes from trialkoxysilanes such as 3-methacryloxypropyltrimethoxysilane (MPTMS) by controlled hydrolysis-condensation reactions has been investigated. A variety of solvent and catalyst systems have been studied in an effort to control the extent of oligomerization, functionality and residual silyl ether and/or silanol content. Thus far from MPTMS, both viscous liquid, multi-methacrylic oligomers (MW > 6,000) and fluid liquids consisting of mainly dimeric products have been obtained. Both types, in contrast to the starting MPTMS, are easily photopolymerized using visible light irradiation. As expected from their silsesquioxane structure, polymers derived from the viscous oligomer exhibited high thermal stability. In addition to their potential use in dental composite, sealant, and adhesive applications, these fast-curing resins also may find use in other fields such as electronic packaging.

External Collaboration

B. O. Fowler, a Guest Scientist from National Institute of Dental Research, characterized reactive organosilsesquioxanes for dental applications.

Accomplishments

- By means of the microbond test, it was demonstrated under accelerated aqueous challenge that 10-methacryloxydecyltrimethoxysilane, a more hydrophobic and flexible silane coupling agent than the widely used 3-methacryloxypropyltrimethoxysilane (MPTMS), generated a more durable interface than MPTMS.

- Demonstrated that the microbond test could be successfully adapted to probe adhesion to a variety of flat substrates, e.g., quartz, dentin, enamel. This new technique facilitates the evaluation of a variety of adhesive agents with diverse substrates.
- Developed facile syntheses for acrylic organosilsesquioxanes from readily available silane coupling agents. These reactive oligomers are readily polymerized and have potential for use in dental composites, sealants and adhesives. Other applications, e.g. in electronic packaging, that require fast-curing resins yielding polymers with high thermal stabilities and low dielectric mass also may be feasible.

Outputs

Publications

W.G. McDonough, J.M. Antonucci and J.P. Dunkers, *Durability of Polymer-Glass Interfaces by the Microbond Test*, J. Dent. Res., 76, 38 Abstract 198 (1997).

W.G. McDonough, J.M. Antonucci and J.P. Dunkers, *A Study of Dental Adhesion by Means of the Microbond Test*, Polymer Preprints 38, 112-113 (1997).

J.M. Antonucci, B.O. Fowler and J.W. Stansbury, *Facile Synthesis of Reactive Organosilsesquioxanes for Dental Applications*, J. Dent. Res., 76, 40 Abstract 214 (1997).

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W.G. McDonough, J.M. Antonucci and J.P. Dunkers, *Shear Strength Measurements of Dental Polymer-Glass Fiber Interfaces Using The Microbond Test*, Tokyo Medical and Dental University, Tokyo, Japan, September, 1996.

W.G. McDonough, J.M. Antonucci and J.P. Dunkers, *Determining Mechanical Strength Mass of Dental Composites*, Tokushima University, Tokushima, Japan, September, 1996.

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Improved Adhesive Systems for Bonding to Tooth Structure

Joseph M. Antonucci

Objectives

The overall objective 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

Recently 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 these unique adhesive systems can be modified by the addition of silane coupling agents without adversely affecting their adhesion to dentin. The presence of silane coupling agents has potential for mediating adhesion to other dental substrates such as porcelain. In addition, mass spectrometry was used to aid in elucidating the mechanism of initiating polymerization with *N*-aryl- α -amino acids. Also, gas chromatography-mass spectrometry has been used to study the Michael addition of primary and secondary aryl amines with several types of acrylic monomers. This type of reaction can provide a facile synthetic method to a variety of arylimino diacids. In order to gain further insight into the etching, priming and polymerization-initiating mass of aryliminodiacetic acids, several analogs of PIDAA have been synthesized and characterized. Evaluation of these potential adhesive agents is in progress. Studies are in progress that seek to elucidate the role(s) of a variety of primers in dentin bonding.

External Collaborations

Dr. Farahani, a Guest Scientist from the American Dental Association Health Foundation's Paffenbarger Research Center, investigated mechanisms of the addition reaction of arylamines with acrylic monomers. Dr. G.E. Schumacher and P.S. Bennett, Guest Scientists from Paffenbarger Research Center, Dr. J.E. Code, a Guest Scientist from the U.S. Public Health

Service, and Dr. T. Nikaido, a Guest Scientist from the Tokyo Medical and Dental University, carried out experiments on *N*-phenyliminodiacetic acids as an etchant/primer for dentin bonding.

Accomplishments

- *N*-phenyliminodiacetic acid (PIDAA) was shown to be a multi-functional dental primer with the ability to etch dentin and at the same time stabilize collagen in demineralized dentin, thereby facilitating adhesive resin infiltration. In addition, PIDAA has the ability to initiate interfacial polymerization. This unique combination of mass in one adhesive agent permits the development of simplified, highly effective dental adhesive systems.
- Demonstrated that silane agents such as 3-methacryloxypropyltrimethoxysilane can be successfully incorporated in two and three component PIDAA adhesive systems to yield high composite-to-dentin shear bond strengths.
- Demonstrated by mass spectrometric analysis techniques that several types of *N*-aryl- α -amino acids can act as polymerization initiators when dissolved in acrylic monomers.
- Demonstrated that the primer 2-hydroxyethyl methacrylate can prevent the collapse of demineralized dentinal collagen, thereby promoting enhanced diffusion of adhesive resins into demineralized dentin.

Impact

A patent (U.S. Patent 5,498,643) has been issued based on self-etching primers of the *N*-aryliminodiacetic acid type. The American Dental Association has licensed this invention and Caulk/Dentsply has recently sublicensed this technology.

Outputs

Publications

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

Joseph M. Antonucci

Objectives

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 mass compared to either dental ceramics or traditional dental composites. Previously, it was shown that a polymer-reinforced interpenetrating composite (IPC) with high strength mass 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. 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 also have been investigated. Silane treatment of the porous ceramic network had a positive effect on the IPC, but the effects of varying resin composition were less clear cut. During the current phase of this research, the effect of using fluorinated monofunctional methacrylates as part of the infiltrating monomer system was explored. Both the strength and durability (after aqueous challenge) of the IPCs were enhanced compared to a control IPC infiltrated with methyl methacrylate.

External Collaboration

Dr. J. R. Kelly, a Guest Scientist from the Naval Dental Research Institute and the Naval Dental School, Bethesda, prepared porous ceramic structures by low temperature pyrolysis of ceramic powders coated with pre-ceramic polymers such as polysiloxanes.

