POLYMERS

1998 PROGRAMS AND ACCOMPLISHMENTS

MATERIALS
SCIENCE AND
ENGINEERING
LABORATORY

NISTIR 6249

UNITED STATES
DEPARTMENT OF
COMMERCE

TECHNOLOGY
ADMINISTRATION

NATIONAL
INSTITUTE OF
STANDARDS AND
TECHNOLOGY

Innovative Uses of Polymers

Polymers are used in almost every medical implant, for example, pacemakers, shunts, and total joint replacements, as well as in dental restoratives. The Polymers Division seeks to build on its strong program in dental restorative materials and orthopaedic devices with new programs in tissue engineering where innovative uses of polymers and biological products hold promise for regeneration and repair of human organs and tissues.

Courtesy of Andrew J. Lovinger, (Division of Materials Research) Chair, NSF Macromolecular Working Group. This image was reproduced from the NSF Report of the Workshop on Interdisciplinary Macromolecular Science and Engineering, 1998.

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DEPARTMENT OF
COMMERCE
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MATERIALS SCIENCE AND ENGINEERING LABORATORY

POLYMERS

1998 PROGRAMS

AND

ACCOMPLISHMENTS

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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.

EXECUTIVE SUMMARY

This report, covering the technical activities of the Polymers Division in fiscal year 1998, is organized according to the major programs of the Division. Each program description includes an overview that describes the motivation for the individual projects, selected accomplishments that we wish to emphasize and project summaries. Relevant publications are referenced for the reader who wants further information.

The Polymers Division provides standards, measurement methods, data and concepts of polymer behavior for the U.S. polymers industries and business enterprises that use polymers in products and services. The Division looks at trends in the production, processing and use of polymers in deciding areas of work. The following stimulates the current focus on electronic applications of polymers, polymer blends and processing, polymer composites, dental and medical materials, and characterization of polymer structure and properties.

- New catalysts systems give polymer producers the ability to control molecular architectures to levels heretofore unknown. The Division creates new tools based on recent advancements in mass spectrometry to characterize molecular structure.

- Most commercial polymeric materials are not single component systems, but mixtures of several polymers along with additives or fillers that improve processibility, enhance properties and/or improve long term performance. As new market opportunities and increased competitive pressures arise from advances in polymer synthesis and the precise control material components, there are increasing demands on polymer suppliers and processors for multifunctional materials with improved performance and ease of production. Current work to provide the measurement tools and knowledge base required in response to these demands includes on-line characterization of temperature and phase behavior, shear effects on phase behavior, morphology and dispersion, influence of compatibilizers and fillers, and control of interfacial interactions.

- The full utilization of fiber reinforced polymers for structural applications is limited by the lack of rapid, reliable, cost-effective fabrication methods and the poor understanding of and predictive capability for long-term performance. Methods are developed to monitor, model and control events that occur during composite fabrication by liquid molding technology and other new fabrication techniques. Test methods are developed for assessing important characteristics such as the resin/fiber interfacial adhesion and the subsequent degradation of this adhesion resulting from fluid attack, particularly moisture.

- Another trend is the increasing importance of polymers in the form of thin films. The microelectronics industry is one example of where polymeric films are used as photoresists, dielectric insulators and encapsulants. The Division develops x-ray and neutron reflectivity techniques to measure the properties of the submicron thick polymer films that are necessary for continued development in the field.

- Health care professionals increasingly use polymeric materials to replace diseased structures. The Division provides basic materials science, test methods and standards for the development of new or improved materials and delivery systems. The focus is on development of improved dental restorative materials with greater durability, wear resistance and clinical acceptability.

These programs are developed with input from sectors of U. S. industry that produce, process or use polymers in essential parts of their business. NIST sponsored workshops are a key way in which industry provides input into planning program direction. In fiscal year 1998, the Division sponsored workshops on Filled Polymers and Nanocomposites, on Properties and Applications of Dendritic Polymers, and on X-ray Microscopy of Synthetic and Natural Polymers.

In the past year the Division made significant contributions to the scientific and technology base that drives commercial advancements in polymeric materials and their uses. A listing of some of these accomplishments is given below; more complete lists and descriptions are contained in the individual sections of this report.

Significant Accomplishments

ELECTRONIC PACKAGING, INTERCONNECTION, AND ASSEMBLY PROGRAM

- A new test specimen design for use as a common dielectric test vehicle has been accepted by the National Center for Manufacturing Sciences (participants: DuPont, IBM, Delco, Raytheon, 3M) for their Embedded Capacitive Materials Project. This test specimen and its associated test procedure were developed by NIST, in collaboration with the industrial partners, for ferroelectric films in the frequency range from 0.5 GHz to 5 GHz.

- A new methodology for characterizing low-k thin film dielectrics has been developed and data have been delivered to Dow Corning Corp. and SEMATECH. A combination of x-ray reflectivity and neutron scattering was used to measure film porosity, pore size and moisture uptake. The results were forwarded to industry to support their efforts to produce new materials needed for next-generation microelectronics.

- The applicability of x-ray reflectivity measurements has been extended to films up to 1 μm thick. This new capacity is essential for many on-going thin film projects in the electronics application program because 1 μm is the nominal thickness for interlevel dielectrics used in today's VLSI circuitry.

- A new test methodology has been certified and is being submitted to the Institute for Interconnecting and Packaging Electronic Circuits as a standard test for measuring the thin film coefficient of thermal expansion normal to the film surface. Certification tests of the newly developed NIST capacitance cell were performed using a <0001> oriented Al_2O_3 single crystal as the test standard. Results were in excellent agreement with literature values.

POLYMER BLENDS AND PROCESSING PROGRAM

- An optical sensor to measure anisotropy during biaxial stretching of polypropylene film in production ovens at high temperature was designed and demonstrated in collaboration with Mobil Chemical Company.

- Spherical and cylindrical composition waves emanating from the boundaries of inclusions in a phase separating blend were predicted by simulations and subsequently confirmed by experiments investigating the microstructure of filled polymer materials.

- An analytical model predicting the viscosity for polymers filled with dispersions of platelet particles was developed and validated with data for a range of particle shapes. The threshold of rigidity where the suspension viscosity diverges is predicted to be inversely proportional to the intrinsic viscosity.

- Alignment of the morphology in a phase separating blend film to an underlying pattern of surface chemistry was shown to improve with decreasing film thickness until reaching a critical value below which spinodal dewetting causes controlled break-up into uniform nanoscale droplets.

- Interpenetrating polymer networks of hydroxyethylmethacrylate with PAMAM dendrimers were prepared, and the individual dendrimers were shown by small angle x-ray scattering and transmission electron microscopy to be uniformly dispersed.

POLYMER COMPOSITES PROGRAM

- Optical coherence tomography was used successfully to rapidly measure the porous structure of a high fiber volume fraction glass fiber reinforcement in sufficient detail to predict the permeability using a 3-D fluid flow simulation based on the lattice-Boltzmann method.

- A database of permeability and other reinforcement properties was released in collaboration with the NIST Standard Reference Data Program.

- A workshop entitled *X-ray Microscopy of Synthetic and Natural Polymers: Towards Chemical Speciation at 10 nm Spatial Resolution. Assessment of Research Opportunities and the Need for X-ray Microscopy Facilities* and co-sponsored by NIST, Department of Energy, Advanced Light Source, North Carolina State University, Carnegie Institution of Washington, Dow Chemical, and General Electric, was held at NIST on May 11-12, 1998. The workshop resulted in a DOE funded proposal for $500,000 to develop an X-ray imaging facility at the Advanced Light Source devoted to the study of polymers.

POLYMER CHARACTERIZATION PROGRAM

- A major obstacle to the use of mass spectrometry to determine the molecular mass distribution of synthetic polymers was overcome through improvements in sample preparation methods that reduced variation of signal intensity from 42% on samples prepared by conventional techniques to below 5% on samples prepared by the new procedures.

- Chemical shift calculations for the ethylene defect in isotactic polypropylene confirmed assignments of experimental NMR data used to establish relationships between molecular defects and crystallinity.

- Research to identify a material for a new Nonlinear Fluid Standard was completed, and an inter-laboratory comparison of the fluid involving 35 researchers from industry (instrument makers and material suppliers) and academe was organized.

- Recommendations for standards for estimation of statistical errors in SAS data sets were made to the Commission on Small-Angle Scattering of the International Union of Crystallography.

- In collaboration with General Electric Company and the University of Pittsburgh, the evolution of the viscoelastic response of a commercial epoxy thermoset during cure was successfully modeled.

DENTAL AND MEDICAL MATERIALS PROGRAM

- A series of highly fluorinated dimethacrylate monomers were prepared and evaluated in homopolymerization studies. Dental composites with enhanced durability and color stability may result from several of the new fluoropolymers that combine excellent mechanical strength with extreme hydrophobicity.

- A new accelerated wear resistance machine was developed in collaboration with the Ceramics Division and the University of Maryland under a NIST research consortium formed by CRADAs with four orthopaedic companies: Biomet Inc. and Zimmer Inc, both of Warsaw, Ind.; Johnson & Johnson Professional Inc., Raynham, Mass.; and Oesteonics Inc., Allendale, New Jersey. The new test machine allows for evaluation of new orthopaedic joint materials in five days or less, under a variety of load, load-cycle and motion conditions promises to hasten the introduction of longer lasting hip, knee, and other orthopaedic joint implants to the market. As a result of this successful development, the four companies elected to seek extension of their CRADAs to September 30, 2000.

- Fluorescent probes were successfully used for cure monitoring of dental bonding resins and bone cements. Improved products will result from the addition of one of the probes to dental bonding resins or bone cements.

TECHNICAL ACTIVITIES

ELECTRONIC PACKAGING, INTERCONNECTION AND ASSEMBLY PROGRAM

The objective of this program is to assist the U.S. microelectronics industry by addressing their most pressing materials measurement and standards issues. These issues are central to the development and utilization of advanced materials and material processes required by new product technologies, as outlined within leading industry roadmaps[1]. This program is part of a broad effort in the NIST Materials Science and Engineering Laboratory with the goal of serving as a key resource within the Federal Government for materials metrology development for commercial microelectronics manufacturing. More specifically the objectives can be categorized in the following four areas:

- Develop and deliver standard measurement methods and data on materials important to the microelectronics industry.
- 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 currently consists of some eleven separate projects dealing in matters such as the electrical, thermal, and mechanical characteristics of polymer thin films; characteristics of interfaces and adhesion; and the nature of the built-up stress and moisture in plastic packages. From beginning to end, these projects are 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)[2]. 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

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[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.eeel.nist.gov/810.01/index.html

(http://www.msel.nist.gov/epia1996/contents.htm). Copies may be obtained by contacting Wen-li Wu at (301) 975-6839 or wenli@nist.gov.

Significant Accomplishments

- A test specimen designed for use as a common dielectric test vehicle has been accepted by the National Center for Manufacturing Sciences (DuPont, IBM, Delco, Raytheon, and 3M) for their Embedded Capacitive Materials Project. This test specimen and its associated test procedure were developed by NIST, in collaboration with the industrial partners, for ferroelectric films in the frequency range from 0.5 GHz to 5 GHz.

- A new test methodology has been certified and is being submitted to the Institute for Interconnecting and Packaging Electronic Circuits as a standard for measuring the thin film coefficient of thermal expansion normal to the film surface. This test is capable of measuring films as thin as 5 µm replacing a standard method certified for films only as thin as 2 mm. Certification tests of this newly-developed NIST capacitance cell were performed using a <0001> oriented Al_2O_3 single crystal as the test standard. Results were in excellent agreement with literature values.

- The presence of a surface-bound negative charge layer, residing within 0.1 µm of the film surface, in polyimide films not previously subjected to an applied voltage was discovered. The electric field associated with this charge is not switchable by a normal bias voltage of either polarity and is stable against heating of the specimen up to about 200 °C. The discovery of charge layers in polyimide films is expected to have significant impacts on electronics applications such as the alignment of liquid crystals in flat panel displays.

- The applicability of x-ray reflectivity measurements to determine film thickness has been extended up to films that are 1 µm thick. This new capacity is essential for many on-going thin film projects in the electronics application program because 1 µm is the nominal thickness for interlevel dielectrics used in today's VLSI circuitry.

- A new methodology for characterizing porous low-k dielectric thin films (<1 Ωm) has been developed. A combination of x-ray reflectivity, neutron scattering, and ion scattering was used to measure film density, pore size, and moisture uptake. The results were forwarded to industry (Dow Corning Corp. and SEMATECH) to support their efforts to produce new materials needed for next-generation microelectronics.

- Shear-induced polymer desorption from an attractive solid substrate was observed by neutron reflectivity for the first time in a highly-entangled polymer melt. The rate of desorption was found to depend strongly on the shear rate. This observation provides a new insight into the underlying mechanism of flow instabilities which lead to defects in products from widely used polymer processes such as extrusion and injection molding.

- A reduction in signal noise at elevated temperatures by a factor of four was achieved in a Tencor residual stress analyzer, an instrument commonly used in microelectronic companies. This resulting precision in measurement of the in-plane coefficient of thermal expansion and elastic modulus of supported thin films is greatly improved over that previously possible.

Measurements of Hygrothermal Expansion of Polymer Thin Films

F. I. Mopsik, C.R. Snyder

Objectives

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

Technical Description

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

External Collaborations

Dr. E.O. Shaffer II of Dow Chemical Company provided materials for CTE measurements.

Planned Outcomes

Improved test method for measuring hygrothermal expansion of thin films providing reliable data on the expansion behavior of electronic packaging materials with variations in temperature and humidity

Accomplishments

Measurements were performed on <0001> oriented Al_2O_3 single crystal samples to demonstrate the ability of the technique to provide accurate values for the thermal expansion coefficient of materials. Results are in excellent agreement with literature values. Additionally, the calculated expansion coefficient of the nichrome-plated fused quartz electrode matches the literature value within the experimental uncertainty.

The uncertainties from the humidity and PVT properties of air and water have been assessed. A relative uncertainty of 1×10^{-6} of the total thickness has been determined for dry conditions by measurements on single crystal Al_2O_3 and 4×10^{-5} for humid conditions (at 60 °C) by theoretical computations.

Validity of the data reduction technique, based upon first principles, was demonstrated by determining the thickness of Zerodur spacers as a function of relative humidity. The determined thicknesses were identical within the experimental uncertainty at 60 °C and 0 %, 20 %, 40 %, 60 %, and 80 % relative humidity.

Outputs

Publications

C.R. Snyder and F.I. Mopsik, *A Precision Capacitance Cell for Measurement of Thin Film Out-of-Plane Expansion. I. Thermal Expansion*, Rev. Sci. Instrum., **69**(1998)3889.

C.R. Snyder and F.I. Mopsik, *A Precision Capacitance Cell for Measurement of Thin Film Out-of-Plane Expansion. II. Hygrothermal Expansion*, J. Appl. Phys., submitted.

C.R. Snyder and F.I. Mopsik, *High Sensitivity Technique for Measurement of Thin Film Out-of-Plane Expansion*, Proceedings of the 1998 International Conference on Characterization and Metrology of ULSI Technology, in press.

E.K. Lin, C.R. Snyder, F.I. Mopsik, W.E. Wallace, W.L. Wu, C.X. Zhang and R.M. Laine, *Characterization of Epoxy-Functionalized Silsequioxanes as Potential Underfill Encapsulants*, Proceedings of the Materials Research Society 1998 Spring Meeting, in press.

Presentations

C.R. Snyder and F.I. Mopsik, *A Precision Capacitance Cell for Measurement of Thin Film Out-of-Plane Expansion: Thermal & Hygrothermal Expansion*, 1998 International Conference on Characterization and Metrology of ULSI Technology, Gaithersburg, MD, March 25, 1998.

C.R. Snyder and F.I. Mopsik, *A Precision Capacitance Cell for Measurement of Thin Film Out-of-Plane Expansion: Thermal & Hygrothermal Expansion*, American Chemical Society National Meeting, Boston, MA, August 22, 1998.

Characterization of Polymer Films and Composites by Dielectric Techniques

Jan Obrzut

Objectives

Develop test procedure for dielectric characterization of thin films at microwave frequencies (up to 20 GHz). Evaluate dielectric properties of polymer composites filled with ferroelectric materials for electronic applications.

Technical Description

Dielectric measurement techniques in the microwave range are of primary importance to industry, and can provide substantial insight into interfacial interactions and molecular dynamics in thin polymer films.

There are two currently available standard testing methods for dielectric permitivity of polymer substrates at microwave frequencies. One is ASTM 3380 – 90/95 and the other is IPC-TM-650, No.: 2.5.5.5, revised in 1998. These test methods employ a strip line resonator circuit covering frequency range from 8 GHz to 12 GHz. The required sample thickness is about 1.6 mm. Substrates thinner than 1.27 mm with dielectric constant greater than 10.5 are not covered by the above testing methods. Many of the polymers in applications are available only in the form of thin films, typically a few micrometers in thickness. As the thickness of the dielectric being measured is reduced, the other dimensions of the test pattern are reduced as well. Such test patterns can only be made using very high-resolution photolithographic techniques. Moreover, the coupling efficiency between the feeding microstrip launchers and the resonating strip rapidly approaches zero, as the test pattern becomes smaller. This makes the dielectric measurements on the thin films in the microwave range rather difficult and unreliable, if performed in accordance with the available testing standards. Therefore, a new testing procedure specifically designed for thin dielectric films and laminates is needed.

To address this issue the applicability of the IPC-TM-650, No.:2.5.5.5 test method to thin films is being extended by designing a new test specimen and by developing a new coupling procedure for microstrip resonators. The first application of this new test method is the characterization of polymer composites for high-dielectric films.

New, chip scale packaging utilizes high-dielectric constant films to form embedded RC cells, which are integrated within the interlevel dielectric structure. Polymer composites filled with ferroelectric powders are candidates for such applications. However, the structure-dielectric property relationship for the high-dielectric constant composites is poorly understood. This situation is mostly due to lack of reliable experimental permittivity data in the frequency range from 0.5 GHz to 20 GHz. Currently, there is no satisfactory test procedure for evaluating dielectric dispersion and relaxation behavior of candidate materials at the above mentioned frequencies. Most of the problems in testing can be attributed to interfacial polarization, to the wave compression effect and to the cutoff frequency effect of distributed circuits.

External Collaborations

Philip Bowles of Delphi-Delco Electronics provided assistance in accelerated stress test of high-k films for their reliability.

Yueh-Ling Lee of DuPont provided copper clad laminates of high dielectric constant films.

John Lauffer of IBM constructed an artwork (mask) of the microwave test specimen.

Dale Murry of Litton Advanced Circuitry manufactured the test boards with embedded a dielectric test pattern.

Dr J. Dougherty of Penn State University provided detailed analysis of molecular dynamics of high-k films.
Dylan Williams of NIST Boulder provided test specimen design.

Planned Outcome
Metrology for Dielectric Permittivity of Thin Polymer Films in the Microwave Range.

A better understanding of coupling mechanism between ferroelectric filler and polymer matrix. There is a question whether and to what extent polarizability of the polymer matrix may control the apparent dielectric permittivity of the composite. The search will focus on model polymer matrices of different molecular structure, such as dielectric polymer matrix (polyimide), poled polymer matrix (PVDF) and an oriented chiral polymer matrix (modified cellulose).

Accomplishments
In collaboration with the industrial partners a test specimen and a test procedure has been developed for ferroelectric films. The method utilizes a modified, airline coaxial probe for frequency range from 0.5 GHz to 5 GHz. The uncertainty is currently about 0.5% for the dielectric constant. This is significant improvement over the existing methods utilizing four terminal fixtures, which have an upper frequency limit of about 800 MHz and uncertainty of about 10%. The test specimen (photo mask) has been accepted by the National Center for Manufacturing Sciences participants (DuPont, IBM, Delco, Raytheon, 3M) as a common dielectric test vehicle for the Embedded Capacitive Materials Project.

In collaboration with MSEL and EEEL staff, a new test specimen has been designed for thin dielectric films. The specimen utilizes triplate, microstrip resonating structures and co-planar waveguides. The microstrip resonators can be used at frequencies up to 20 GHz. The co-planar waveguiding structure can be used to test thin dielectric films at higher frequencies, above 20 GHz (Boulder). A new measurement protocol has been developed for resonators, which are end-fire coupled to microwave launchers. The implemented alignment procedure is analogous to those used in aligning fiber-optics devices. It allows precise controlling of coupling conditions, which eliminates a major source of experimental errors and improves overall accuracy.

An experimental set-up has been developed for dielectric relaxation spectroscopy and DC conductivity of composite materials. Currently, the experiment can be conducted in the frequency range of 1 mHz to 1 MHz and temperatures from –150 ° C to 200 °C. The temperature stability is about ± 1 °C. The set-up has been used for dielectric evaluation of DuPont High Dielectric Constant films. The dielectric permittivity and the DC conductivity of the DuPont 3579 high-k material have been evaluated and a summary report (6 pages) has been transmitted to DuPont and IBM. IBM plans to use the DuPont materials in new chip carrier applications.

Outputs

Publications
J. Obrzut, and Miguel Jimarez, *Plastic Flip-Chip-BGA Carrier with Microvias for Chip Scale Packaging*, SMTA, International Conference on Electronic Assembly, Atlanta, GA, June 16-18, 1998, pp. 31 - 38.

J. Obrzut, *Interconnection Continuity Test for Packaged, Functional Modules,* Proceedings of the 1998 International Conference on Characterization and Metrology of ULSI Technology, in press.

M. A. Jimarez, L. Li and J. Obrzut, *Elastic Thermal Compensation of Chip Carriers*, IBM Tech. Discl. Bull., **40**(1997)85.

Patents
"Compliant Surface Layer for Flip-Chip Electronic Packages" IBM Docket #EN997150

"UV Absorbing Glass Cloth and Use Thereof" IBM Docket #EN996136

Presentations
J. Obrzut, and M. Jimarez, *Plastic Flip-Chip-BGA Carrier with Microvias for Chip Scale Packaging*, SMTA, International Conference on Electronic Assembly, Atlanta, GA, June 16, 1998.

M. Jimarez, C. Tytran, C. Loveland, and J. Obrzut, *Technical Evaluation of CPS-BGA Carrier*, 48th Electronic Components & Technology Conference, CPMT/IEEE, Seattle, WA, May 25, 1998.

J. Obrzut, *Interconnection Continuity Test for Packaged, Functional Modules*, 1998 International Conference on Characterization and Metrology of ULSI Technology, NIST Gaithersburg, MD, March 25, 1998.

J. Obrzut, *Prototyping Electrooptic Devices using Polymer Waveguides*, MRS Fall Meeting, Boston, MA, Dec. 3, 1997.

Miscellaneous
Membership on the IPC High Density Interconnect Task Force Committee.
Contributions to the following, new standard test methods:
- IPC -TM-650-2.5.5.5.1; Stripline test for complex relative permittivity of circuit board materials to 14 GHz.
- IPC-TM-650-2.5.5.5.9; "Permittivity and loss tangent, parallel plate, 1 MHz to 1.5 GHz.
- IPC-TM-650-2.2.2.1; "Planarization of dielectrics for build-up technology.
- IPC-CC-830-A; "Qualification and performance of electrical insulating compounds for printed board assemblies

Dielectric Measurements of Thin Films from DC to 1 GHZ

F. I. Mopsik

Objective

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 (> 5 µm) of importance to the electronic packaging industry.

Technical Description

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 and extend the measurement range in a known way. Sample configurations and data reduction methods will be developed to optimize the measurements.

Planned Outcomes

We expect to develop a sample configuration and measurement protocol for the accurate measurement of dielectric constant and loss of thin films(> 5 µm) 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 coaxial holder was constructed, allowing a single sample to be measured with accuracy better than 1 % from 1 kHz to 30 MHz, 1 % up to 500 MHz and less than 5 % to 1 GHz., as measured on a 25 µm thick polypropylene film. The film was metallized on one side and on a central 5 mm spot on the other, using a simple punch and mask. Reproducibility from sample to sample is within 1 %. This includes all sources, including sample variation, variations in metallization geometry and sample insertion.

The residuals of the holder have been determined with the main contribution being 3 pF from the coaxial adapter and line. The fringing fields for the sample and holder were evaluated and shown to be small. The uncertainty in this evaluation was shown to be less than the 1 % goal for the total measurement uncertainty. When this is complete, a test method will be proposed that will be capable of good reproducibility, limited mainly by determination of sample thickness at the 10 µm level.

Commercial capacitor-grade polypropylene film was acquired and initial measurements were made in the sample holder and the thin film two-fluid cell. Also, thickness determinations were made both by the thin film capacitance cell and a precision micrometer assembly. There was some discrepancy that has to be evaluated so that reliable thickness data can be used for data reduction.

Outputs

Presentations
F. I. Mopsik, *Extended Frequency Range Dielectric Measurements of Thin Films*, 1998 International on Characterization and Metrology of ULSI Technology, Gaithersburg, MD, March 25, 1998.

Measurement of the Thermal Properties of Polymer Thin Films

A. S. DeReggi, Peter Bloss, Chad Snyder

Objective

Improve the methodology for measuring the thermal properties of substrate-supported and free-standing polymer thin films (>5 μm), important for *in-situ* characterization of the thermal performance of materials used in microelectronics.

Technical Description

Laser pulse heating of the surface of an electroded and voltage-biased polymer film generates a transient pyroelectric-like response as the polymer first expands inhomogeneously and then contracts to its original thickness as it loses heat to the substrate (or to the surrounding air for the free-standing film) . The response depends on the bias voltage, temperature profile (which depends on the thermal properties of the polymer and time), and the electric field profile produced by the bias voltage (for nonpolar polymers) or by pre-existing charges and dipoles (for general or specially treated polymers). Theoretical modeling of the problem and deconvolution of the measured response using advanced numerical techniques yield the thermal properties and the electric field profile.

External Collaborations

Dr. Mel Zussman of Dupont provided test materials and material data.
Dr. Thomas Avedesian of Cornell/SRC collaborated in developing alternative test methods and reference samples.
Dr. Eberhard Hartman of Institute of Surface Modification at Leipzig provided test samples and conducted complementary measurements that resulted in one joint publication.
Dr. Gerhard Sessler of Technical University at Darmstadt collaborated in developing alternative test methods and this work has resulted in one joint publication.

Planned Outcomes

New metrology for measuring thin film thermal and electrical properties.

Development of superior reference materials in the form of thin films for thermal and electrical properties.

Reliable thermal and collateral electrical data on polymeric microelectronics packaging materials.

Accomplishments

Noise-subtraction techniques have allowed signal acquisition to begin at 10^{-7} s, the nominal end of the laser pulse, and consequently, resolution of electrical features within 0.1 micrometers of the incident surface.

A surface-bound negative charge layers in polyimide residing within 0.1 μm of the surface was discovered. These charges are present in polyimide specimens not previously subjected to an applied voltage. The electric field associated with these charges is not switchable by a normal bias voltage of either polarity. They are stable against heating of the specimen up to about 200 °C. These charge layers are significant because the electrical properties of thin films will become increasingly surface-sensitive as their thicknesses are decreased to the point where they can no longer be considered as large compared to the thickness of the charge layers.

The electric field associated with these charge layers may affect the operation of field-effect transistors and charged coupled devices and may raise or lower the dielectric breakdown voltage depending on the direction of the local field due to designed operating voltages between conductors in close proximity.

Preliminary surface-sensitive thermal pulse measurements were conducted in polyimide with thicknesses as small as 1.7 micrometers and found a decrease in thermal conductivity as compared to the value for bulk samples.

A steady state heat flow measurement apparatus to determine the thermal conductivity of thin films averaged over their thickness was designed and is under construction. Measurements obtained on the same samples with this apparatus and with the thermal pulse method will allow estimates to be made of the variation of thermal properties near the surface.

Charge distribution measurements were made on electron-beam-irradiated fluoroethylene propylene by using thermal pulse and acoustic pulse methods. This material is being considered as a reference material for the measurement of long-term (> 10 y) trapped-charge stability.

Poling effects in electron-beam-cured nanocomposites of powdered ferroelectric barium titanate dispersed in the polar binder tripropylene glycol diacrylate were observed. These nanocomposites are materials with a high dielectric permittivity with microelectronics application as the dielectric of integrated capacitors. The thermal pulse methods provides detailed information about the polarization profile and thus indirectly about the homogeneity of the dispersion.

Outputs

Publications

Aime S. DeReggi, *Space charge characterization for the 21st century: from high voltage cables to microelectronics*, Proc. 3rd Int. Conf. on Electric Charge in Solid Insulators, published in Le Vide: Science, Technique, et Applications, **287** Supp., 165-174 (1998).

Peter Bloss, Aime S. DeReggi, and Hartmut Schafer, *Elecric field profile and thermal properties in substrate-supported dielectric films*, Phys. Rev. B, submitted.

Peter Bloss, and Aime S. DeReggi, *Electrode thermal mass effects in thin film thermal pulse measurements*, IEEE Trans. on Dielectrics. and Electr. Insul., submitted.

Peter Bloss, and Aime S. DeReggi, *Electric field profiles in 1.7 micrometwer polyimide using improved thermal pulse method: Influence of water uptake*, IEEE Trans. on Dielectrics and Electr. Insul., submitted.

Peter Bloss, Aime S. DeReggi, Hans-Jurgen Glasel, and Eberhard Hartmann, *Thermal pulse investigation of polarization distribution in ceramic-polymer nanocomposites*, Proc. World Ceramics Congress and Forum on New Materials (CIMTEC '98), in press.

P. Bloss, A. S. DeReggi, G.-M. Yang, G.M. Sessler, and H. Schafer, *Thermal and acoustic pulse studies of space charge profiles in electron-irradiated fluoroethylene propylene*, 1998 Annual Report on Conf. on Electr. Insul. and Diel. Phenom., in press.

Surface Roughness as Measured by Total-reflection X-ray Fluorescence

Wen-li Wu, William E. Wallace

Objective

Develop metrology for measuring thin film surface roughness and planarity, which are important parameters for interlevel dielectric process control in microelectronics manufacture.

Technical Description

Total-reflection x-ray fluorescence is employed. This is a technique which has been used in the semiconductor industry to measure wafer metal contamination before processing, (a so-called front-end of fabrication line measurement). Application of this technique to the determination of low-k dielectric (e.g. polymer) thin film roughness (e.g. planarity over metal topography) would extend the use of the technique to the back-end of the fabrication line. Industry would gain a new use for an existing tool. At present time there is no suitable non-contact technique for measuring dielectric film roughness when the film materials are transparent, as is the case in most instances.

Accomplishments

Experiments have been performed using the new Philips x-ray reflectometer on phase-separated polystyrene/poly(vinyl methyl ether) thin films. These results were compared to atomic force microscope measurements. Indications are that that TXRF is sensitive to low amplitude (~10 nm RMS) but long wavelength (~0.1 Ωm) roughness. Most scanning techniques, such as AFM, have difficulty measuring long wavelength roughness especially if the wavelength is on the order of the maximum scan length. Thus, TXRF, a technique already familiar to industry, obtains a new application as a technique for roughness measurement.

Output

Publications

W. L. Wu, and W. E. Wallace, *Microroughness of Thin Polymer Coatings Studied by Total External Reflection X-ray Fluorescence*, Journal of Vacuum Science and Technology B **16**(1998)1958.

W. L. Wu and W. E. Wallace, *Characterization of Planarity of Polymer Thin Films on Rough Surfaces*, Proceedings of the SPIE **3426**(1998)222.

Polymer Precursors for Inorganic Low-k Dielectrics for Integrated Circuitry

William E. Wallace

Objective

Provide thin film measurement support to an industrially-led initiative to develop a novel polysilsesquioxane spin-on-glass.

Technical Description

Polysilsesquioxanes are a type of silicon-oxygen polymer that can readily be converted to silica, or organically-modified silica, by the application of heat or ultraviolet radiation. The polysilsesquioxane precursor must be stable enough to allow for room temperature processing (e.g. spin coating) but reactive enough to form an insoluble monolith with a modest heating or radiation schedule. For this reason many types of polysilsesquioxanes are being studied by a host of industrial concerns. Two of the major properties of the final monolith that affect it performance in service are density and composition, chiefly residual carbon content. For example, these two properties go a long way toward determining the dielectric constant for the final spin-on-glass thin film. Dielectric constant of the insulating material is an important design parameter in very large scale integration circuitry and of great concern to the microelectronics industry. NIST provides accurate thin film density measurements, a key metric in determining film performance.