Accomplishments

- Demonstrated that the incorporation of monofunctional fluorinated methacrylates in the infiltrating monomer system of IPCs can have a positive effect on their mass.

Impacts

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

Outputs

Publications

C.R. Fahncke, J.R. Kelly and J.M. Antonucci, *Influence of Veneering Material on Failure of In-CERAM FPD Analogs*, J. Dent. Res., 76, 311 Abstract #2378 (1997).

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Patents

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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. The fluorescence wavelength of the probe decreases with decreasing mobility of the probe. Since the mobility of the probe molecules decreases upon their attachment to sodium alginate the fluorescence spectrum is a measure of 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.

Measurement methods described above can also be used to monitor other functionalization processes and other crosslinking reactions. For example, the reaction of tetrahydroxy polyethylene glycol with acryloyl chloride, the photo-induced crosslinking reaction of polyethylene glycol functionalized with acrylate moieties, and the crosslinking reaction of acrylamide and bis-acrylamide can all be monitored in the manner described above.

Planned Outcome

Technology transfer, to small biotechnology companies, of process control methods for functionalization and cross-linking of sodium alginate and other water-soluble polymers 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. It was demonstrated that when a bifunctional fluorescent probe was dissolved in a buffer solution containing acrylamide and a bis-acrylamide, the crosslinking reaction can be monitored by measuring the change in the excitation spectrum of the probe.

Outputs

Presentations

F.W. Wang, *Applications of Fluorescence Spectroscopy in Polymer Systems*. Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz, Poland, November, 1996.

F.W. Wang, *Wavelength-shift Fluorescent Probes for Monitoring of Polymerization*, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland, November, 1996.

F.W. Wang, *Applications of Fluorescence Spectroscopy in Polymer Systems*, Institute of Polymer Chemistry, Polish Academy of Sciences, Zabrze, Poland, November, 1996.

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

Joseph M. Antonucci

Objective

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

Technical Description

ACP, a highly soluble, non-crystalline calcium phosphate with a propensity for facile conversion to hydroxyapatite (HAP), has potential as remineralizing agent for defective mineralized tissues. Previous studies in this laboratory have shown that polymeric composites derived from dental acrylic polymers and stabilized ACP powders give sustained release of calcium and phosphate ions over extended periods of time. It was demonstrated that caries-like lesions in extracted bovine enamel that were covered with a sealant layer of a photocured ACP-composite regained considerably more of their lost mineral than did lesions coated with a similar HAP-filled composite. It also was demonstrated that glass forming agents such as tetraethoxysilane and zirconyl chloride can be used to prepare modified ACP fillers for bioactive composites. These new bioactive composites exhibited both adequate release of calcium and phosphate ions on exposure to oral-simulative environments sufficient for remineralization, and also had improved mechanical strength compared to an unmodified ACP composite control. In the present study the mechanical properties of a BisGMA/ACP composite were evaluated to determine its applicability as a base/liner material. Biaxial flexure, diametral tensile and compression tests were performed on this experimental composite comprising a BisGMA resin that was filled with 40 mass % of stabilized ACP.

External Collaborations

Dr. E.D. Eanes and Mr. A.W. Hailer of NIDR, Dr. D. Skrtic of the American Dental Association Health Foundation's Paffenbarger Research Center and Dr. M.S. Park of Phil Dental Clinic, Seoul, Korea carried out the experimental development of bioactive polymeric composites with remineralization potential.

Accomplishment

The results of this study demonstrated that experimental, visible-light curable ACP-BisGMA resin composites with remineralizing properties and with mechanical properties suitable for use as base/liners or pit and fissure sealants can be prepared.

Impact

A patent has been issued based on the use of ACP as a bioactive filler in polymeric dental materials. Several companies have expressed interest in this technology.

Outputs

Publications

D. Skrtic, J.M. Antonucci and E.D. Eanes, *Improved Properties of Amorphous Calcium Phosphate Fillers in Remineralizing Resin Composites*, Dent. Mater., 12:295-301(1996).

M.S. Park, E.D. Eanes, J.M. Antonucci and D. Skrtic, *Mechanical Properties of Bioactive ACP/methacrylate Composites*, J. Dent. Res. 76 :76 (Abstract No. 504) (1997).

Presentations

M.S. Park, E.D. Eanes, J.M. Antonucci and D. Skrtic, *Mechanical Properties of Bioactive ACP/methacrylate Composites*, 75th General Session of the International Association for Dental Research, Orlando, FL, March 19-23, 1997.

Support for the Biomaterials Integrated Products Industries

J.A. Tesk, Steve Hsu¹, Kenzo Asaoka², Alan Litsky³

¹ Ceramics Division, NIST; ² Tokushima University; ³ Ohio State University

Objective

The objective is to provide support for the American Biomedical industry via development of test methods, provision of reference materials, development of standards useful to the industry, and exploratory research into new materials and properties with useful benefits, such as: employment of cyclopolymerizable monomers as substitutes for poly(methylmethacrylate) in orthopaedic bone cement; metallic glasses for wear resistant coatings of orthopaedic implant bearing surfaces, and modeling of processing variables on the mechanical behavior of dental/medical materials.

Technical Description

Objectives 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. New materials and properties benefits will be explored via collaborations within NIST and with universities and industry.

External Collaborations

Biomet Inc. (Warsaw Ind.), Johnson & Johnson Professional, Inc. (Raynham, Mass.), Ostenoics Inc. (Allendale, N.J.), Smith & Nephew Richards, Inc. (Memphis, Tenn.), Wright Medical Technology, Inc. (Arlington, Tenn.), and Zimmer, Inc. (Warsaw, Ind.), which are members of the Cooperative Research and Development Agreement (CRADA) Consortium established to evaluate test methods for the wear properties of orthopedic materials, provided insight into the needs of the orthopedic industry and partial financial support. Poly Hi Solidur (Fort Wayne, Ind) and Teledyne Allvac/Vasco (Monroe,NC) contributed materials to the CRADA Consortium. Professor K. Asaoka of Tokushima University modeled the effects of processing variables in dental investments.

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; New materials with features of interest for potential applications to improve biomedical products; Understanding of processing effects on mechanical behavior of dental/medical materials; Foreshortening the time for acceptance of device submissions to the FDA (an industry estimate is that shortening acceptance time by two weeks for only one device would recoup the research expenditures).

Accomplishments

Completed one year of Cooperative Research & Development Agreement (CRADAs) research with six (6) orthopaedic companies, formed as a CRADA consortium, to identify accelerated methods for evaluation of the wear properties of orthopaedic joint materials. Based on results from first year, four (4) of the six (6) companies voted to amend the CRADAs to change the direction of the research according to a proposal recommended by NIST. Amended the CRADAs, with additional support provided by the companies.

Facilitating NIST-NIH-FDA-Industry collaboration for NIST dissemination of Industry Developed Polyetherurethane Reference Materials, useful for development of Cardiovascular devices.

A Memorandum of Understanding (MOU) was signed by three government agencies--- NIST (Polymers Division and Standard Reference Materials Program), the Food and Drug Administration, and the National Institute of Health---for the development of reference materials for biomaterials. The MOU may facilitate the cooperative efforts of these agencies to produce reference materials that are intended for use in quality assurance of biomaterials for medical devices.

Developed method for use of methacrylate powders with co-monomers of cyclopolymerizable and methylacrylate types to produce doughs in times comparable to those used for orthopaedic bone cement (BC) and dental denture bases (DB), but which can persist for a couple of days. Extended-time dough state could be expected to make insertion time of a BC less critical and the

use as a DB material potentially labor saving. Other potential benefits include: lower exotherm, less tissue damage (BC; DB reline material), higher conversion, less residual monomer, (BC; DB & DB reline), large monomer size (BC, no blood pressure drop due to monomer absorption; DB & DB reline), Reduced polymerization shrinkage (BC, DB, & DB reline; improved fit).

Outputs/Interactions

Publications/Reports

K. Asaoka and J.A. Tesk, *Simulation of Transient Thermal Stress in Gypsum-bonded Investment*, Dent. Mater., December 1996.

J.A. Tesk and O. Okuno, *High-Temperature Investments*, In: Dental Materials and Their Selection, 2nd ed., W.J. O'Brien Editor, Quintessence Pub. Co., Chapter 18, 1997.

J.A. Tesk and E.P. Mueller, *Reference Materials in Standards for Tissue-Engineered Products*, Proceedings of ASTM Workshop on Tissue Engineering: The Role of ASTM, May 1997.

J.A. Tesk, *Review of Dental School Departmental Programs*, Report of Expert Advisory Panel on 20 Years of Dental Research at Tokushima University, February 1997.

J.A. Tesk, S. Hsu, and M. Shen, Quarterly Reports (confidential) to Orthopaedic CRADA Research Consortium, September 1996, December 1996, March 1997, June 1997.

Presentations

J.A. Tesk, *Implant Retrieval: Reference Materials, Standards, and Analysis*, Tokushima University Tokushima, Japan, March 1997.

J.A. Tesk, *Needs for Reference Materials in Standards*, ASTM Workshop on Tissue Engineering, St. Louis MO, May 6-7, 1997.

THEORY AND MODELING

Materials science and engineering is on the threshold of a fundamental transformation. Spectacular advances in computer processor power, memory, and computational methodologies now allow researchers to simulate highly complex materials behavior and microstructures. In FY97, the MSEL Theory and Modeling Program's activities continued their focus on the behavior and properties of materials over length scales extending from atoms to bulk materials. For example, MSEL researchers performed molecular dynamics simulations to study relaxation and glass formation in supercooled liquids, employed mesoscopic phase field and reaction-diffusion models of alloys, polymers and liquid crystals to study phase behavior, stability, separation kinetics, and morphological evolution in these materials, designed cellular automata models to investigate solidification in alloys, and developed finite-element software tools to model solder drops in microelectronic interconnects, domain formation in micromagnetic materials, and mechanical properties of composite microstructures.

In FY97 MSEL's Center for Theoretical and Computational Materials Science (CTCMS) facilitated numerous interactions between industry, academia, NIST and other government labs in the development and application of state-of-the-art theoretical and computational 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 FY97, CTCMS researchers within MSEL developed powerful new materials modeling tools and addressed critical technical issues 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, and object-oriented finite-element modeling of composite microstructures.

Significant Accomplishments

- A path-integral description is deduced and explicitly calculated using fractional calculus methods for the virial coefficient of flexible polymers with objects having complex shape and general interaction (dendrimers, colloid particles, proteins). This theory is potentially important for describing the role of particle shape and polymer-particle interaction on the binding of polymers to filler particles. This contribution also introduces new mathematical

methods which should be broadly applicable to condensed matter.

- Developed a statistical mechanics based theory that connects the kinetics of glass formation to the underlying thermodynamics. This leads to a formula to replace the Vogel-Fulcher law.
- Discovered a new polymer phase transition involving a polymer molecule threading a membrane separating two solutions. The transition is first-order.

Theory and Modeling of Polymer Phase Transitions

E. A. Di Marzio

Objectives

The objectives are: *i.* Develop a relationship between the kinetic properties and thermodynamic properties of glass forming systems. *ii.* Discover, classify and understand all the polymer phase transitions. *iii.* Determine how different phase transitions couple to one another. *iv.* Use polymer phase transitions as models for self-assembly. *v.* Investigate the coupled phase transitions as technology opportunities.

Technical Description

The principle of detailed balance is taken to connect thermodynamic properties to the kinetic properties of polymer glasses and compared the results with the classical Vogel-Fulcher law for the temperature dependence of, e.g., the viscosity.

A statistical mechanical analysis of a polymer molecule which is allowed to translocate through a small hole in an otherwise impenetrable partition separating two solutions shows that the molecule undergoes a first-order phase transition. A classification scheme is developed for coupled pairs, triplets, etc. of polymer phase transitions. An attempt is being made to collect, catalogue, and classify the various examples of coupled polymeric phase transitions in order to determine what technology opportunities exist in the area of self-assembly.

External Collaborations

Arthur J-M Yang while at Armstrong World Industries; now at Industrial Science and Technology Network, Inc.

Arnold Mandell, Emory University

Planned Outcomes

- A model for the temperature dependence of the viscosity of glass forming polymers from a rigorous statistical mechanics basis.
- A methodology for classifying phase transitions in polymers.

Accomplishments

- Developed a statistical mechanics based theory that connects the kinetics of glass formation to the underlying thermodynamics. This leads to a formula to replace the Vogel-Fulcher law. Derived formulas for the frequency dependence of viscosity and dielectric susceptibility.
- Discovered a new first-order polymer phase transition. It is that of a polymer molecule threading a membrane separating two solutions. In addition, an important insight was obtained which shows why linear macromolecules display phase transitions in abundance.
- Investigated the extent to which self-assembly in polymeric systems can be viewed as thermodynamic phase transition phenomena. It is concluded that self-assembly in polymers is essentially nothing more than the equilibrium, kinetic and pattern formation aspects of polymeric phase transitions.