External Collaborations

Barry Arkles of Gelest, Inc. has been collaborating on the preparation of monomers and the synthesis of novel polysilsesquioxanes.

Accomplishments

The density and composition of polysilsesquioxane-derived silica thin films processed with UV light were measured by energy-dispersive x-ray reflectivity and ion scattering respectively. Exposure to 12 min of intense UV light was found to produce the same level of conversion to organically-modified silica of essentially the same composition as heating at 350 °C for 4 h. Such a drastic reduction in processing time is of great interest to industry. Conversion by UV light also allows for the possibility of patterning the dielectric, a necessary step for damascene processing the new lithographic technique for ultra-large scale integration processing.

Work also continued on improved methods to more accurately measure thin film density because, generally speaking, density is the underlying parameter that controls many thin film properties of interest for glassy materials, for example, dielectric constant. Polystyrene continued to be used as the example material.

Outputs

Publications

Q. Pan, G. B. Gonzales, R. J. Composto, W. E. Wallace, B. Arkles, L. K. Figge, and D. H. Berry, *Spin-on-Glass Thin Films Prepared form a Novel Polysilsesquioxane by Thermal and Ultraviolet-Irradiation Methods*, Thin Solid Films, acccepted.

E. K. Lin, C. R. Snyder, F. I. Mopsik, W. E. Wallace, W. L. Wu, C. X. Zhang, and R. M. Laine, *Characterization of Epoxy-Functionalized Silsesquioxanes as Potential Underfill Encapsulants*, Materials Research Society Proceedings, in press.

W. E. Wallace, C. K. Chiang, and W. L. Wu, *Energy-Dispersive X-ray Reflectivity and the Measurement of Thin Film Density for Interlevel Dielectric Optimization*, Proceedings of the 1998 International Conference on Characterization and Metrology for ULSI Technology, in press.

W. E. Wallace, N. C. Beck Tan, S. Satija, and W. L. Wu, *Mass Density of Polystyrene Thin Films Measured by Twin Neutron Reflectivity*, Journal of Chemical Physics **108**, 3798 (1998).

N. C. Beck Tan, W. L. Wu, W. E. Wallace, and G. T. Davis, *Interface Effects on Moisture Absorption in Ultrathin Polyimide Films*, Journal of Polymer Science B: Polymer Physics **36**, 155 (1998).

Presentations

W. E. Wallace, *Mass Density of Polystyrene Thin Films*, American Physical Society March Meeting, Los Angeles, CA, March 1998.

W. E. Wallace, *Measurement of Thin Film Thermomechanical Properties for Polymer Interlevel Dielectric Optimization*, 1998 International Conference on Characterization and Metrology for ULSI Technology, Gaithersburg, MD, March 25, 1998.

Confinement Effects on Polymer Thin Film T_g and Morphology

Darrin Pochan, Eric Lin, Wen-li Wu

Objective

To determine the effects of polymer/solid substrate interaction and the presence of a polymer free surface on thin film properties such as the coefficient of thermal expansion (CTE), glass transition temperatures T_g and crystalline structure using x-ray and neutron reflectivity and diffraction. Both semicrystalline and amorphous polymers were included in this work.

Technical Description

Thin film thermal expansion/glass transition: The thermal expansion as a function of film thickness for thin deuterated polystyrene films is measured via neutron reflectometry. In addition, measurements are performed on samples with a free surface and subsequently on the same samples without free surfaces by capping them with a high Tg polymer confinement layer. Two confinement materials are used, bisphenol-A polycarbonate (Tg=150 °C) and a unique, soluble polyimide (Tg=300 °C) synthesized from 2,2'-bis(3,4-dicarboxyphenylhexafluoropropane dianhydride and 2,2'-(trifluoromethyl 4,4'-biphenyldiamine). The polymer layer to be studied, deuterated polystyrene, has a repulsive segmental interaction energy with both of the above materials thereby focusing on confinement as the root cause of any unique thermal behavior. Above film thicknesses (d) of 80.0 nm the thin films were found to exhibit bulk thermal expansion behavior and a transition from the bulk glass CTE to bulk rubber CTE at approximately 100 °C. In films with 40.0 nm. > d > 70.0 nm a transition was found to occur between capped and uncapped samples. Uncapped d-PS layers were again found to exhibit bulk thermal expansion/Tg. However, after capping the glassy CTE persisted 20-40 °C above the bulk Tg of 100 °C while the rubber CTE was found to be lower than the bulk rubber CTE. Film thicknesses > 35.0 nm were found to have glassy thermal expansion throughout the temperature range studied in both the uncapped and capped geometries. Therefore, only in the transition region of thickness (40.0 nm. > d > 70.0 nm and 3-5 Rg) is the effect of the free surface noticeable (a transition from bulk-like behavior with the free surface to a glassy state without the free surface). Below this transition region, the material expands as a glass throughout the temperature range studied (<180 °C)

Thin film crystallization: Initial neutron and x-ray reflectivity and diffraction experiments are carried out in an attempt to discern the effects of confinement in a thin-film geometry on the morphology and phase behavior of semi-crystalline polymers. Deuterated polypropylene was chosen as the model material. Neutron diffraction in transmission mode and synchrotron diffraction in reflection mode revealed strong orientation of crystallites with a monoclinic unit cell within the plane of the film. Neutron Reflectivity performed through the silicon substrate revealed a homogeneous polymer sublayer of constant density next to the substrate. Similar levels of crystallinity are observed in both as-cast and melt/slow cooled films despite gross differences in superstructure as determined via AFM measurements.

External Collaborations

Rainer Kolb of Exxon provided synchrotron beam time and performed experiments, including WAXS and SAXS, on thin semi-crystalline films.

Steven Z.D. Cheng of University of Akron provided high T_g soluble polyimide for confinement material.

Ron Trolard of Cambridge Isotope Laboratories provided detailed molecular analysis of deuterated semi-crystalline polymers, and custom synthesis of other deuterated polymers.

Planned Outcome

The thermomechanical behavior of thin, amorphous polymer films in the film thickness region of 40 nm > d > 70 nm will be focussed on to confirm the transition from bulk-like to completely glassy thermal expansion. Also, the interfacial energy of the substrate and capping materials will be altered in order to monitor its effect on the entire film's thermomechanical properties

The unit cell, crystalline orientation and melting point of semi-crystalline polymers with a depth resolution of few nanometers will be determined. The emphasis will be placed in the region next to the substrates.

Accomplishments

Polystyrene: The effect of a free surface on thin film properties was determined using polystyrene as a model material. Thickness limits were determined. Above one limit the films exhibit bulk thermal expansion (90 nm) while below a second limit below glassy behavior persists throughout temperature range studied (30nm).

Transition region was mapped out in which free surface results in bulk-like thermal behavior. After capping the film behaves like a glass to temperatures ~20-40 °C above the bulk Tg and exhibits a CTE less than the bulk rubbery CTE.

Polypropylene: Unit cell of deuterated polypropylene ultra thin films was determined to be monoclinic ϑ type. Diffraction studies suggest strong orientation of the c axis within the plane of the films.

A sublayer adjacent to the silicon substrate was observed via neutron reflectivity ; this sublayer was found to have a density different from the rest of the polypropylene thin film.

Outputs

Presentations

D. J. Pochan, E. K. Lin, R. Kolb, W-L Wu, and S. Satija, *Neutron Reflectometry for Interfacial Materials Characterization*, 1998 International Conference on Characterization and Metrology for ULSI Technology, NIST, Gaithersburg, MD., March 23, 1998.

D. J. Pochan, E. K. Lin, W-L Wu, and S. Satija, *Confinement Effects on the Thermal Expansion and Glass Transition Behavior of Thin Polymer Films Sandwiched between Polymer Layers*, American Physical Society Meeting, Los Angeles, CA., March 16,1998.

D. J. Pochan, E. K. Lin, W-L Wu, and S. Satija, *Confinement Effects on the Thermal Expansion and Glass Transition Behavior of Thin Polymer Films Sandwiched between Polymer Layers*, American Chemical Society Meeting, Boston, MA., August 24, 1998.

Polymer Ultra-Thin Films - CTE and Viscoelastic Properties

Chris White, William E. Wallace, Wen-li Wu

Objective

Develop a dual quartz resonator technique for measuring the viscoelastic properties of polymer films as thin as several hundred Angstroms. Thin film viscoelastic properties and their temperature dependence will further our understanding of the fundamentals of polymer at interface. Determining the anomalous thin film thermomechanical properties is necessary to the design and implementation of novel thin film organic layers in modern microelectronics.

Technical Description

Development of a instrumental design for quantitative measurement of the viscoelastic properties of thin polymer films has not been possible in the past due to the lack of relevant working equations for this condition. The two widely used simplifying limits of the force balance equation, surface loading and gap loading are not applicable for ultra-thin polymer films. New working equations have been developed that do not rely on either of these simplifying limits. With this development, an instrument based on resonating quartz crystals has been designed. With an ultra-thin polymer layer attached, the resonance condition of the quartz crystal is shifted slightly and the width of the frequency peak is also broadened. At temperatures below Tg , the rigid glassy polymer film, moves in phase and with similar amplitude to the quartz driving surface. As the temperature is raised through the Tg of the polymer, the polymer film becomes more lossy and begins to move with a motion that is out of phase and with a different amplitude than that of the quartz driving surface. These changes in properties are measured by determining the resonance frequency of the quartz crystal and broadening of the resonance frequency peak.

External Collaboration

Barry Lucas, Nanoprobe Corporation, will conduct joint measurement and analysis of thin polymer films using nano-indentation techniques.

Planned Outcome

A state-of-the-art and high precision technique for measuring the viscoelastic properties of polymer films (< 1 Ωm).

Accomplishments

A dual quartz crystal resonator has been designed, constructed, and tested. It currently has a dynamic range of 12 kHz-500kHz. It has temperature control of better than 0.1°C within a range of 25-200 °C. The measurement precision has been determined to be better than 1 part in 10^8 for the resonance frequency measurement and slightly lower precision for the resonance peak width measurement.

Films of 570 nm and 370 nm thick have been measured. They both show significant temperature dependence in resonance frequency shift and peak width. These are the first measurements of the viscoelastic properties of ultra-thin polymer films.

Output

Publications

C. C. White, and W. L. Wu, *A Novel Method to Determine the Mechanical Properties of Ultra-Thin Films,* Proceedings of the Materials Research Society Spring 1998 meeting, San Francisco, Ca., in press.

Presentations

C. C. White, and W. L. Wu, *A Novel Method to Determine the Mechanical Properties of Ultra-Thin Films*, Materials Research Society Meeting, San Francisco, CA., April 15, 1998.

C. C. White, and W. L. Wu, *Determining The Viscoelastic Properties Of Ultra-Thin Polymer Films*, 1998 Gordon Research Conference on Thin Film Mechanical Behavior, Plymouth, New Hampshire, June 24, 1998

C. C. White, and W. L. Wu, *Determining The Viscoelastic Properties Of Ultra-Thin Polymer Films*, American Chemical Society Meeting, Boston, MA, August 23, 1998.

Measuring Polymer Mobility near Solid Surfaces

Eric K. Lin, Rainer Kolb, Wen-li Wu

Objective

To gain a fundamental understanding of the effect of molecular size, surface interaction energy, and mechanical deformation on the mobility of polymer chains near the polymer/solid interface. This information is critical for understanding important physical properties such as the glass transition temperature of polymer chains in confined geometries, the dynamics of adhesion between polymer layers, and the effect of flow processing on entangled polymers at the polymer/solid interface.

Technical Description

The mobility of polymer chains over distances comparable to the size of the polymer chain is measured near the polymer/solid interface using neutron reflectometry which monitors the rate of interdiffusion between layers of deuterated poly(methyl methacrylate) (d-PMMA) and hydrogenated PMMA supported on polished silicon wafers. The thickness of the d-PMMA layer located next to the solid substrate is varied to investigate changes in polymer mobility as a function of distance from the substrate. Molecular size effects were investigated using different molecular weight pairs of d-PMMA and h-PMMA. The surface interaction energy between d-PMMA and the silicon surface was varied chemically through the use of different silane coupling agents. The effect of a shear deformation on the surface adsorption/desorption kinetics of an entangled polymer melt was measured in a newly constructed shearing device.

Accomplishments

Polymer mobility from different molecular weight pairs near an attractive solid substrate is found to dramatically decrease for polymer chains located less than 3 R_g (radius-of-gyration) from the surface. No changes in polymer mobility are observed at distances more than 5 R_g from the solid substrate.

Decreases in the polymer chain mobility are observed near the substrate surface for various substrate surface energies ranging from hydrophilic to hydrophobic.

Shear-induced polymer desorption from an attractive solid substrate is observed for the first time in a highly entangled polymer melt. The rate of desorption increases with increasing shear rate.

Output

Publications

E. K. Lin, R. Kolb, W. L. Wu, and and S. K. Satija, *Shear Induced Polymer Desorption at the Melt/Solid Interface*, Macromolecules, submitted.

E. K. Lin, W. L. Wu, and S. K. Satija, *Polymer Mobility near the Melt/Solid Interface*, Macromolecules, submitted.

E. K. Lin, d. J. Pochan, R. Kolb, W. L. Wu, and S. K. Satija, *Neutron Reflectometry for Interfacial Materials Characterization*, Proc. 1998 International Conference on Characterization and Metrology for ULSI Technology, 1998, in press.

Presentations

E. K. Lin, R. Kolb, W. L. Wu, and S. K. Satija, *Shear-induced Polymer Melt Desorption*, Gordon Conference: Polymer Physics, Newport, RI, August 17, 1998.

W. L. Wu, E. K. Lin, R. Kolb, S. K. Satija, *Polymer Desorption at the Melt/Solid Interface after a Shear Deformation*, American Physical Society, Los Angeles, CA, March 19, 1998.

R. Kolb, E. K. Lin, W. L. Wu, and S. K. Satija, *Polymer Interdiffusion near Varying Solid Surfaces*, American Physical Society, Los Angeles, CA, March 18, 1998.

W. L. Wu, E. K. Lin, R. Kolb, and S. K. Satija, *Polymer Interdiffusion near Attractive Walls*, Materials Research Society, San Francisco, CA, December 7, 1997.

E. K. Lin, R. Kolb, W. L. Wu, and S. K. Satija, *Polymer Interdiffusion at the Melt/Solid Interface*, American Institute of Chemical Engineers, Los Angeles, CA, November 18, 1997.

Novel Underfill Materials and Underfill Flow Modeling

Eric K. Lin, William E. Wallace, Wen-li Wu

Objective

To evaluate physical properties of novel epoxide functionalized silsesquioxane cubes critical to their application as potential underfill materials in flip-chip packaging. To develop the Lattice Boltzmann method as a new tool to model the complex multiphase underfill flow process.

Technical Description

Underfill materials are used to improve device reliability in flip-chip electronic packages by reducing stresses due to differences in the coefficients of thermal expansion between the silicon die and organic substrates. Current formulations are multiphase fluids consisting of low viscosity epoxy resins highly filled with silica particles. The underfill material is flowed under capillary action into the narrow gap between the chip and the substrate and in between the solder bump interconnects. The underfill materials exhibit complicated rheology and complex formulations due to the requirement of a dense suspension of silica particles. Inorganic/organic hybrid materials such as epoxy functionalized silsesquioxane cubes may provide a single phase fluid alternative to current underfill formulations. The critical physical properties of the hybrid material to be evaluated include the coefficient of thermal expansion of the cured material, viscosity, and glass transition temperature. These properties are measured with a variety of methods including X-ray reflectometry, differential scanning calorimetry, and rheometry.

Since the rheology and composition of current underfill materials are complex, computer modeling of underfill flow has been difficult to achieve because of the high filler content, the presence of a free surface, and the complex geometry of the flow volume with surfaces with different wetting characteristics. A working flow model is helpful in determining metrics to apply to new underfill formulations and to evaluate innovative underfill dispension technologies. The Lattice Boltzmann method is a new flow modeling technique which can model complex flow problems by solving a discretized version of the Boltzmann kinetic equations. The advantages of the technique include a straightforward inclusion of multiphase flow in complex geometries and easily parallelizable coding and has been successfully applied to many other technologically important problems such as multiphase flow through porous media. Here, the Lattice Boltzmann method is developed for application to the underfill flow process.