Outputs

Publications

E. A. Di Marzio and A. J-M Yang, *Configurational Entropy Approach to the Kinetics of Glasses*, J. Research NIST, 102, 135 (1997).

E. A. Di Marzio, *The Use of Configurational Entropy to Derive the Kinetic Properties of Polymer Glasses*, ACS Books, Symposium on Polymer Glasses, San Francisco, April, 1997, in press.

E. A. Di Marzio and A. Mandell, *Phase Transition Behavior of a Linear Macromolecule Threading a Membrane*, J. Chem. Phys., in press.

Presentations

E. A. Di Marzio, *The Glass Transition in Polymers*, Chemical Engineering Department, Johns Hopkins, Baltimore, MD, October 1996.

E. A. Di Marzio, *Phase Transitions in Polymers: Their use as Models for Self-Assembly*, Physics Department, University of Maryland, Baltimore Campus, October 1996.

E. A. Di Marzio, *Phase Transitions in Polymers: Their use as Models for Self-Assembly*, Polymer Science Department, University of Massachusetts, Amherst, MA, October 1996.

E. A. Di Marzio, *The Glass Transition in Polymers*, Polymer Science Department, University of Massachusetts, Amherst, MA, October 1996.

E. A. Di Marzio, *The Use of Configurational Entropy to Derive the Kinetic Properties of Polymer Glasses*, American Chemical Society Meeting, San Francisco, CA, April 1997.

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

J. F. Douglas

Objectives

The objectives are: *i.* describe the influence of solvent quality on the morphology of adsorbed and grafted polymer layers, *ii.* develop theoretical approach for deducing shift of phase boundary for polymer blends under steady shear in the two phase region, *iii.* introduce novel fractional calculus methods for solving boundary value problems involving rough surfaces such as polymers, *iv.* investigate influence of blend incompatibility on the tendency for block copolymers to become localized at the interface of phase separated blends and *v.* calculate swelling of polymers subject to a power law potential to describe chain swelling of block copolymers over a range from weak to strong segregation.

Technical Description

The properties of polymer blends, films and solutions are studied through analytical path-integration and other functional (integral equation, renormalization group, fractional calculus) methods, and analytic calculations for lattice models of polymers in combination with numerical calculations based on polymer lattice models of interacting polymers, numerical simulation of polymer layer deposition processes, and lattice gas simulations of phase separation of fluids with surfactants.

Accomplishments

- Developed theoretical method for deducing shift of critical temperature of blends in the two-phase region under conditions of steady shear. Provided interpretation to renormalization of critical exponents (β and ν) in diluted polymer blends. Results used to predict the exponent governing the shear shift of the critical temperature.
- The inhomogeneity of polymers adsorbed and grafted on surfaces is modeled by a generalized random sequential adsorption model in which the adaptability of chain shape to changes in surface accessibility in the deposition process is modeled by taking the size of depositing species to be variable. Properties of polymer layers grown adsorbed under non-equilibrium conditions are shown to be qualitatively different from polymer films at equilibrium and predictions of the model are verified experimentally.
- Numerical calculations with Bruce Berghosian of Boston University indicate that surfactants such as block copolymers exert a very different influence on phase separation depending on the degree of fluid immiscibility. For weak segregation the surfactant exerts a weak influence on the phase separation kinetics, while the coarsening is arrested in the strong segregation regime where the surfactant becomes localized at the interfaces between the phase separated domains.
- A path-integral description is deduced and explicitly calculated using fractional calculus methods for the virial coefficient of flexible polymers with objects having complex shape and

general interaction (dendrimers, colloid particles, proteins). This theory is potentially important for describing the role of particle shape and polymer-particle interaction on the binding of polymers to filler particles. This contribution also introduces new mathematical methods which should be broadly applicable to condensed matter.

- Model calculations are applied to the swelling of block copolymers from the disordered to ordered regimes and to the density profile of end-tethered polymer layers with a parabolic potential interaction modeling the interchain interactions in the grafted layer. Renormalization group calculations were performed to describe the influence of chain excluded volume on the density profile of end-grafted brushes.

External Collaboration

Modeling of the deposition of polymer layers under non-equilibrium conditions was performed in collaboration with Professor Steve Granick of the University of Illinois and Dr. Hildegard Schneider of 3M Corporation.

Outputs

Publications

J. Yu, J. Douglas, E. Hobbie and C. Han, *Homogenization of Polymer Blends Under Shear*, Phys. Rev. Ltrs., 78, 2664 (1997).

J.F. Douglas, *Some Applications of Fractional Calculus to Polymer Science*, Advances in Chemical Physics, in press.

J.F. Douglas, H. Schneider, P. Frantz, R. Lipman and S. Granick, *Origin and Characterization of Conformational Heterogeneity in Adsorbed Polymer Layers*, Journal of Physics: Condensed Matter, 9, 7699 (1997).

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

J.F. Douglas and K.F. Freed, *Modification of Continuum Chain Model of Surface-Interacting Polymers to Describe the Crossover between Weak and Strong Polymer Adsorption*, Macromolecules, 30, 1813 (1997).

C. Donati, J.F. Douglas, W. Kob, S.J. Plimpton, P.H. Poole and S.C. Glotzer, *String-Like Clusters in a Supercooled Liquid*, Phys. Rev. Ltrs, submitted.

J.F. Douglas, C.M. Guttman, A. Mah and T. Ishinabe, *Spectrum of Self-Avoiding Walk Exponents*, Physical Review E, 55, 738 (1997).

J.A. Given, J.B. Hubbard and J.F. Douglas, *A First-Passage Time Algorithm for the*

Hydrodynamic Friction and Diffusion-Limited Reaction Rate of Macromolecules, J. Chem. Phys., 106, 3761 (1997).

Presentations

Jack Douglas and Mark Mansfield, *Treatment of Fluctuation Effects in Mean-Field Models of Chain Stretching*, American Physical Society March Meeting, Kansas City, MO, March 1997.

Jack Douglas, *Coping with Complex Boundaries*, American Mathematical Society, April 1997.

Jack Douglas, *Transport Properties of Complex-Shaped Particles and Polymers*, Chemistry Department, New York University, New York, NY, August 1997.