External Collaborations

Professor Richard M. Laine and Chunxin Zhang from the University of Michigan-Ann Arbor collaborated by preparing both tetra- and octa-epoxide functionalized silsesquioxane cube materials.

Dr. Michael A. A. Spaid from Corning, Inc. collaborated in code development of the Lattice Boltzmann method.

Accomplishments

Thin films of the tetra- and octa-epoxide functionalized silsesquioxane cubes cured with structurally different diamines were successfully prepared.

The glass transition temperature of the cured epoxy-functionalized cube material is found to be more than 200 °C, a necessary condition for a useful underfill material..

The coefficient of thermal expansion is found to strongly depend upon the structure of the curing agent. Tailoring the thermal expansion is critical for a successful underfill material.

A working three dimensional multi-phase code using the Lattice Boltzmann method has been successfully developed and applied to model test problems.

Outputs

Publications

E. K. Lin, C. R. Snyder, F. I. Mopsik, W. E. Wallace, W. L., Wu, C. W. Zhang, and R. M. Laine, *Characterization of Epoxy-Functionalized Silsesquioxanes as Potential Underfill Encapsulants*, in Organic/Inorganic Hybrid Materials, ed. by R. M. Laine, C. Sanchez, E. Giannelis, and C. J. Brinker, Mat. Res. Soc. Proc., San Francisco, CA, in press.

Presentations

E. K. Lin, C. R. Snyder, F. I. Mopsik, W. E. Wallace, W. L., Wu, C. X. Zhang, and R. M. Laine, *Characterization of Epoxy-functionalized Silsesquioxanes as Potential Underfill Encapsulants*, Materials Research Society, San Francisco, CA, April 13, 1998.

Residual Stress in Polymer Films Adhered to Silicon Substrates

C. K. Chiang and A. S. DeReggi

Objective

To develop a test method based on a residual stress measurement for determining coefficient of thermal expansion and in-plane elastic modulus of thin polymer coatings.

Technical Description

Differences in coefficient of thermal expansion, CTE, between polymer coating and substrate lead to residual stress during a temperature excursion. For example, there always exists a tensile residual stress in polymer coatings prepared at elevated temperatures onto a low CTE substrate such as silicon wafer. Provided the elastic constants of the wafer are known quantities the bending or the warpage of the wafer can be used to determine residual stress. Depending on the substrate CTE and elastic modulus the residual stress of a polymer coating can be markedly different. By measuring the residual stress of a pair of identically prepared thin coatings on two different substrates with known properties, the CTE and elastic modulus of the coating can be deduced. By conducting this measurement at different temperatures one can measure the temperature dependence of CTE and elastic modulus. The above mentioned procedure was first used for investigating the properties of refractory films by Retajczyk and Sinha, (Appl. Phys. Lett. **36**, 162 (1980)). In our work silicon wafer and GaAs wafer were chosen as the substrates because of their wide usage in electronic industries.

External Collaborators

Dr. David Babb of Dow Chemical Company provided data on the thermal and mechanical properties of spin-on polymer films.

Dr. David Feiler and Dr. Wei Xia of Rockwell Semiconductor System provided test samples and their properties of spin-on low-k dielectric materials.

Accomplishments

A modification of a Tencor residual stress analyzer, an instrument commonly used in most microelectronic companies, resulted in a significant reduction of thermal noise. For example, our data collected at 180 °C showed that the random noise level was reduced by a factor of four with our modification. A reduction in thermal noise significantly improves the accuracy of stress measurement, and hence the accuracy of CTE and modulus values of the polymer coatings or films.

Output

Presentation

C. K. Chiang, and Aime S. DeReggi, *Measurement of In-Plane CTE and Elastic Modulus of Polymer Thin-Films Using Bending Plate Technique*, 1998 International Conference on Characterization and Metrology for ULSI Technology, Gaithersburg, MD, March 25, 1998.

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 are further sharpened by the advent of methods that provide better control in polymer synthesis, more precise molecular structure, and new nanoscale 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 that in thin films at interfaces, and the effects of complex thermal and mechanical histories on the phase separation process. Fundamental advances in theory and modeling in collaboration with CTCMS continue to guide and interpret these measurements.

Current research in the program has four areas of emphasis: (1) measurement technology for on-line characterization of phase behavior, deformation, and dispersion; (2) shear effects on phase diagrams and blend morphology; (3) interfacial interactions in compatibilized blends, filled polymers, and nanocomposites; and (4) control thin films morphology by surface interactions and finite size effects. Active industrial collaborators include: Dow Chemical, Dow Corning, Eastman Chemical, Exxon, GE, Goodyear, Lucent Technologies, Mobil, ChemElectroPhys, Packard Electric, Dendritech, and DSM for development of measurements using fluorescence, light scattering, neutron scattering and reflectivity, x-ray scattering, birefringence, microscopy (AFM, TEM, phase contrast), and rheology.

In fiscal year 1998 special emphasis was put on developing the programs in polymer fillers and nanocomposites and applications of dendritic polymers. Two NIST/Industry workshops were held to identify and prioritize the critical technical issues hindering new applications in these two areas. For fillers and nanocomposites a number of important needs were identified with the conclusion that the most critical were controlling molecular level interactions and measuring dynamics of polymers at the filler interface. For dendritic polymers important issues included direct comparisons of structures of dendritic polymers, characterization of interactions with other polymers, and, most critically, properties of dendritic polymers at interfaces. The workshops also provided an opportunity to communicate the cutting edge work of the blends and processing program.

Significant Accomplishments

- The versatility of hydrogen-bonded polymer blends for advanced materials was demonstrated and a new phenomenological model for the strength of the bonding interaction was tested and confirmed by small angle neutron scattering.

- A model based on normal stress differences was developed which predicts the onset of highly anisotropic structures in the vorticity direction for phase separated blends under shear when the droplet first normal stress difference exceeds that of the matrix.

- An optical sensor to measure anisotropy during biaxial stretching of polypropylene film in production ovens at high temperature was designed and demonstrated in collaboration with Mobil Chemical Company.

- Spherical and cylindrical composition waves emanating from the boundaries of inclusions in a phase separating blend were predicted by simulations and subsequently confirmed by experiments investigating the microstructure of filled model polymer blends.

- An analytical model predicting the viscosity for polymers filled with dispersions of platelet particles was developed and validated with data for a range of particle shapes. The threshold of rigidity where the suspension viscosity diverges was predicted to be inversely proportional to the intrinsic viscosity.

- Modeling of finite size effects agrees with measurements by showing that surface confinement can shift phase boundaries in compressible blends up or down depending on the strength of polymer-surface interactions

- Theoretical concepts and simulations were developed to describe the growth of dynamical correlations that are related to slow dynamics in glass forming materials.

- X-ray reflectivity and atomic force microscopy methods were developed to characterize interactions between clay and polymer in nanocomposite films under well defined conditions.

- Alignment of the morphology in a phase separating blend film to an underlying pattern of surface chemisty was shown to improve with decreasing film thickness until reaching a critical value below which spinodal dewetting causes controlled break-up into uniform nanoscale droplets.

- Interpenetrating polymer networks of hydroxyethylmethacrylate with polyamidoamine (PAMAM) dendrimers were prepared and the individual dendrimers were shown by small angle x-ray scattering and transmission electron microscopy to be uniformly dispersed.

- Thorough characterization of the size, shape, and molecular conformation of PAMAM dendrimer molecules of generations 5 through 10 was achieved with a combination of small angle neutron and x-ray scattering and transmission electron microscopy.

- The single chain dimensions of polyelectrolytes as measured by zero-average-contrast small angle neutron scattering, were shown to be consistent with semiflexible rods in the presence of monovalent counterions and random coils in the presence of divalent counterions.

Phase Behavior in Polymer Blends

C. C. Han, H. Gruell[1], A. Esker[2], R. Xie[2], A. I. Nakatani, C. L. Jackson, A. Karim, and G. Kim[3]
[1]Alexander von Humboldt Foundation, Germany
[2]University of Connecticut, Storrs, Connecticut
[3]Stevens Institute of Technology, Hoboken, New Jersey

Objectives

The objectives are to develop experimental techniques and capabilities for studying morphologies of polymer blends resulting from phase separation and crystallization both at surfaces and in the bulk in order to understand the mechanisms by which these processes occur. Of particular interest are questions about: the interplay between crystallization and phase separation in blends and in microphase separated copolymers where both processes are present; the role strong and steric interactions have on the stabilization of phase separated morphologies; finite size effects, which influence and control film stability and polymer miscibility in nanotechnology applications; the role of the preferential interaction of polymer components with a surface and the growth of adsorbed layers (pre-transition) and subsequent phase separation; and finally, the effect semi-permeable, ultra-thin, barrier layers (membranes) have on selective polymer transport process.

Technical Description

Small angle neutron scattering (SANS), light scattering (LS), optical microscopy (OM), transmission electron microscopy (TEM), atomic force microscopy (AFM), and reflectivity (x-ray (XR) and neutron (NR)) are being used and modified to examine the time dependent evolution of morphologies associated with preferential adsorption, wetting/dewetting, mixing/demixing and crystallization in polymer blends at surfaces, in confined geometries and in the bulk.

- AFM capabilities will be developed to probe the role surface interactions have on polymer film stability (wetting/dewetting) with homopolymers for subsequent blend studies of these phenomena.
- Polystyrene/polybutadiene and polybutadiene/polyisoprene on flat silicon surfaces are being studied by NR and SANS and followed by a bulk system with fine silica particles.
- The phase behavior of polymer blends stabilized by H-bonding and metal ion complexes have been studied by SANS.
- The effect of conformational changes on steric interactions induced through photoisomerization has been examined by SANS.
- Blends of polystyrene and polycaprolactone which have an upper critical solution temperature will be examined as to the interplay of crystallization and phase separation on

both the kinetics of phase separation and the ultimate morphologies, at appropriate relative quench depths by LS and microscopy.

- Microphase separation and crystallization in semi-crystalline block copolymers of polystyrene(S)-polybutadiene(B)-polycaprolactone(C) and diblocks SC and BC will be studied using optical microscopy (OM), transmission electron microscopy (TEM) and scattering techniques.
- Alkyl branch modification of stiff rods (thereby forming "hairy-rods") in bulk and on a surface are being studied by the aforementioned techniques.
- Trilayer thin films of spin-coated deuterated polystyrene, membranes prepared by the Langmuir-Blodgett technique, and hydrogenated polystyrene will be prepared and characterized where the membrane consists of a blend of photo-crosslinkable cellulose "hairy-rods" and polystyrene. NR provides a convenient way to study the diffusion of this system, while characterization of the membrane and layer thicknesses are readily obtained from the other techniques.

External Collaborators

A. Halasa, Y. Feng, Goodyear Tire and Rubber Company, Akron, Ohio - Collaboration and supply of elastomers and filled elastomers for various experiments.

R. A. Weiss, University of Connecticut, Storrs, Connecticut - Collaboration and supply of ionomer blend materials.

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

T. Hashimoto, H. Jinnai, ERATO, Japan Science and Technology Corporation, Kyoto, Japan

O. Urakawa, Q. Tran-Cong, Kyoto Institute of Technology, Kyoto, Japan - Collaboration and supply of materials for SANS experiments on the effect of photoisomerization in polymer blends.

M. Libera, Stevens Institute of Technology, Hoboken, New Jersey - Collaboration on TEM of block copolymers.

G. Wegner, Max-Planck-Institut für Polymerforschung, Mainz, Germany

Accomplishments

- The role of capillary waves on film breakup was investigated and a conceptual model was introduced involving three film thickness regimes defined in terms of the amplitude of capillary waves relative to the film thickness. The "spinodal dewetting" mechanism characterizing the ultrathin film regime was observed by AFM.
- The bulk phase behavior of a polyisoprene/deuterated polybutadiene blend was determined by SANS measurements. The system shows lower critical solution temperature (LCST) behavior with a bulk critical temperature of 55 °C and a critical composition of $\phi_{dPB} = 0.45$ (where ϕ_{dPB} is the volume fraction of deuterated polybutadiene). The phase behavior of this blend in a thin film geometry was investigated by multiple neutron reflection experiments as a function of temperature ($298\text{ K} < T < 408\text{ K}$) and film thickness ($400\text{ Å} < d < 2000\text{ Å}$). The depth profile shows a preferential symmetric adsorption of polyisoprene at both interfaces consistent with Monte Carlo simulation studies. The surface excess, z^*, of polyisoprene as a function of temperature shows a maximum around the bulk critical temperature and linearly increases with the logarithm of film thickness for a given temperature. The results suggest

that in the one phase region adsorption layers of polyisoprene are formed which grow in size with increasing film thickness and as the critical temperature is approached. In the two-phase region, phase separation occurs inside the film with the polyisoprene rich phase wetting both interfaces. For thick films, a trilayer structure is formed with the polybutadiene rich phase in the center of the film and the polyisoprene rich phase wetting both interfaces (polymer/air and polymer/Si). This structure becomes more and more unstable with decreasing film thickness leading to lateral inhomogeneities inside the film.

- A phenomenological model was formulated for how the strength of the binding interaction in hydrogen-bonded polymer blends depends on the density of the hydroxyl group. This model was tested by SANS in order to deduce the hydrogen bond enthalpy. The demonstrated complexity of the low-q structure in these materials was linked to the equilibrium properties of the condensed phase. The use and versatility of this type of chemical modification technique for enhancing polymer-polymer miscibility for advanced materials processing was also demonstrated.
- Control over the miscibility of polymer blends by manipulating steric interactions through controlled photoisomerization of labeled polymer chains was demonstrated by SANS measurements.
- A model blend system of polystyrene and polycaprolactone was purified and cloud point experiments planned to study the competition between crystallization and phase separation. Necessary modifications have been initiated for the existing temperature jump light scattering instrument to study phase separation kinetics and subsequently probe crystallization kinetics following a second temperature quench.
- TEM was used to study thick films (5-10 μm) and bulk specimens of polystyrene(S)-polybutadiene(B)-polycaprolactone(C) (SBC) triblock and BC diblock copolymers prepared by various annealing conditions, with or without spherulitic crystalline morphology. A comparison of the macroscopic crystalline superstructure (optical range 4-1000 μm) and microphase separated morphology (TEM range 5-100 nm) showed that crystallization into spherulites can either distort or completely destroy the microphase-separated morphology. In the SBC triblock, long range crystallization of the C block can be suppressed by appropriate annealing conditions, as seen by TEM and OM. In this case, the microphase-separated structure resembles that seen for ABC type amorphous block copolymers; for $S_{35}B_{15}C_{50}$ a lamellar microstructure with B cylinders at the interphase boundaries is observed. The competition between microphase separation and crystallization of the C block depends strongly on the rubbery or glassy character of the amorphous blocks and the overall composition. SC diblock copolymers form a lamellar microphase separated structure which is prevented from spherulitic crystallization due to the glassy S blocks at 62 mass %.
- Langmuir-Blodgett thin film blends of cellulose ethers with polystyrene were characterized by XR and AFM for use as membrane materials. Crystallization conditions were determined for bulk blends of cellulose ethers and esters with polycaprolactone and poly(ethylene oxide) for use as model systems for studying crystallization kinetics by LS where the rigidity of the cellulose backbone may induce substantial changes in morphology.
- NR measurements were performed to characterize the interdiffusion of deuterated and protonated polystyrene in the presence and absence of a membrane. The porosity of the membrane can be controlled by mixing 0 to 40 % polystyrene into the cellulose ether to form a phase separated structure. The membrane thickness can be varied in increments of 10 Å

corresponding to the thickness of a single monolayer. The presence of a 60 Å thick membrane containing 34% PS substantially retards interdiffusion. Movement of the membrane as a function of annealing time is observed and may be represent a polymeric analog to similar observations for barrier layers in metallic systems.

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Mixing and Structure Formation Under Shear Flow

C. C. Han, F. Qiao, L. Kielhorn[1], H. S. Jeon[2], A. I. Nakatani, E. K. Hobbie[3], K. B. Migler, and C. Huang[4]
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Objectives

The objectives are to understand the fundamental mechanisms and to explore the possible applications in the framework of mixing and morphology control of polymer blends as a function of shear rate, temperature, composition, and compatibilizer concentration. The fundamental studies are aimed at: understanding the relationship between the mean-field, the Ising, and the shear generated mean-field-like phase behavior in binary blends; explanation and possible applications for the shear induced promotion and suppression of various phase transition temperatures in blends of homopolymers and block copolymers; the effects of the shear induced distortion of fluctuation waves on phase separated morphology and the orientation of the ordered state of the block copolymers involved; the development of in-situ characterization of multiphase materials. By working in collaboration with industry, the current goal is to demonstrate the use of these characterization methods and to apply the knowledge gained from the structure-rheology relationships of multiphase systems to help determine the range of critical processing parameters for specific applications, such as molding, extruding, compounding, and dynamic phase inversion processes.

Technical Description

The success of this study could lead to a better understanding and even comprehensive prediction of morphology/property of extruded resin and molded parts. Phase inversion under shear has been studied heavily by the extrusion community from an engineering perspective. A more scientific understanding of the phenomena would be important for future polymer alloying efforts.

- The effect of shear on the phase separation temperature of binary blends, and on the order disorder transition temperature of block copolymers, will be studied as fluctuation waves are either suppressed or distorted by the shear wave.
- The shear induced morphological structure of polyisoprene with high 1,2-microstructure content and polyisoprene or polybutadiene with high 1,4-microstructure content are being studied as two-phase blends to evaluate the elastic effect in these visco-elastic fluids.
- The structure changes, especially at high shear rate will be emphasized and compared with the entangled network chain deformation and with the flow instability.
- The concept of forming string (or fibril like) morphology at lowered interfacial tension condition will be tested by the LCP/thermoplastic blends with grafting reaction on the interface to introduce block copolymers as compatibilizer.
- The use aligned rod-like LCP polymer will be explored for an elongated fibril structure to stabilize the Rayleigh instability in order to maintain a desired morphology for applications.

- Time resolved video optical microscopy will be used to study anisotropically deformed droplets under shear jump or shear quench and measure the retraction and undulation/breakup predicted by Rayleigh instability.
- Viscoelastic systems will be compared with viscous systems and also with rigid rod chain stabilized systems.
- The steady state viscosity and dynamic modulus of multiphase polymer blends will be studied to investigate the relationship between rheological properties and structure formation (domain deformation, break-up etc.).
- The phenomena of phase inversion during shear flow will be investigated. The primary focus of the work is to find a suitable polymer blend system for which these phenomena can be directly observed through microscopy and/or light scattering.
- On-line light scattering and optical microscopy techniques will be used to demonstrate the in-situ structure characterization and to locate the narrow processing window of fiber formation in a LCP/amorphous polymer blends at elevated temperature and high shear rate with a conical twin screw extruder.
- The mechanical modulus and fracture toughness are being evaluated jointly with composite group, and correlated with the morphology characterized by the on-line LS/Optical microscope apparatus for the LCP containing blends. Different LCP's will be studied with and without in-situ grafting reaction for reactive compatibilization.
- The phenomena of dynamic phase inversion under shear flow and its relationship with composition, temperature, and viscosity are being studied.

External Collaborators

A. Halasa, Y. Feng, Goodyear Tire and Rubber Company, Akron, Ohio
Don Wiff, Wright Patterson Air Force Research Lab
H. Yang, Eastman Chemical
T. P. Lodge, University of Minnesota - Collaboration and supply of block copolymers for SANS experiments on shear behavior of block copolymers in various solvents.
R. Colby, Pennsylvania State University, State College, Pennsylvania
M. D. Dadmun, University of Tennessee, Knoxville, Tennessee - Collaboration and supply of materials for shear SANS experiments on LCP materials.
F. A. Morrison, Michigan Technological University, Houghton, Michigan - Collaboration for shear SANS experiments on cylindrical diblock copolymer melts.
J. W. Mays, University of Alabama, Birmingham, Alabama - Collaboration and synthesis of material for shear SANS experiments on cylindrical diblock copolymer melts.

Accomplishments

- Work on shear behavior of blend with external added copolymer has been completed, resulting in some fundamental understanding of compatibilizer distribution under shear and phenomena of phase separation within phase separated domain/matrix morphology.
- Shear-induced behavior on solutions of block copolymers in neutral and selective solvents has been examined by SANS.
- Interface evolution in a reactively blended liquid crystal polymer/poly(ethylene terephthalate) (LCP/PET) system has been studied by FTIR, SEM and torque-time monitoring process. The

effectiveness of using a multi-functional epoxy as reactive-coupler to produce compatibilizer in-situ for morphology control of this blend has been demonstrated.

- With the use of the on line LS/Optical microscope system, a narrow processing window for LCP/PET alloying has been located and optimized.
- A droplet-fiber transition has been observed in the slit channel of the extruder for the above reactively blended LCP/PET system by the in-line light scattering and optical microscopy. This is in contrast with the droplet morphology of the uncompatibilized system.
- The stability of fibrillation has been studied under different flow conditions by the LS pattern and the Optical microscopy images. The results indicate that LCP is highly oriented under proper flow conditions, and the formation of fiber microstructure is strongly dependent on the flow and interfacial conditions.
- Fracture strength has been measured by biaxial tensile testing with preliminary results showing improved mechanical properties along the machine direction.
- Phase contrast optical microscopy and light scattering experiments were performed for critical and off-critical polybutadiene/polyisoprene blends after the cessation of shear. Time evolution data of anisotropy and other quantities are being collected.
- Computer programs for time-resolved data analysis of scattering and optical microscopy results have been developed.
- Several types of relaxation behavior due to the interplay of thermodynamics and elastic behavior have been classified. A non-linear response of the system under shear has been observed; the domain structure becomes ‘cleaner’ with increasing shear rate and the relaxation becomes faster. This implies that mixing of polymer blends at high shear rates might actually induce more unmixing at later times if the mixed morphology is not stabilized.

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Interfaces in Immiscible Multiphase Systems

A. Karim, J. F. Douglas, D. Liu, B. Bauer, and C. Han

Objectives

The objectives are to characterize interfaces in immiscible, reactive and strongly interacting homopolymer/random/ block copolymer systems for studying compatibilization effects and to test the validity of extending the binary interaction parameter theory to pseudo-ternary systems. Interface profiles will be measured in glassy polymeric systems to delineate equilibrium from non-equilibrium effects, utilizing thin film neutron and X-ray reflectometry methods.

Technical Description

Many industrially important polymer systems tend to be multiphase in nature, which are often stabilized through the addition of compatibilizing or dispersing agents. These agents are usually copolymer materials or are generated in-situ by reaction of the blend components. The thin film geometry provides ideal interfaces by which the compatibilizing effect of a copolymer can be accurately quantified. A homopolymer/random copolymer is one of the simplest representative multiphase system. Theories on interfacial characteristics exist for such systems, yet verification through controlled experimentation is lacking. A measure of the interfacial properties in such systems is important since adhesive strength and other mechanical properties of laminates hinges critically on interface width and profile shape. Knowledge of these parameters is expected to lead to improved predictive behavior for such materials. Likewise, the control and estimation of reactively generated copolymer is important to correlate structure - property relationship in reactive polymer blends.

- Measure interface profiles in deuterated poly(phenylene oxide)/styrene acrylonitrile (PPO/SAN) and poly(phenylene oxide)/styrene maleic anhydride (PPO/SMA) bilayer films as a function of AN and MA fraction and compare with predictions from binary interaction parameter theories.
- Quantify morphological characteristics of frustrated coalescence in polycarbonate/ poly(methyl methacrylate) (PC/PMMA) films using atomic force microscopy and determine reactively generated copolymer fraction using NR.
- Compare phase separation in the PC/PMMA reactive blends to PS/PB regular blends with model PS-b-PB block copolymer surfactants in the strong segregation limit.
- Characterize interfacial width in hyperbranched poly(ethylene oxazoline) (PEOX)/linear PS bilayers samples by NR to estimate entropic contribution to adhesive strength and other interfacial properties in exploratory blend materials.
- Evaluate interface profile development occurring by segmental relaxation in dPS/PS bilayers below the bulk glass transition temperature (T_g) using NR and compare with equilibrium interface widths in immiscible bilayer systems. Compare with recent theories on interfacial mobility near deformable and hard walls.

External Collaborators

G. D. Merfeld, D. R. Paul, Center for Polymer Research, University of Texas, Austin - Collaboration on NR measurements, data fitting and analysis and supply of SAN and SMA polymers.

B. Majumdar, GE Plastics, Schenectady, New York - Collaboration and supply of dPPO samples.

G. P. Felcher, R. J. Goyette, Materials Science Department, Argonne National Laboratories, Illinois - NR measurements of glassy PS interface development.

K. F. Freed, University of Chicago, Illinois - Collaboration on theoretical aspects of sub-T_g bilayer interfacial profile development.

S. K. Satija, NIST Center for Neutron Research - Collaboration utilizing NR for interface characterization of dPPO/SAN and dPPO/SMA samples.

Accomplishments

- Characterized dependence of interface profiles in dPPO/SAN and dPPO/SMA bilayer samples for full range of copolymer composition by NR. Results validate theories on applicability of binary interaction theories to these pseudo-ternary systems.
- Observed dramatic reduction of interfacial tension in thin blend films of PS/PB with less than 1% addition of PS-b-PB, leading to suppression of lateral phase separation induced surface patterns. Instead, temporal patterns corresponding to critical fluctuations are observed. These results suggest an amplification of surfactant interfacial activity in thin films due to the layered interfacial geometry.
- Characterized the interfacial width of PEOX/PS bilayers samples as a function of PEOX branching content, from linear to highly branched, using NR. Increase of branching content induced a systematic increase of the interface width. Such novel blend systems provide a means for investigating contributions to interfacial broadening arising solely from entropic variations (rather than enthalpic), a subject of significant scientific importance and controversy in recent years.

- Confirmed an inhibition of the late-stage coalescence of droplets during phase separation in PC/PMMA reactive blends as due to the presence of a surfactant layer "frustrating" phase separation. The thickness of the reactively generated copolymer layer was measured by NR. OM measurements indicate a plateau in the structure factor of the evolving droplets due to the frustration of coalescence. Factors controlling inhibited coalescence were identified and the mechanism for droplet distortions explained.

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Phase Behavior of Polyolefin Blends

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Objectives

The objectives are to maximize the benefits to suppliers and users of new metallocene catalyzed polyolefin materials for expanded commercial opportunities by providing a greater understanding of the interplay between chain architecture (branching) and ultimate morphological properties. The ultimate aim is to control crystal structure, phase morphology and surface properties based on a rational understanding of the underlying thermodynamics and kinetic processes.

Technical Description

Blends of polyolefin materials allow the supplier to customize the material for a particular end-use. The miscibility of these blends under typical processing conditions of high temperature, pressure and shear is critical to the state of the final product. The measurements of the miscibility under pressure will allow suppliers to modify their material formulation to suit a particular processing and end-use application. Final mechanical properties in polyolefin blends are strongly influenced by crystal morphology. The question of whether phase separation precedes crystallization or is caused by it remains unresolved. Control of these processes enables the intelligent choice of blend components to achieve desired final properties.

- Crystallization of a series of polyolefins via simultaneous small angle x-ray scattering and wide-angle x-ray diffraction will be studied.
- The phase separation and relative surface layering in a model compatibilized polyolefin blend will be determined via neutron and x-ray reflectivity .
- The NIST neutron scattering shear cell and the NIST pressure cell will be utilized to measure the effects of external fields on polyolefin blend interactions and miscibility.
- The origins of the composition dependence of the interaction parameter of polyolefin blends will be explored by probing the response of these systems to pressure.
- Optical and neutron scattering will be utilized to study the effects of pressure on the interaction and phase behavior of model and commercial polyolefin blends.
- Data analysis and theoretical understanding of pressure induced changes in the interaction parameter will be emphasized.
- The phase behavior between blends of polyethylene and a copolymer with side chain branching will be studied to examine the competition between crystallization and phase separation.
- Neutron scattering and small angle light scattering will be used to examine the occurrence of phase separation and the kinetics of crystallization.

External Collaborators

D. J. Lohse and M. Rabeony, Exxon Research and Engineering Company, Annandale, New Jersey - CRADA developed to measure the pressure and shear rate dependence of the phase behavior of metallocene catalyzed polyolefin blends by SANS and optical techniques.

N. Balsara, Polytechnic University, Brooklyn, New York - Special synthesis of model polyolefins and study of the effects of external fields.

Accomplishments

- Two distinct behaviors of structure growth were discovered during the early stages of crystallization using monodisperse polyethylene at low undercooling. Time resolved small and wide angle x-ray scattering (SAXS and WAXS) measurements found that in the first regime, density fluctuations increase in size and amplitude as a result of the development of local order in the sample. In the second regime, these dense regions evolve into the growing lamellar crystals. The second regime growth process is temperature dependent.
- The kinetics of crystallization in model polyolefin materials were measured as a function of short side chain branch content. Large length scale density fluctuations were found to precede the onset of crystal structure.

- In thin films (200-400 Å) of compatibilized model polyolefin blends the onset of lateral phase separation decreases with film thickness. Neutron reflectivity demonstrates that a compatibilizing agent alters the kinetics of phase separation but does not change the final shape of the density profile.

Outputs

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In-Line Optical Characterization of Polymer Extrusion and Blend Morphology

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[1]University of Pennsylvania, Philadelphia, Pennsylvania

Objectives

The objectives are to develop a flexible set of optical based tools for measurement of critical processing parameters and demonstrate their value to industry. Utilization of optical tools will deepen the understanding of processing phenomena which occur under high shear conditions, such as morphology development, fiber formation, and slippage.

Technical Description

Ultimate blend properties depend critically on the structural morphology. Manufacturers have little understanding of how to generate desired morphologies. This work will generate characterization of the powerful effects of normal forces on the morphology. While polymer melt processing is carried out under conditions of extreme shear stresses and normal forces, laboratory measurements of droplet morphology have been confined to the low shear regime. We have evidence of profound changes in droplet morphology as shear rates enter the processing regime.

- An extrusion slit die with optical access for in-situ microscopy and light scattering enables measurement of polymer blend morphology and polymer flow profiles.
- Microscopy permits measurements of structures in the 2 - 200 micron range while light scattering can measure structures at length scales down to 0.1 micron.
- The morphology of polymeric droplets are measured as a function of depth and shear stress in the flow channel.
- The effect on viscosity ratio on polymer deformation and breakup are measured.

- Key processing variables in the control of material structure are identified.
- The influence of processing on the development of morphology for representative classes of polymer blends are examined.
- Measurements in both the twin screw extruder and the optical cone and plate device will be continued.
- Complimentary rheological measurements in the pure homopolymers will be conducted and used to identify the relevant rheological conditions that create these unusual shapes.
- Theoretical models of the morphology utilizing normal force concepts will be developed.

External Collaborators

3M Corporation, St. Paul, Minnesota - Velocity profile measurements/Polymer processing additives.

Exxon Research and Engineering Company, Annandale, New Jersey - Measurements of polyolefin blends structure during extrusion.

Accomplishments

- Discovery of a blend system, which exhibits highly anisotropic structures in the vorticity direction, was made as part of a systematic investigation of the vorticity alignment in sheared polymeric blends. A theoretical model based on normal stress differences was developed that predicts that the onset of this novel phenomenon when the droplet first normal stress difference exceeds that of the matrix. Rheological measurements carried out on the same materials demonstrate qualitative agreement between the experiment and theory.
- A comprehensive study of morphology as a function of viscosity ratio, screw rotation rate and channel depth was completed. A dramatic effect of viscosity ratio on the creation of strings was observed. Depth resolved optical microscopy revealed that morphology of droplets is a strong function of position. In the low shear limit, local stress is the controlling parameter, whereas at high shear stress, a transition to pure droplets occurs. Discovery that the surface can act as a compatibilizing agent to create strings in the presence of shear flow.
- The first direct measurements of slippage at the melt-wall interface upon introduction of a polymer processing additive was conducted. The efficiency and performance of wall-slip additives with regards to processing optimization were investigated.
- Measurements were performed that further our fundamental understanding of the role of compatibilizers in polymer processing, particularly with regard to shear-induced structures in polymer blends and thermoplastic/polymer - liquid crystal blends.