J.F. Douglas, R. Lipman, A. Karim and S. Granick, *Models of the Influence of Excluded Volume on the Formation of Polymer Layers*, American Chemical Society, Las Vegas, NV, September 1997.

J.F. Douglas, *A Model of the Viscoelasticity and Mass Transport in Glass Forming Liquids*, Third International Discussion Meeting on Relaxations in Complex Systems, Vigo, Spain, July 1997.

OTHER PROJECTS

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.

Development and Utilization of Test Methods for Qualification of Passport Laminates

W.G. McDonough and D.L. Hunston

Objectives

One objective is to perform testing and provide consultation to assist the Bureau of Consular Affairs, 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. Another objective is to perform testing and provide consultation on the development of the next generation 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.

With the ultimate goal to have a more secure U.S. Passport, work on the next generation of US Passports involves evaluating techniques to put down a digitized image onto the data page in lieu of the currently used photograph. By combining a digitized image with state-of-the-art security devices, the security of the US Passport should be greatly enhanced.

Accomplishments

For work on passport laminates, 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 digital image technology were evaluated and the results served as a guide for future directions for this field. NIST helped review the current solicitation to make the next generation passports and this solicitation is now in the evaluation stage.

Outputs

Reports on the work are provided to the State Department on a periodic basis.

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
Wen-Li Wu
Phone: (301) 975-6839
e-mail: wen-li.wu@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

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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 Dendrimers and dendritic polymers

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

- o Synthetic and polymer chemistry
- o Dental composites, cements and adhesion
- o Initiator systems
- o Interfacial coupling agents
- o Remineralizing polymer systems

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

*Research Associate

⁺Guest Scientist

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

- o Dielectric measurements
- o Piezoelectric and pyroelectric modeling and theory
- o Equation of state of polymers
- o Ionic conduction

Bur, Anthony J.
anthony.bur@nist.gov

- o Dielectric properties of polymers
- o Fluorescence and optical monitoring of polymer processing
- o Piezoelectric, pyroelectric polymers
- o Viscoelastic properties of polymers

Campbell, Jr., Gordon C.⁺

- o Solid state NMR of polymers
- o Off-resonance proton irradiation techniques

Carey, Clifton M.*
clifton.carey@nist.gov

- o Dental plaque
- o Microanalytical analysis techniques
- o Phosphate chemistry
- o Ion-selective electrodes

Cerrada, Maria⁺
maria.cerrada@nist.gov

- o structure property relations
- o physical aging

Chang, Shu Sing⁺

- 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

Cherng, Maria*
maria.cherng@nist.gov

- o Calcium phosphate biomaterials

Chiang, Chwan K.
c.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

*Research Associate

⁺Guest Scientist

Choi, Kyung Moon⁺
kyung.choi@nist.gov

o Polymer composites

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

*Research Associate

⁺Guest Scientist

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

- o Scaling and renormalization group calculation
- o Optical coherence tomography of composites
- o Image analysis
- o Fiber optics spectroscopy
- o Process monitoring and control
- o Infrared microspectroscopy of polymers

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 Atomic force microscopy
- o Strong interactions in polymer solvent systems
- o Polyelectrolytes

Ettedgui, Emile E.+
emile.ettedgui@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, Hanqiao+
hanqiao.feng@nist.gov

- o Solid state NMR of polymers
- o Measurement of polymer morphology of the 2-50nm scale

*Research Associate

+Guest Scientist

- 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 Raman spectroscopy
 - o Structure of calcium phosphates, bones, and teeth
 - o Composites
- 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
- Glotzer, Sharon C.
sharon.glotzer@nist.gov
- o Theoretical and computational materials science
 - o Disordered systems
 - o Liquid crystals glasses
- Gruell, Holger[†]
- o Surface wetting
 - o Phase decomposition on surfaces
- Guttman, Charles M.
charles.guttman@nist.gov
- o Solution properties of polymers
 - o Size exclusion chromatography
 - o Mass spectroscopy of polymers
 - o Diffusion and absorption of gases by polymers
- 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

*Research Associate

[†]Guest Scientist

- 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, Erik 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
- Hoffman, Kathleen M.^{*}
kathleen.hoffman@nist.gov
- o Amalgam alternative material
 - o Scanning electron microscopy
 - o Nuclear magnetic resonance spectroscopy
- 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
- 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
- Hussain, Latiff^{*}
latiff.hussain@nist.gov
- o Monomer synthesis and testing
- Huynh, Hai⁺
- o Rubber recycling
 - o Mechanical properties of concrete
- Ishikawa, Kunio^{*}
- o Calcium phosphate compounds
- Ivkov, Robert⁺
- o Biopolymers

*Research Associate

⁺Guest Scientist

robert.ivkov@nist.gov

- o Polymer solutions
- o Polyelectrolytes

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

Jeon, Hyun Sik⁺

- o shear light scattering and optical microscopy
- o structure and morphology of two-phase elastomer blends under shear

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 Calcium phosphate cements
- o Clinical-laboratory test correlation
- o Dental ceramics
- o Failure analysis; dental prostheses
- o Finite element analysis
- o Weibull analysis

Khatri, Chetan A.⁺

- o Monomer/polymer synthesis and characterization

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, Ginam⁺
ginam.kim@nist.gov

- o Structure and morphology of polymers
- o Transmission and scanning electron microscopy
- o cryo-electron microscopy