Outputs

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Fluorescence, Dielectrics and Ultrasonics Monitoring for Polymer Processing

A. J. Bur, K. B. Migler, S. C. Roth

Objectives

The objectives are to develop experimental methodology using fluorescence spectroscopy, ultrasonics, and dielectrics for monitoring temperature profiles, shear heating, pressure effects, molecular orientation, strain rate, and blend and filler composition as a function of processing conditions.

Technical Description

- A strain rate measurement sensor will be developed using the method of fluorescence recovery after photobleaching. We will employ the confocal optics hardware in order to obtain spatially resolved strain-rates and to focus photobleaching energy. The strain rate measurement will yield information about the viscoelastic character of a resin during flow.

- The confocal optics probe will be used to measure temperature profiles during extrusion and injection molding for various processing conditions.
- Residence times and residence time profiles will be measured as a function of position along an extruder and as a function of the depth in the flow stream. Direct industry participation is planned for this task. The experiments will be carried out in collaboration with a guest scientist from 3M Co. The confocal optics sensor will be used for the depth profiling measurements.
- A film processing machine will be instrumented with optical equipment to measure temperature and to measure the molecular orientation via fluorescence anisotropy and birefringence during the stretching phase of the process.
- The temperature and pressure behavior of fluorescence band broadening dyes will be examined by statistical, experimental, and model concepts.
- An in-line dielectric sensor will be placed on the NIST twin extruder and used to study the dielectric properties of polymer blends and filled polymers.
- Shear and longitudinal ultrasonic transducers will be developed for high temperature environments of polymer processing. Measurements of ultrasonics velocity and attenuation will be combined with models to use ultrasonics for monitoring temperature and orientation.

External Collaborators

M. McBrearty, Chemical Electrophysics Corporation, Hockessin, Delaware - Chemical ElectroPhysics will contribute dielectric spectrometer equipment and conduct experiments to measure dielectric properties of filled polymers.

M. Amon, Mobil Chemical Company, Rochester, New York - Mobil Chemical will contribute optical equipment and access to a pilot plant process line for the measurement of fluorescence anisotropy of stretched films during processing.

C. L. Thomas, Department of Mechanical Engineering, University of Utah, Salt Lake City, Utah - The University of Utah will provide a polymer injection molding machine that will be instrumented with optical sensors for the purpose of studying physical properties of resins during molding.

Accomplishments:

- In collaboration with Chemical Electrophysics Corp., dielectric measurements of filled polymers during twin screw extrusion were performed using a new in-line dielectric sensor. The measurements yielded information about mixing ratios, residence time and sensor performance. The dielectric data are being used by Electro ChemicalPhysics Corp. to improve their dielectric sensor and to develop models for sensor behavior. The in-line application of this sensor yields real-time information about dielectric constant and dielectric loss and the composition of mixtures.
- In collaboration with Mobil Chemical, a new optical sensor was designed for real time measurements of fluorescence anisotropy during the biaxial stretching of polypropylene films that have been doped with a fluorescent dye. The sensor contains polarizing elements, focusing optics, and fiber optics for monitoring the polarization content of fluorescence radiation and for monitoring temperature using the spectral characteristics of the dye. The

NIST anisotropy sensor, which is the subject of a patent application, is being used by Mobil Chemical Co. because the sensor can be deployed at high temperatures in the production oven during biaxial stretching of polypropylene film. The real-time information about molecular orientation will be used to determine final properties of the film.

- The temperature and pressure dependence of spectra from fluorescence band broadening dyes were evaluated by acquiring arrays of temperature/pressure data for four fluorescent dyes, bis di-tert-butylphenyl perylenedicarboximide (BTBP), perylene, and diphenyl octatriene (DPO) doped into PDMS and benzoxazolyl stilbene (BOS) doped into polystyrene. Statistical analysis of the data by the method of principal components is being carried out in order to separate pressure and temperature effects.
- A model for an optical interferometer sensor that was developed and employed to measure resin shrinkage during injection molding. The optical sensor that has been used to monitor injection molding has yielded multi-parameter information about resin properties including crystallization and shrinkage. Asymmetric shrinkage patterns can be used to predict warpage in the final product.

Outputs:

Publications

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Theory for Phase Separation and Transport in Polymer Liquids

J. F. Douglas, B. P. Lee, and S. C. Glotzer

Objectives

The objectives are to develop theoretical models of blend phase separation subject to perturbing influences (finite size, filler particles, shear flow) and of the transport properties of polymeric liquids with and without filler particles; to investigate and model properties of glass-forming liquids; and to provide guidance for ongoing experimental studies by the Polymer Blends and Processing Group.

Technical Description

- A general model of the viscosity of complex-shaped particle dispersions is developed based on a mathematical analogy between the hydrodynamics of concentrated particle dispersions and the problem of calculating the conductivity of a suspension of insulating particles in a conductive matrix. The use of percolation theory concepts leads to a description of the viscosity of dispersions as a function of a reduced concentration dependent on particle shape, interparticle interaction and shear rate.
- The influence of shape and surface interactions on blend phase separation is investigated numerically within a Cahn-Hilliard theory framework.
- The influence of interacting boundaries on the phase stability of compressible blends is examined by Monte Carlo simulation and analytic (mean-field) modeling of the blend phase diagram.
- Lattice Boltzmann numerical computations are utilized to evaluate the appropriateness of this technique for modeling blend phase separation. Phase separation under steady shear flow is also investigated by this method in order to compare with ongoing measurements in the Polymers Division.
- Simulations are performed to test a proposed model of the heterogeneity occurring in supercooled liquids. Analytic modeling of diffusion in supercooled liquids was performed based on effective medium theory and a model of the structural heterogeneity in supercooled liquids based on simulation observations.
- Theories of film breakup by capillary wave instability are applied to spinodal dewetting measurements. Theoretical ramifications for polymer liquids were briefly investigated to guide future measurements.

External Collaborators

J. Bicerano, Dow Chemical Company, Midland Michigan - Collaborator on modeling the transport properties of filled polymers.

N. Martys, E. Garboczi, NIST, Building and Fire Research Laboratory - Collaborator in modeling fluid phase separation by lattice Boltzmann methods.

S. Kumar, Pennsylvania State University, State College, Pennsylvania. Collaborator in modeling finite-size effects on phase separation and the glass transition.

K. Freed, University of Chicago, Chicago, Illinois - Collaborator in modeling the effect of molecular structure on polymer mixture miscibility and molecular structure effects on the glass transition.

D. Leporini, University of Pisa, Italy - Collaborator in modeling the effect fluid heterogeneity on diffusion in supercooled liquids.

Accomplishments

- The simulation of phase separation on patterned substrates indicated that surface-directed waves should form transverse to the solid substrate and that modulation of the composition should also occur in the plane of the substrate, resulting in a checkerboard composition pattern. These predictions indicated that initial polymer blend separation studies should be restricted to "ultrathin" films where the surface-directed composition waves are suppressed. The verification of the checkerboard composition pattern remains a challenge for future measurements.
- Phase separation simulations with filler particle inclusions showed the development of spherical and cylindrical composition waves developing from the inclusion boundaries. Since many commercially encountered blends have filler additives and are thermodynamically unstable these novel predicted phase separation structures likely have an important influence on the properties of these materials. These simulations provided guidance in designing experiments that confirmed simulation predictions, and are a first step in understanding how blend microstructure is affected by the presence of fillers.
- The predicted form of the viscosity of particle dispersions based on percolation concepts was validated for data involving a wide range of particle shapes. A very good approximation was found between the percolation threshold of overlapping particles and the leading concentration virial coefficient for the suspension viscosity, the intrinsic viscosity. The hydrodynamic-electrostatic analogy further indicated that the percolation threshold for rigidity, where the suspension viscosity diverges, is inversely proportional to the intrinsic viscosity. These connections provide a basis for modeling aggregating suspensions and other complex rheological problems arising in processing filled polymers. The analytic dispersion viscosity model of filled polymers is currently being utilized by industry for process design of mica platelet filled polymers. The modeling can be extended to many other properties of commercial interest (electrical and thermal conductivity, dielectric constant, and gas permeability).
- The modeling of surface confinement on a polymer blend indicated that the phase boundary can be shifted either up or down in compressible blends, depending on the strength of the polymer-surface interaction. This finding seems in accord with existing measurements, but further experiments are planned to check the theoretical predictions. The simulation and analytical modeling also predict that finite size effects on the phase boundary of polymer blends arise sooner in much thicker films than in the case of small molecule fluid mixtures. These findings indicate that finite size effects can play a significant role in the miscibility of thin polymer films increasingly utilized in applications.

- The critical properties of Lattice Boltzmann fluids (coexistence curves, surface tension, interfacial tension, correlation length, and scattering intensity) were determined and the results expressed in a form comparable to measurements on polymer blends. The critical phenomena exhibited by these computational liquids could be described by mean-field theory making the Lattice Boltzman model best suited to the description of high molecular weight blends where mean-field theory is a good approximation.
- The calculated diffusion coefficient of a particle in an inhomogeneous environment of ideally fixed obstructions was found to deviate from the Stokes-Einstein relation. This deviation arises from the different effect of the heterogeneities on the mass and momentum diffusion coefficients (viscosity). An effective medium theory indicates a fractional power relation between the viscosity and diffusion coefficient in heterogeneous fluids. Fractional Stokes-Einstein relations of this kind are commonly observed in supercooled liquids with exponents close to that predicted by the obstruction model of fluid heterogeneity. This simple model provides significant insight into the origin and nature of the anomalously large rates of diffusion observed in supercooled liquids and other heterogeneous materials.
- Theoretical models of spinodal dewetting were generalized through the introduction of a conceptual model involving three film thickness regimes defined in terms of the amplitude of equilibrium capillary waves relative to the film thickness. The formation of holes at random positions in thicker films is interpreted as a nucleation process while the random height fluctuations occurring uniformly in the thinner films reflect random phase height fluctuations similar to spinodal decomposition in polymer blends. Height fluctuations of the dewetting film correspond to composition fluctuations in the phase separating blend. This theoretical modeling has many ramifications for the problem of creating dewetted film morphologies of controlled architecture, which are important for the modification of surface properties of polymers.
- Accurate measurements of the Soret coefficient as a function of concentration were made for the first time, and universal scaling functions deduced from renormalization group theory were introduced to describe these data. Polymer solutions are particularly sensitive to temperature gradients because of the large thermophoretic forces on large macromolecules. Thermally induced concentration gradients can cause large shifts in the apparent phase boundary of polymer solutions and can give rise to complex surface pattern formation in drying polymer films. An understanding of the factors influencing the formation of defect structures in drying polymer films has many applications to polymer coatings technology.
- A new and general theory of condensed matter relaxation was introduced based on fractional calculus methods and the fluctuation theory of recurrent events. This modeling shows that classical models of exponential relaxation become generalized to a two-parameter family of functions. The two parameters of this model characterize the degree of intermittency in the relaxation process in time and the geometrical form and distribution of the material heterogeneity. This model shows promise for understanding the occurrence and form of universality in relaxation processes in condensed materials, and experiments are planned to test the proposed relaxation functions on model polymeric materials.

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Publications
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B. D. Ermi, A. Karim, and J. F. Douglas, *Formation and Dissolution of Phase-Separated Structures in Ultrathin Blend Films*, Journal of Polymer Science, Polymer Physics Edition **36**, 191 (1998).

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C. Donati, **J. F. Douglas**, W. Kob, S. J. Plimpton, P. H. Poole, and S. C. Glotzer, *Observation of Polymer-like Structures in a Model Supercooled Liquid*, Poster at Polymer Physics Gordon Research Conference, Newport, RI, August, 1998.

Microstructure and Dynamics of Heterogeneous Materials

S. C. Glotzer, J. F. Douglas, C. Donati, A. Al-Sunaidi[1], B. P. Lee, P. Allegrini, T. Schroeder, and S. Sastry[2]
[1]University of Maryland, College Park
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Objectives
The objectives are to demonstrate the existence of microstructural and dynamical heterogeneity in frustrated materials and phase separated blends, and to develop theoretical and computational tools to characterize heterogeneity and establish a theoretical understanding of heterogeneity.

Technical Description

The relationship between microstructure, dynamics, and properties in the broad class of "frustrated" materials is poorly understood. Demonstration of heterogeneity provides a new paradigm to describe these materials, and will allow us to develop new theories and tools that industry needs to predict material behavior. For polymer blends, these tools must account for phase separation and processing conditions, especially conditions that may be perturbative to normal phase separation.

- Computer simulations will be developed to measure and characterize heterogeneity in materials approaching a glass transition, a spinodal, or a jamming transition.
- Molecular dynamics simulations of polymer melts and other liquids will provide details inaccessible to experiments on microstructure, dynamics, and cooperative molecular motion.
- Measurements will be designed, theories tested, and realistic models of frustrated materials developed.
- Computational tools will be developed to model heterogeneous, multiphase materials under various processing conditions, with an emphasis on filled polymer blends.
- Comparisons between new Lattice Boltzmann methods and traditional Cahn-Hilliard methods for phase-separating blends will be conducted to determine the future method of choice for blend modeling.
- Simulations will be designed and performed at the Center for Theoretical and Computational Materials Science (CTCMS) in conjunction with the filled polymers project.

External Collaborators

P. H. Poole, University of Western Ontario, Department of Applied Mathematics, London, Ontario, Canada - Performed computer simulations of a glass-forming paramagnet and participated in development of measurement quantities.

S. J. Plimpton, Sandia National Laboratories, Albuquerque, New Mexico - Provided computer code for performing massively parallel computer simulations of glassforming liquids.

A. J. Liu, A. Lapena and R. Nyquist, University of California, Los Angeles, Department of Chemistry and Biochemistry, Los Angeles, California - Participated in CTCMS Heterogeneous Structures project to investigate pattern formation in polymer-dispersed liquid crystals through simulation. Contributed to theory and performed simulations and analytical calculations.

W. Kob, Johannes-Gutenberg University, Mainz, Germany - Participated in CTCMS Glasses Working group.

J. Baschnagel, Johannes-Gutenberg University, Mainz, Germany - Participated in CTCMS Glasses Working group

C. Bennemann, Johannes-Gutenberg University, Mainz, Germany - Performed computer simulations of polymer melts

N. Martys, NIST, Building and Fire Research Laboratory - Co-organized CTCMS workshop on Computational Methods for Modeling Multiphase Polymers.

S. A. Langer, NIST, Information Technology Laboratory - Participated in CTCMS Heterogeneous Structures project to investigate pattern formation in polymer-dispersed liquid crystals through simulation. Developed computer code and performed simulations and analytical calculations.

Accomplishments

- New theoretical and simulation ideas were developed for glassforming polymers and simple liquids that allowed the description of growing dynamical correlations for the first time. This work will lead to a fundamental understanding of slow dynamics and related phenomena in glasses and glassforming materials.
- The extent of dynamical heterogeneity in a model glassforming paramagnet was defined and calculated for the first time. Work in this program on dynamical heterogeneity in liquids and polymers is built upon the key ideas developed here.
- Dynamical heterogeneity and cooperative molecular motion in molecular dynamics simulations of glass-forming simple liquids and polymers were identified and quantified. It was shown for the first time in both systems that particle motion involves larger and larger groups of particles as temperature decreases. While this concept is at the heart of many models of glass formation, it has not been previously demonstrated. Identified the mode-coupling temperature with a percolation transition. This work will provide further insight into the physical mechanism underlying the mode coupling theory.
- A new correlation function that measures the extent to which the local molecular motion of a liquid is spatially correlated was defined. This work will provide the underpinning for a comprehensive theoretical framework to describe any system in which the local particle motions are correlated on some time scale. The work is expected to have important implications for the interpretation of data in a variety of fields, including glasses, polymeric materials, foams, polyelectrolytes, colloids, granular materials, and dense liquids.
- Simulations have shown that exploration of the potential energy landscape by a model glassforming paramagnet exhibits the same behavior as recently reported in Nature for a glassforming liquid. This result is important because it shows that the origin of slow dynamics in all frustrated systems, including polymer melts, may have a similar origin.
- Simulations have shown that the structural relaxation of a binary mixture is governed by "basin hopping" of the system on its potential energy landscape, and that basin hopping is achieved through cooperative rearrangements of groups of particles. While this idea has been discussed prominently in the literature for years, this is the first clear demonstration.
- CTCMS Multiphase Polymers working group conducted large-scale simulations to study the interference between ordering and spinodal decomposition in polymer dispersed liquid crystal (PDLC) materials, and compared resulting morphologies with those found in experiments by ALCOM and industrial researchers. Both global anisotropy and local anisotropy of PDLC domain orientation that was observed experimentally were reproduced. The results guided experimentalists in designing new "standard" experimental measurements.
- CTCMS workshop on Computational Methods for Modeling Heterogeneous Polymer Materials: A Critical Comparison, was organized and held on May 1998.

Outputs

Publications

C. Donati, J. F. Douglas, W. Kob, S. J. Plimpton, P. H. Poole, and S. C. Glotzer, *Stringlike Cooperative Motion in a Glass-forming Liquid*, Physical Review Letters **80**, 2338 (1998).

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S. C. Glotzer, *Dynamically Heterogeneous Materials*, Catholic University, Johns Hopkins University, University of Maryland, University of Pennsylvania, and George Mason University.

Polymer-Filler Interactions

A. Karim, A. I. Nakatani, K. A. Barnes, E. K. Hobbie[1], R. Ivkov, D. Liu, B. J. Bauer, B. D. Ermi[1], J. F. Douglas, C. L. Jackson, and E. J. Amis
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Objectives

The objectives are to address critical issues hindering progress in filled polymer and nanocomposites technology by developing advanced measurement techniques suitable for quantifying filler/polymer interactions, both as to structure and dynamics, by utilizing expertise in scattering, rheology, and on-line microscopy. Concurrent modeling efforts will predict the viscosity of filled polymers as a function of filler dispersion and interactions.

Technical Description

Filled polymers and nanocomposites represent a significant share of the world plastics market. However a major limitation to further growth and development of this industry is the lack of understanding and measurements tools for interactions between the fillers and the polymer matrix. Industry is thus forced to adopt empirical approaches which usually lead to long product development cycles. Quantification of polymer-surface interactions will improve techniques for modifying polymer-surface interactions and validate models predicting material properties. Untested Monte Carlo simulations predict the radius of gyration in the presence and absence of filler particles of various sizes. Measurements of stress relaxation and local rheology of filled polymers are critical for improvements in mixing, stabilization, and performance of filled polymer materials. The most recent advance to filled polymers is the area of clay-nanocomposites where similar types of measurements are also needed for further developments in the field.

- The phase behavior of polymer blends (e.g. PS/PB) in the presence of fillers will be examined by light scattering, small angle neutron scattering (SANS), atomic force microscopy (AFM) and optical microscopy.
- SANS will be used to characterize polymer molecular dimensions, domain sizes and interaction parameters of poly(dimethyl siloxane) (PDMS) blended with treated silica fillers, and polybutadiene (PB) mixed with carbon black. Rheological tests on these systems will be used to relate scattering results and mechanical behavior.
- Model filler surfaces will be prepared on silicon wafers by depositing a carbon film, treating by plasma etching or chemical modification with coupling agents to mimic carbon black. Homopolymers and polymer blends will be coated on the treated surfaces and the polymer-surface interactions characterized by AFM and reflectivity. Neutron reflectivity of polymer blends with finely dispersed fillers and on model filler surfaces will be examined.
- Digital-video microscopy will be developed as a measurement technique to study kinetics, structure, collective dynamics, and viscoelastic relaxation in polymer-colloid complexes and dispersed filler particles in entangled polymers.

- The structure and dynamics (segmental and chain) of polymers such as polyethylene oxide (PEO) intercalated into clay-polymer nanocomposites will be characterized using inelastic neutron scattering techniques such as filter-analyzer spectroscopy, neutron time-of-flight and spin-echo spectroscopy.
- SANS will be utilized for investigating clay/polymer suspensions to characterize the nature of clay/polymer interactions.
- Methods will be developed to quantify and characterize the static and dynamic interactions of various polymers with the clays by x-ray and neutron reflectometry and atomic force microscopy (AFM).

External Collaborators

W. Chen, G. V. Gordon, R. G. Schmidt, Dow Corning Corporation, Midland, Michigan - Collaboration and supply of materials for experiments on chain dimensions of filled polymers and phase separation behavior of filled blends.

A. Halasa, Y. Feng, Goodyear Tire and Rubber Company, Akron, Ohio - Collaboration and supply of materials for SANS characterization of filled polymers.

B. Majumdar, GE Plastics, Schenectady, New York - Collaboration and supply of polymers for filled materials.

N. Moll, Dow Chemical Company, Midland, Michigan - Collaboration and supply of clay materials.

J. Gilman, T. Kashiwagi, NIST, Building and Fire Research Laboratory - Collaboration and supply of materials for SANS characterization of filled polypropylenes.

N. Malizsewskyi, P. Gehring, NIST Center for Neutron Research - Collaboration on inelastic neutron scattering from intercalated clays.

R. Krishnamoorti, University of Houston - Supply of clay nanocomposites for inelastic neutron scattering.

Accomplishments

- A workshop entitled “Interactions of Polymers with Fillers and Nanocomposites” was organized and held at NIST on June 18-19, 1998. Of the 75 non-NIST participants, 2/3 were industry experts in filled polymer technology. Control of molecular level interactions and measuring the dynamics of polymers at the filler interface were identified as the most critical issues in this field.
- Perturbations of polymer blend phase separation by fillers were shown to provide sensitive measures of preferential interfacial interactions. With this discovery, expertise in measurements of polymer blends can be applied to characterize polymer nanocomposites where production, as well as their high value properties, are dominated by polymer-filler interactions.
- Extensive cloudpoint measurements confirm filler induced shifts in phase boundary of polystyrene/polybutadiene (PS/PB) blends. Measurements were performed as a function of several different filler types and blend compositions. Filler types include three different fumed silicas with and without grafted polystyrene, and silica beads of 0.5 μm size, both without and with surface treatment by a silane coupling agent. Cloudpoints for the fumed silica filled sample were shifted to higher temperatures, and the extent of the shifts depended on the type of fumed silica used. The destabilization of the blend by filler is unexpected, and

suggests that the interactions between the filler and PB phase are strong. These measurements demonstrate that the phase separation behavior of polymer blends is sensitive to differences in fillers undetectable by conventional means such as TEM and N_2 adsorption methods currently used by industry.

- The amount of PS grafted to the fumed silica was characterized by TGA and the amount of grafted polymer was related to the cloudpoint shift in the model blend filled with fumed silica. This indicates that differences in the number of surface groups on the different fumed silicas may be responsible for the variations in the observed cloudpoint behavior.
- Characterization of the size and morphology of phase separating PS/PB and PS/PVME blends filled with fumed silica, PS latex, colloidal gold and tetrapropyl orthosilicate (TPOS) and tetraethyl orthosilicate (TEOS) based silica beads by AFM, OM, and SEM indicate different types of phase separation regimes. In the case of small particles, the blend phase separation predominates while large filler particles lead to a phase separation dominated by the wetting of these particles.
- Morphological regimes of phase separating PS/PB and PS/PVME blends were identified in thin films as a function of filler particle mobility. In order of increasing mobility, the particles included fumed silica, silica beads (commercial and synthesized), colloidal silicas, colloidal gold, and bucky balls.
- In the limit of low filler mobility, wetting of the filler by one component dominates and pins the blend morphology. At the other extreme of high filler mobility, blend phase separation dominates the process. In the cases of intermediate mobility, both interfacial segregation and temporal phase migration of filler are observed.
- A TEM staining technique was developed and it was found that the fumed silica surface is preferentially wetted by the PB phase (stained with OsO_4).
- Small angle neutron scattering measurements were performed on fumed silica filled polybutadienes with four different surface treatments at a fixed concentration of coupling agent as well as five different concentrations of the coupling agent with a fixed surface treatment. The filled samples with different coupling agent concentrations were mixed under two different mixing protocols. No differences in the scattering were observed for all conditions tested, suggesting that correlations in filled homopolymer systems are unaffected by filler surface treatment.
- Preliminary observations indicated suppression of dewetting by addition of trace amounts of bucky balls to thin PS and PB films. This phenomenon has important implications for thin film inhibiting defects in polymer coatings.
- SANS measurements were performed on three component mixtures of labeled PDMS, unlabeled PDMS, and filler. An analysis scheme was developed for extraction of the single chain structure factors of each polymer component by assuming the filler can be treated as a solvent molecule. From the analysis, the single chain dimensions of labeled and unlabeled polymers larger than the filler particle size increase at low filler concentrations (mass fractions <0.10) then decrease to values slightly larger than the unfilled dimensions at higher filler concentrations. For polymers approximately the same size as the filler particles, the chain dimensions are slightly smaller than the unfilled chain dimensions.
- Neutron measurements have shown that confinement of polymer chains to spaces (~1.4 nm) that accompany intercalation in nanocomposites significantly restricts the mobility of the

chains. An increase of only 0.4 nm in the spacing can produce a noticeable change in the polymer chain mobility, so that some bulk polymer features are recovered.

- Methods were established to prepare clay (laponite)/polymer films on silicon with varied and controlled thickness and to characterize them by x-ray reflectivity and atomic force microscopy. Potential applications for creating ordered nanostructure coatings and for opportunities for investigating structure and interactions between clay and polymer under more ideal conditions are evident through these studies.
- SANS observation on PAA-clay in solutions where the long range ordering is suppressed under the influence of shear, provided important structural information on clay-polymer suspensions. This demonstrates the potential utility of SANS for measuring clay-polymer interactions.

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Phase Separated Polymer Blend Coatings and Thin Films

A. Karim, B. D. Ermi[1], J. F. Douglas, D. Liu, G. Nisato[1], B. P. Lee, and S. C. Glotzer
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Objectives

The objectives are to develop techniques and methodologies for controlling surface adhesion and wetting in thin films by characterizing pattern formation in polymer blend films through phase separation, substrate patterning and surface reaction. Utilize surface probe microscopy (SPM) techniques such as atomic force microscopy (AFM) and near surface optical microscopy (NSOM) as measurement tools for characterization of nanoscale pattern formation.

Technical Description

A quantitative technique for measuring kinetics and morphology development through phase separation in thin polymer blend films is vital for validating any predictive model or theory on wetting and adhesion of blends on surfaces. Scanning probe microscopy (SPM) provides unique opportunities for characterizing phase separation phenomena in real space. Identifying the important controlling factors affecting localized blend phase separation in the vicinity of heterogeneous surfaces is important since most real surfaces tend to be heterogeneous.

- The kinetics and morphology of phase separation of PS/PB and PS/PVME blend films on homogeneous and patterned self-assembled monolayer (SAM) surfaces will be characterized using a combination of AFM, optical microscopy (OM), and neutron reflection (NR).
- Regimes of blend film thickness defining transitions in the nature and alignment of induced patterns through pattern-directed phase separation will be identified. The possibility of creating patterned spinodally-dewet films will be investigated.
- 2-D FFT analysis methods already developed for optical image studies will be extended to analysis of AFM topographical data from blends on patterned surfaces. The kinetics of isotropic phase separation will be discriminated from the anisotropic morphology evolution by selective averaging of the 2-D FFT data.
- Equilibrium analytical theory will be used to predict aspect ratio of steady state laterally phase-separated structures. Modified Cahn-Hilliard-Cook (CHC) based computer simulations will be used for predicting the morphology of phase separating mixture films on periodically modulated surfaces. Experimental results from model blend films of varying composition and thickness will be used to validate the analytical model and simulations of ultrathin film phase separation on patterned surfaces.
- Nucleation and growth versus spinodal decomposition regimes in blend films will be distinguished by varying blend composition and studying changes in film morphology. Two-

phase to single phase temperature jump measurements will be performed to test reversibility of surface topology for the different blend compositions.

- NSOM will be used to investigate sub-surface morphology development in phase separated conducting/non-conducting (thiophene/PS) polymer blend films prepared by spin coating.

External Collaborators

G. M. Whitesides, R. J. Jackman, Department of Chemistry, Harvard University, Cambridge, Massachusetts - Supply of SAM patterned substrates.

J. A. Rogers, Lucent Technologies, Murray Hill, New Jersey - Collaboration and supply of SAM patterned substrates.

M. Walker, NIST, Surface and Microanalysis Division - Phase-mode AFM characterization of coating films.

L. Goldner, NIST, Physics Division - Near surface optical microscopy (NSOM) measurements of phase separated blend films

Accomplishments

- A coupling was discovered between phase separation and surface deformation modes of phase separating blends on chemically patterned self assembled monolayer (SAM) substrates. The surface deformation modes induced by phase separation contain excited transient harmonics, which are close to the harmonics of the SAM pattern. Recognition of the SAM pattern by the phase separating blend thus occurs at early times when the phase separation length scale is only a fraction of the SAM pattern scale (few µm).
- The perfection of steady state alignment of the morphology of a phase separated blend to an underlying SAM pattern was demonstrated as a function of decreasing film thickness. Furthermore, the reduction in film thickness below a critical value was shown to cause a break-up of the aligned strips into uniform droplets via spinodal dewetting. This phenomenon produces aligned nano-droplet arrays, a process that may be technologically significant for applications requiring control of surface wetting properties at the nanometer level.
- A theoretical perspective for coupling between phase separation and surface deformation modes in terms of theory of shallow fluid channels was developed. An analytical model for predicting steady state topography of blend films of PS/PB, PS/PVME and poly(ethylene propylene (PEP)/dPEP in terms of surface and interfacial tension ratios was verified. Computer simulations of phase separation with periodic surface modulations using modified CHC equations were used to generate novel transverse checkerboard blend composition profiles in 2-D.
- Thermodynamic reversibility of phase separated structures in thin films for all compositions was demonstrated. The kinetics of the dissolution process was different from the phase separation process for the same quench depth conditions. These measurements confirm the phase separation origin of surface modulated structures in thin blend films.
- Preliminary success was achieved in the characterization of sub-surface phase distribution of polythiophene in PS matrix (chemical sensitivity) using NSOM with sub-micron resolution. Such non-destructive determination of polymer phase distribution in thin films is not possible by conventional microscopy techniques.

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Characterization of Dendrimers with Polymers, Metals, and Small Molecules

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[1]Max Planck Institute of Colloids and Interfaces, Teltow, Germany,
[2]DSM Corporation, The Netherlands
[3]University of Köln, Germany
[4]University of Pennsylvania, Philadelphia, Pennsylvania
[5]Chinese University of Hong Kong

Objectives

The objectives are to characterized materials containing dendrimers with other polymers, small molecules, and metals, with regard to their assembly in bulk, in solution, and on surfaces. Dendrimer size and shape will be characterized in order to calibrate analytical methods and equipment and to explore applications of dendrimers as unique and precise macromolecules.

Technical Description

Dendrimers studied in solution have demonstrated the ability to solubilize, encapsulate, and present functional groups but little is known about immobilizing them in a polymeric matrix. Such incorporation would lead to stable nanoscopic structures. Incorporation of metals into the dendrimers would lead to materials with unique electronic and magnetic properties. Dendrimers modified with molecules such as fatty acids can emphasize their micellar character and further promote dispersion of materials. Characterization of dendrimers shows that their uniformity in size and shape makes them excellent candidates for standards in the critical 1 to 15 nm size range.

- Produce and characterize molecularly dispersed dendrimers in polymeric matrices by blending and interpenetrating polymer network (IPN) techniques.
- Characterize fatty acid modified dendrimers in bulk and in solution and in blends for both single chain structure and multi-chain morphology.
- Produce and characterize metal containing dendrimers

- Measure the dendrimers size variation in solvents of different quality and in aqueous solutions of different pH and ionic strengths.

External Collaborators

Dendritech and Michigan Molecular Institute, Midland, Michigan - CRADA developed for supply of materials, custom synthesis and joint research.

DSM - Collaboration has been established for supply of materials and a guest researcher spent 7 months at NIST on joint research.

Army Research Office - Grant (35109-CH) for work on dendrimer blends; Collaboration with Army scientists.

M. Gauthier, University of Waterloo - Collaboration has been established for supply of materials for joint research.

N. Mishenko, Catholic University of Leuven - Collaboration has been established to spend part of a year at NIST doing SANS of supplied materials.

I. Gitsov, Cornell University, Ithaca, New York - Collaboration has been established to time at NIST doing SANS of supplied materials.

M. Diallo, California Institute of Technology/Howard University - Collaboration has been established to spend part of a year at NIST doing SANS of supplied materials.