Kolb, Rainer⁺
kolb@shine.nist.gov

- o X-ray reflectivity
- o Neutron reflectivity

*Research Associate

⁺Guest Scientist

Kryder, Samuel J. ⁺	<ul style="list-style-type: none"> o Electronic circuit design and construction o Electronic troubleshooting and repair
Kurakawa, Hidenobu ⁺	<ul style="list-style-type: none"> o Polymer solution thermodynamics o Small angle neutron scattering
Lee, Benjamin P. benjamin.lee@nist.gov	<ul style="list-style-type: none"> o Theory of polymer blends o Theory of phase separation kinetics
Lenhart, Joseph L. ⁺	<ul style="list-style-type: none"> o Sensors o Interphase structure
Li, Shuiqiang ⁺ shuiqiang.li@nist.gov	<ul style="list-style-type: none"> o Instrument design and building for light scattering and microscope with twin screw extruder
Liao, Hongyan [*] hongyan.liao@nist.gov	<ul style="list-style-type: none"> o Statistical data analysis o Experimental design
Liao, Kin ⁺ kin.liao@nist.gov	<ul style="list-style-type: none"> o Fatigue, damage, and NDE of composites o Environmental durability of composites o Behavior of ceramic composites
Lin, Nam S. [*] nam.liao@nist.gov	<ul style="list-style-type: none"> o Synthesis and testing of dental adhesives
Lin, Eric K. eric.lin@nist.gov	<ul style="list-style-type: none"> o Statistical mechanics o X-ray and neutron reflectivity
Liu, D.-W. da-wei.liu@nist.gov	<ul style="list-style-type: none"> o Polymer synthesis o Polymer characterization - thermal gravimetric analysis, differential scanning calorimetry, gel permeation chromatography, infrared spectroscopy, nuclear magnetic resonance, scanning electron microscopy
Ly, Agnes K. [*] agnes.ly@nist.gov	<ul style="list-style-type: none"> o Clinical dental assistant o Adhesion measurements
Mager, Carie ⁺ carie.mager@nist.gov	<ul style="list-style-type: none"> o Toughening Bioceramics o Fracture mechanics
Marjenhoff, William A. [*] william.marjenhoff@nist.gov	<ul style="list-style-type: none"> o Research Administration

*Research Associate

⁺Guest Scientist

- 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
- 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
- Miyagi, Zenichi*
zenichi.miyagi@nist.gov
- o Adhesion
 - o Polymer mechanics
 - o Experimental design
- Mopsik, Frederick L.
- o Dielectric measurements and behavior

*Research Associate

⁺Guest Scientist

frederick.mopsik@nist.gov

- 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

Nisato, Giovanni
giovanni.nisato@nist.gov

- o Polymer gels
- o Polyelectrolytes
- o Dynamic light scattering

O'Connell, Paul A.
paul.oconnell@nist.gov

- o Nonlinear viscoelasticity
- o Physical aging
- o Torsional testing

Obrzut, Jan
jan.obrzut@nist.gov

- o Electronic properties of polymers and composites
- o Photoelectron spectroscopy (X-ray and UV)
- o Dielectric relaxation spectroscopy
- o Electronic packaging
- o Reliability, stress testing
- o Microwave and optical waveguides
- o Data acquisition
- o Patent process (in electronic packaging)

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
- o Processing and failure behavior of polymer composites
- o Resin transfer molding: modeling and processing studies
- o Viscoelastic flow modeling
- o Flow in porous media

Phelan, Jr., Frederick R.
frederick.phelan@nist.gov

*Research Associate

*Guest Scientist

- | | |
|--|---|
| Pochan, Darrin
darrin.pochan@nist.gov | <ul style="list-style-type: none"> o Lattice Boltzmann methods o SEM & TEM of polymeric materials o Wide-angle and small-angle x-ray scattering o Block copolymer phase behavior |
| Prosa, Ty J.
ty.prosa@nist.gov | <ul style="list-style-type: none"> o X-ray scattering o Dendrimers o Conducting polymers |
| Qiao, Fang | <ul style="list-style-type: none"> o Polymer mixing and compounding o Liquid crystalline polymer/thermal plastic polymer mixing |
| Raghavan, Dharmaraj T. ⁺
Dharmaraj.Raghavan@nist.gov | <ul style="list-style-type: none"> o Rubber recycling o Interface chemistry o Mechanical properties of concrete |
| Reed, Benjamin B. [*]
benjamin.reed@nist.gov | <ul style="list-style-type: none"> o Synthetic and polymer chemistry o Polymerization expanding monomers o Laboratory automation |
| Reiff, Andrea
andrea.reiff@nist.gov | <ul style="list-style-type: none"> o Viscoelastic flow modeling o Hyperbolic systems o Numerical modeling |
| Rolnick, Robert A. | <ul style="list-style-type: none"> o Network administrator (Blends Group) o Computer maintenance |
| Rose, Karen J. [*]
karen.rose@nist.gov | <ul style="list-style-type: none"> o Topical fluoridation for professional application |
| Roth, Steven C.
steven.roth@nist.gov | <ul style="list-style-type: none"> 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 | <ul style="list-style-type: none"> o Viscoelasticity o Polyurethane creep |
| Rupp, Nelson W. [*] | <ul style="list-style-type: none"> o Clinical dentistry |

^{*}Research Associate

⁺Guest Scientist

- | | |
|---|--|
| | <ul style="list-style-type: none"> o Amalgams o Direct golds o Composites o Microleakage o Dentin adhesives |
| Sanin, Norman D.*
norman.sanin@nist.gov | <ul style="list-style-type: none"> o Topical dental fluorides o Calcium phosphate cements |
| Schen, Michael A.
michael.schen@nist.gov | <ul style="list-style-type: none"> 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 | <ul style="list-style-type: none"> o Failure of composites o Experimental mechanics o Torsional dilatometry o Physics of polymer glasses o Polymer rheology |
| Schumacher, Gary E.*
gary.schumacher@nist.gov | <ul style="list-style-type: none"> o Clinical dentistry o Composites o Dentin adhesives |
| Sieck, Barbara A.*
barbara.sieck@nist.gov | <ul style="list-style-type: none"> o Calcium phosphate compounds o Chemical analysis o Remineralization |
| Skrtic, Drago*
drago.skrtic@nist.gov | <ul style="list-style-type: none"> o Calcium phosphates as dental materials o Liposome studies |
| Smith, Leslie E.
leslie.smith@nist.gov | <ul style="list-style-type: none"> o Adsorption of polymers o Polymer degradation reactions |
| Snyder, Chad
chad.snyder@nist.gov | <ul style="list-style-type: none"> o Polymer crystallization o WAXD and SAXS of polymeric materials o Thermal expansion measurements o Thermal analysis of polymers |
| Stansbury, Jeffrey W.
jeffrey.stansbury@nist.gov | <ul style="list-style-type: none"> o Synthetic chemistry o Polymers and polymer composites |

- o Polymerization of expanding monomers
 - o Fluorinated polymers
 - o Polymerization kinetics
- 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
 - o Reference biomaterials
- 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
- Vogel, Gerald L.*
- o Dental plaque chemistry, chemistry of calcium

- gerald.vogel@nist.gov
- 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
- White, Christopher
christopher.white@nist.gov
- o Viscoelastic properties of polymers
 - o Shear wave propagation
 - o Atomic force microscopy
 - o Measuring complex modulus of polymers
- 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
- Xie, Rui⁺
- o Metal ion complexation in polymer blends
 - o phase behavior of polymer blends
- Xu, Huakun^{*}
hockin.xu@nist.gov
- o Silver alloy alternative to amalgam
 - o Wear and fatigue
 - o Ceramic-reinforced composite resin
- Zhang, Yubao
yubao.zhang@nist.gov
- o Dynamic light scattering
 - o Polyelectrolytes
 - o Small angle neutron scattering
- Zhou, Chunlin⁺
clzhou@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
- Zhang, Zhen^{*}
- o Microanalysis of dental plaque

jane.zhang@nist.gov

Zimba, Carl G.
carl.zimba@nist.gov

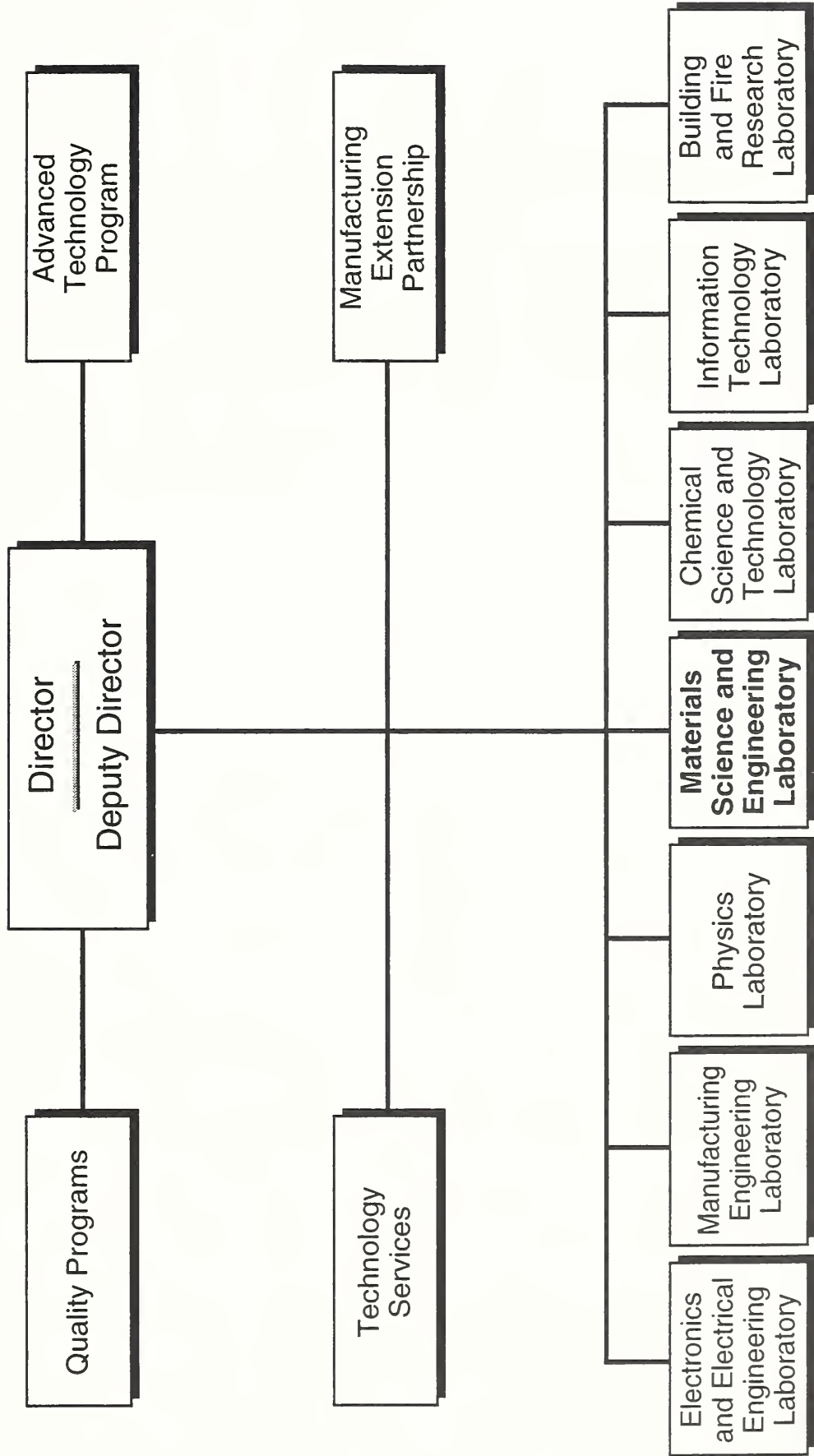
- o Infrared spectroscopy
- o Raman spectroscopy
- o X-ray microscopy
- o Chemical imaging
- o Fiber-optics
- o Optical design
- o Synchrotron radiation
- o General spectroscopy

Dear Mr. [Name],
I am writing to you regarding the [Project Name] project. I have reviewed the [Document Name] and have some questions. I would like to discuss this with you at your earliest convenience. Please let me know when you are available for a meeting. Thank you for your time and attention.

Jane Zhang @ [Company Name]
[Address]
[City, State, ZIP]

National Institute of Standards and Technology

Organizational Chart



**MATERIALS SCIENCE AND
ENGINEERING LABORATORY**
D.E. Hall, Acting Director
S.J. Dapkunas, Acting Deputy Director

Ceramics
S.W. Freiman, Chief
S.J. Dapkunas, Deputy

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

Metallurgy
C.A. Handwerker, Chief
R.J. Schaefer, Deputy

**NIST Center for
Neutron Research**
J.M. Rowe, Director
T.M. Raby, Deputy

**Materials
Reliability**
H.I. McHenry, Chief
T.A. Siewert, Deputy

Smith, Leslie E., Dr., Chief
Fanconi, Bruno M., Dr., Deputy Chief
Han, Charles C., Dr., NIST Fellow
Lightbody, Sonja C., Mrs., Admin. Officer.
Green, Janice M., Mrs., Secretary

ELECTRONICS APPLICATIONS

Wu, Wen-li, Dr., Ldr.
Webb, Bronny, Mrs., Secy.
Chiang, Chwan K., Dr.
Davis, G. Tom, Dr.
DeReggi, Aime S., Dr.
Lin, Eric, Dr.
Mopsik, Frederick I., Dr.
Obrzut, Jan, Dr.
Pochan, Darrin, Dr.
Roth, Steven C., Mr.
Schen, Michael A., Dr.
Snyder, Chad R., Dr.
Wallace, William E., Dr.
White, Christopher F., Dr.

Guest Scientists

Beck Tan, Nora C., Dr.
Bloss, Peter, Dr.
Dickens, Brian, Dr.
Edelman, Seymour, Mr.
Genzer, Jan, Dr.
Kolb, Rainer, Dr.
Kramer, Edward, Dr.
Lynn, Gary W., Mr.
VanZanten, John H., Dr.
Welp, Keith A., Mr.

Students

Yeh, Chi-Yje Jacob, Mr.

POLYMER BLENDS & PROCESSING

Amis, Eric J., Dr., Leader
Hollingsworth, Karen E., Mrs.
Secretary
Barnes, Kathleen A., Dr.
Bauer, Barry J., Dr.
Bur, Tony J., Dr.
Douglas, Jack F., Dr.
Glotzer, Sharon C., Dr.
Ivkov, Robert D., Dr.
Karim, Alamgir, Dr.
Lee, Benjamin, Dr.
Liu, Da-Wei, Mr.
Migler, Kalman, Dr.
Nakatani, Alan I., Dr.

Research Associates

Chen, Wei, Dr.
Lohse, David, Dr.
Thudium, Richard N., Mr.

Guest Scientists

Akpalu, Yvonne A., Ms. (10/97)
Arcarese, Elizabeth B., Mrs.
Balsara, Nitash P., Dr.
Briber, Robert M., Dr.
Choi, Sangwook, Mr.
Dadmun, Mark D., Dr.
Daniel, Christophe, Dr.
Ermi, Brett D., Mr.
Esker, Alan R., Dr.
Gamer, Richard T., Dr.
Gettinger, Constance L., Dr.
Groehn, Franziska, Dr. (11/97)
Gruell, Holger, Dr.
Hayashi, Masaki, Mr.
Ho, Li-Te., Mr.
Hobbie, Erik K., Dr.
Huang, Ching-I, Dr. (10/97)
Huber, Dale, Mr.
Jao, Tze C., Dr.
Jeon, Hyunsik, Dr.
Jinnai, Hiroshi

POLYMER STRUCTURE AND MECHANICS

Parnas, Richard S., Dr., Leader
Ruff, Joan E., Mrs., Secretary
Dunkers, Joy P., Dr.
Flynn, Kathy M., Ms.
Holmes, Gale A., Dr.
Hunston, Donald L., Dr.
McDonough, Walter G., Mr.
Peterson, Richard C., Dr.
Phelan, Frederick R., Dr.
Reiff, Andrea M., Dr.
Zimba, Carl G., Dr.

Guest Scientists

Cerrada, Maria L., Dr.
Delin, Mats, Dr.
Drzal, Peter L., Mr.
Fernandez-Garcia, Marta, Dr.
Han, Won Hee, Dr.
Horkay, Ferenc, Dr.
Kearsley, Elliott A., Dr.
Kofinas, Peter, Dr.
O'Connell, Paul A., Dr.
Othieno, Maurice O., Mr.
Park, Joon-Yong, Dr.
Purohit, Vandana, Ms.
Rouiller, Vincent, Mr.
Simon, Sindee L., Dr.
Soulivong, Vanarong, Mr.
Stiehler, Robert D., Dr.
Yang, Arthur J., Dr.

Students

Cheng, June F., Ms.

POLYMER CHARACTERIZATION

Fanconi, Bruno M., Dr., Leader
Webb, Bronny, Mrs., Secretary
Blair, Bill R., Mr.
Broadhurst, Martin J., Dr.
Guttman, Charles M., Dr.
Jackson, Catheryn L., Dr.
Khoury, Freddy A., Dr.
VanderHart, David L., Dr.

Guest Scientists

Feng, Hanqiao, Dr.
Flynn, Joseph H., Dr.
Kim, Ginam, Dr.
Kryder, Samuel J., Mr.
Maurey, John R., Dr.
Santore, Maria M., Dr.
Verdier, Peter H., Dr.

Students

Oh, Simon, J-H., Mr.

DENTAL & MEDICAL MATERIALS

Wang, Francis W., Dr., Leader
Burton, June S., Ms., 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

Birch, April A., Ms.
Choi, Kyung Moon, Dr.
Geiger, Selly B., Dr.
Kelly, J. Robert, Cmdr.
Konnatsu, Koichi, Dr.
Lowry, Robert E., Mr.
Sauder, Deborah G., Dr.
Shimada, Yasushi, Dr. (11/1)
Wu, En S., Dr.

Students

Tu, Raymond, Mr.

American Dental Association

Eichmiller, Fred, Dr., Director
Bowen, Rafael L., Dr.
Carey, Clifton M., Dr.
Cherng, Maria, Dr.
Chow, Laurence C., Dr.
Dickens, Sabine, Dr.
Duppins, Gretchen, Ms.
Eidelman, Naomi, Dr.
Farahani, Mahnaz, Dr.
Flaim, Glenn M., Mr.
George, Laurie A., Mrs.
Giuseppetti, Anthony A., Mr.
Hoffman, Kathleen M., Miss

-----continued-----

**POLYMER BLENDS &
PROCESSING**

Guest Scientists

Kumar, Sanat, Dr.
Marr, David, Dr.
Morrison, Faith A., Dr.
Mullins, Carol A., Mrs.
Nisato, Giovanni, Dr.
Qiao, Feng, Mr.
Rabeony, Manese H., Dr.
Ramzi, Aissa, Dr.
Seery, Thomas A.P., Dr. (10/97)
Topp, Andreas, Dr.
Xie, Rui, Dr.
Zhang, Yubao, Dr.

Students

Rolnick, Robert A., Mr.

**DENTAL & MEDICAL
MATERIALS**

American Dental Association

Jordan, Truman H., Dr.
Khatri, Chetan A., Dr.
Liao, Hongyan, Mrs.
Liao, Nam S.
Ly, Agnes K., Dr.
Marjenhoff, William A., Dr.
Markovic, Milenko, Dr.
Mathew, Mathai, Dr.
Misra, Dwarika N., Dr.
Mueller, Herbert J., Dr.
Parry, Edward E., Mr.
Reed, Benjamin B., Mr.
Rose, Karen J., Dr.
Rupp, Nelson W., Dr.
Sanin, Norman D., Mr.
Schumacher, Gary E., Dr.
Shore, Noble A., Mr.
Sieck, Barbara A., Ms.
Skrtic, Drago, Dr.
Smythers, Christine, Ms.
Takagi, Shozo, Dr.
Tung, Ming S., Dr.
Vogel, Gerald L., Dr.
Xu, Huakun, Dr.
Zhang, Zhen, Mrs.