C. Gorman, North Carolina State University - Collaboration has been established for supply of materials for joint research.

H. D. Chanzy, CERMAV and CNRS, Grenoble, France - TEM of dendrimers

F. P. Booy, Laboratory of Structural Biology, NIAMS, NIH, Bethesda, Maryland - Cryo-TEM of dendrimers

Accomplishments

- A workshop was organized and held on July 9-10 on the properties and applications of dendritic polymers. All of the dendrimer producers and many of the dendrimer users and resellers were represented. Lack of knowledge about the properties of dendritic polymers at interfaces was identified as a critical barrier to full exploitation of these unique polymers. Other needs identified by the attendees included direct comparisons of structures of dendritic polymers and characterization of interactions with other polymers.
- PAMAM dendrimers were uniformly dispersed in IPN's of hydroxyethylmethacrylate up to 25% by mass. TEM of thin sections show the dendrimers were well dispersed and visible as individual molecules, in good agreement with SAXS results. This is the first confirmation of large PAMAM dendrimers molecularly dispersed in a polymeric matrix.
- The characterization of PAMAM dendrimer molecules was achieved for generation ten (G10) to generation five (G5), ranging in size from 14.7 nm to 4.5 nm, respectively. SANS, SAX and TEM characterizations were combined for complete analysis of size, shape, and molecular conformation. These measurements establish PAMAM dendrimers as the most thoroughly characterized dendritic molecules to date.
- Methods have been developed to characterize the nanoscale phase structure of fatty acid modified dendrimers. Contrast matching methods with SANS were successful in measuring the size of different parts of these dendrimers in solution and bulk.

- Fatty acid modified dendrimers have been shown by SANS to be immiscible with polyolefins on a molecular scale, even though they can disperse pigments on a much larger size scale. This proves that miscibility is not the primary criterion in dispersion techniques.
- The structure of dendrimers with Fe covalently bound to the core was determined by SAXS. Dendrimers with attached Au were prepared and characterization of bulk and surface structures has begun.
- The size of dendrimers of a variety of generations has been measured in a complete range of solvents and varies by 10% or less over the whole series. Dendrimer size response to variations of ionic strength, pH, and presence of polymer was measured using SANS. The radius of gyration of G8 PAMAM dendrimers is rather insensitive to the solution environment, making them suitable for characterization and use as size standards.
- Small quantities of dendritic materials have a large impact on the rheological properties of PS/PVME blends. Continuing work is aimed at showing that the rheological changes are beyond the demonstrated enhancement shown with industrial fillers in blends and that these additions effect the morphology of phase separation in the blend.
- SANS on branched PS was used to determine effect of branching on miscibility with linear polymers and on size in blends and different in solvents. The fact that the highly branched PS has a smaller size in blends than it does in solution suggests that small molecules penetrate dendrimers more easily than linear polymers.
- Polyelectrolyte behavior of charged PAMAM (G5) dendrimer solutions was investigated using SANS. Repulsive interactions between dendrimers were always present even at very high (monovalent) salt concentration, in contrast to latex particles and surfactant micelles.

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A. Ramzi, *SANS Study of Fatty Acid Modified Dendrimers*, American Chemical Society Meeting, Boston, MA, August, 1998.

B. J. Bauer, *Size Changes and Interpenetration within Concentrated Dendrimer Solutions*, American Chemical Society Meeting, Boston, MA, August, 1998.

E. J. Amis, *Dendrimers: Polymers of Unique Dimension*, Kyushu University, Department of Polymer Science, Fukuoka, Japan, August, 1998.

E. J. Amis, *Dendrimers: Polymers of Unique Dimension*, Osaka University, Department of Macromolecular Science, Osaka, Japan, September, 1998.

Polymer Solutions

E. J. Amis, G. Nisato[1], Y. Zhang[2], R. Ivkov, B. J. Bauer, D. Liu, and B. D. Ermi[1]
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Objectives

The objectives are to develop measurement methods to characterize the interactions of polymers in solution and their properties as stabilizers, flocculants, rheology modifiers, and gels. New experimental methodology recently developed at NIST will be applied to characterize the mechanisms of polyelectrolyte interactions with simple ions, macroions, neutrals, and surfaces.

Technical Description

Aqueous solutions and gels represent a growing polymer market and polyelectrolytes comprise the major class of water compatible polymers. Although polyelectrolytes are notoriously difficult to characterize, their most dramatic properties are nearly universal and therefore new measurement methods and descriptions of properties will have a broad impact. Recent experimental and theoretical advances offer this promise. Associative polymers are widely used by industry as viscosity modifiers in food, consumer products, and industrial fluids. Improved characterization and methods of characterization will enhance both quality control and ability to predict behavior of new formulations.

- The critical issue of competitive long and short range interactions in polyelectrolyte solutions will be characterized by SANS, SAXS, and LS.
- Contrast labeling methods will be developed to measure systems that model classes of behavior representative of commercially important polyelectrolyte solutions.
- The effects of counterion charge, polyion molar mass, and variations with charge density will be characterized.
- Associative polymers and their transient gels will be measured by the combination of scattering and rheology to characterize mechanisms of shear thickening, thinning, and gelation.
- Thermoreversible polyolefin physical gels of ethylene/propylene copolymers will be characterized in organic solvents and in simulated motor oil.

External Collaborators

A. Gast, J. Hur, J. Pople, R. Waymouth, Department of Chemical Engineering, Stanford University, Center for Polymer Interfaces and Macromolecular Assemblies, Stanford, California - Collaboration on structure, rheology and mixing in polymer/colloid suspensions; Collaboration on network structure in metallocene polymerized thermoplastic polyolefins.

T. Jao, C. Daniel, Ethyl Corporation, Richmond, Virginia - Collaboration on mechanism of oil additive gelation; Synthesis of deuterated copolymers; Joint measurements at NIST

Accomplishments

- Large differences were shown for the types of gels formed from ethylene/propylene copolymers with small variations of ethylene content in toluene and methyl cyclohexane. Such differences are reflected in significant rheological changes which are important for applications as motor oil additives. The understanding gained from these studies is being used by industry to develop new products that prevent low temperature oil gelation.
- Single chain dimensions of polyelectrolytes without added salt were measured as a function of concentration, polymer molar mass, and valency of the counterion in dilute, semidilute and concentrated solutions by the neutron zero-average-contrast method. The chain dimensions and scaling with molar mass show features of semiflexible rods in the presence of monovalent counterions and random coils in the presence of divalent counterions. Neither extreme of rod-like expansion or coil collapse is observed at finite concentration.
- The microstructure of salt free polyelectrolyte solutions throughout the semidilute regime was shown to be determined by the valency, rather than the size or the chemical identity of the counterions. This observation is linked directly to previous work at NIST showing that long range and short range electrostatic interactions, as opposed to hydrophobic interactions, dominate the structure and dynamics of these solutions.
- The polyelectrolyte behavior characterized by the correlation peak in the SANS profile, was found to show a continuous growth and transition with increasing charge density from neutral poly(2-vinylpyridine) to charged poly(N-methyl-2-vinylpyridinium chloride). The peak position was found to vary as C_p^{α} with α increasing with the charge density.

Outputs

Publications

B. D. Ermi and E. J. Amis, *Influence of Backbone Solvation on Small Angle Neutron Scattering from Polyelectrolyte Solutions,* Macromolecules **30,** 6937 (1997).

B. D. Ermi, Y. Zhang, and E. J. Amis, *Counterion Valence Effects on Inter- and Intramolecular Interactions in Polyelectrolyte Solutions,* American Chemical Society PMSE Proceedings **77,** 304 (1998).

B. D. Ermi and E. J. Amis, *Domain Structures in Low Ionic Strength Polyelectrolyte Solutions,* Macromolecules, **31,** 7378 (1998).

Presentations

E. J. Amis, *Structure and Dynamics in Polyelectrolyte Solutions*, University of Maine, Department of Chemical Engineering, Orono, ME, November, 1997.

E. J. Amis, *Shining New Light (and Neutrons) on the Puzzles of Polyelectrolytes*, North Carolina State University, Materials Science and Engineering, Raleigh, NC, November, 1997

E. J. Amis, *Shining Light (Neutrons and X-Rays) on the Puzzles of Polyelectrolytes*, Gordon Research Conference, Colloidal, Macromolecular and Polyelectrolyte Solutions, Ventura, CA, February, 1998.

Y. Zhang, *Small Angle Neutron Scattering Studies of Polystyrene Sulfonate Solutions with Mono- and Divalent Counterions,* Poster at Gordon Research Conference, Colloidal, Macromolecular and Polyelectrolyte Solutions, Ventura, CA, February, 1998.

R. Ivkov, *SANS Investigation of the Structure and Equilibrium Polymerization of Muscle Actin,* Poster at Gordon Research Conference, Colloidal, Macromolecular and Polyelectrolyte Solutions, Ventura, CA, February, 1998.

G. Nisato, *Structure of Charged Dendrimer Solutions as Studied by SANS,* Poster at Gordon Research Conference, Colloidal, Macromolecular and Polyelectrolyte Solutions, Ventura, CA, February, 1998.

E. J. Amis, B. D. Ermi, and Y. Zhang, *Low-Charge Density Polyelectrolytes in Good Solvent,* American Physical Society National Meeting, Los Angeles, CA, March, 1998.

B. D. Ermi, *Development of Measurement Tools to Characterize Polyelectrolyte Solutions and Polymer Films,* National Starch and Chemical Company, Bridgewater, NJ, August, 1998.

E. J. Amis, B. D. Ermi, and Y. Zhang, *Unveiling the Puzzles of Polyelectrolytes with Small Angle Neutron Scattering*, Multicomponent Polymers and Polyelectrolytes, Closing Symposium of ERATO Hashimoto Phasing Project, Kyoto, Japan, September, 1998.

B. D. Ermi, *Development of Measurement Tools to Characterize Polyelectrolyte Solutions and Polymer Films,* Kodak, Rochester, NY, September, 1998.

E. J. Amis, *Unveiling Polyelectrolytes with Small Angle Neutron Scattering*, Center for Interfacial Engineering Industrial Workshop, University of Minnesota, Minneapolis, MN, September, 1998.

Polymer Blends and Processing Program Outreach

E. J. Amis, C. C. Han, S. C. Glotzer, B. J. Bauer, A. I. Nakatani, A. Karim, and J. F. Douglas

Objectives

The objectives of the outreach activities of the Polymer Blends and Processing Group are to expand the opportunities to communicate NIST work, to obtain feedback from the external technical community, and to facilitate more efficient adoption of NIST measurement methods.

Technical Description

Several activities serve to facilitate planning and maximize the impact of the Polymer Blends and Processing Program. Work in this area also focuses on reducing the learning curve for internal and external collaborators, and assuring reliability of reported results.

- Provide NIST sponsored workshops or NIST organized meeting sessions in support of program objectives.
- Develop facilities in support of collaborations for light, neutron, and x-ray scattering.
- Develop user protocol for standard methods of analysis of scattering data including documentation, instructions, and validated examples.

External Collaborators

C. Glinka, S. Kline, P. Butler, NIST Center for Neutron Research - Joint project on analysis protocol for small angle neutron scattering.

M. Vangel, NIST Information Technologies Laboratory - Statistical analysis and advice on implementation of scattering analysis methods.

Accomplishments

- Several model data sets were used to evaluate data analysis software packages. Validated nonlinear regression results were reproduced with DATAPLOT (NIST), S-Plus (MathSoft, Inc.), and Igor (WaveMetrics, Inc.). A systematic protocol has been designed to provide validated scattering data analysis models for users.

Workshops, Symposia, Outreach

A. Karim, Symposium Organizer for "*Synthetic Design and Characterization of Surfaces and Interfaces*," American Chemical Society Meeting, Las Vegas, NV, September 1997.

S. C. Glotzer, Organized symposium on "Phase Transitions in Polymers," NIST, Gaithersburg, November 1997, in honor of the work of E. A. DiMarzio.

A. Karim, Chaired session, "Surfaces and Interfaces," Materials Research Society Meeting, Boston, MA, December 1997.

E. J. Amis, Vice Chair of Colloidal, Macromolecular and Polyelectrolyte Solutions Gordon Conference, February 1998; Organizing conference in 2000.

S. C. Glotzer, Organized session on "Mesoscale Modeling of Materials," Conference on Complex Phenomena in Physics, Barbados, West Indies, January 1998, to highlight important new developments in materials modeling at the mesoscale.

E. J. Amis, Serves as Chair of the Division of High Polymer Physics of the American Physical Society, 1998-99.

S. C. Glotzer, Organized and chaired CTCMS workshop on "Computational Methods for Modeling Heterogeneous Polymer Materials: A Critical Comparison," May 1998, to discuss polymer modeling methods and identify future methods.

E. J. Amis, Served on workshop panel for Vision 2020 Chemistry Roadmap on "Polymer Research in Green Chemistry and Engineering," Amherst, MA, July 1998.

A. Karim, Organized industrial workshop on "Interactions of Polymers with Fillers and Nanocomposites," at NIST held June 18-19, 1998 leading to prioritizing tasks on characterizing dynamics at filler-polymer interface and polymer-filler interactions.

B. J. Bauer, Organized a workshop held July 9-10, 1998 on "Properties and Applications of Dendritic Polymers." All of the dendrimer producers and many of the dendrimer users and resellers were represented. Feedback was obtained on the important measurement needs to facilitate applications of dendritic polymers.

E. J. Amis, Serves on Technical Advisory Panel for Multiuniversity Research Initiative on Dendritic Polymers (Illinois, lead institution) sponsored by the Army Research Office

S. C. Glotzer, Organized discussion panel session on "Theory and Simulation of Glasses and Glass-forming Liquids, Pisa, Italy, September 1998, to discuss recent developments in the field, and identify new modeling opportunities.

J. F. Douglas, Organized Informal Meeting on Cold Liquids at the NIST Center for Theoretical and Computational Materials Science, 1998.

E. J. Amis, Organizing workshop on "Materials Measurements and Characterization" for the Vision 2020 Materials Technology Roadmap, November 1998.

Outputs

Publications
J. F. Douglas, *NIST Meeting on Multicomponent Polymers and Polyelectrolytes*, J. Res. NIST **103**, 225 (1998).

J. F. Douglas, *Annual Compilations of Publications by the NIST Polymer Blends and Processing Group* covering the years: 1995, 1996, and 1997.

F. Gröhn, B. J. Bauer, E. J. Amis, *Characterization, Modeling, and Applications of Dendritic Polymers,* Literature review compiled for Dendrimer Workshop, 1998

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 beginning to make significant use of these materials. For this to continue, however, two significant barriers must be addressed: the lack of rapid, reliable, cost-effective fabrication methods; and the poor understanding of and predictive capability for long term performance. These barriers were identified in a series of industry workshops, exchange visits, and consultations. In response to these challenges, two tasks were initiated, one on processing science and the other on microstructure, which constitute the composites program. A knowledge of microstructure and how it changes with time is a key factor for understanding long term performance. The automotive industry strongly influenced the composites program initially since the processing and durability issues span many automotive applications. Currently, the group interacts with the automotive, offshore oil, infrastructure, and aerospace industries.

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. Liquid composite molding (LCM) simulations were developed since this fabrication method is of 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 work has since broadened to involve the development of generic measurement tools to characterize material properties that control processing, for example, permeability and fiber architecture. General multiphase flow models are being formulated that can be applied to a variety of composites processes including those involving viscoelastic flow of thermoplastics. 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 six projects, including the support of a database and a SBIR collaboration to develop a commercial sensor system.

The work in the Microstructure Task is currently developing methods for characterizing and interpreting test data on hybrid reinforced composites. Hybrid reinforcements consisting of glass/carbon mixtures are currently of intense interest in the off-shore oil, infrastructure, and automotive industries due to the desirable mix of properties and economics that are obtainable. The particular microstructural features of interest include resin/fiber interfacial adhesion, especially under moisture attack, fiber architecture, and imperfections in composites such as voids, cracks and delaminations. The long term plan is to first develop effective test methods, and then to use the tests to identify the failure mechanisms in hybrids, particularly when synergistic reinforcement effects are present, and finally to formulate reliable predictive models useful for design. Microscale tests such as the single fiber fragmentation test have been put on a firm theoretical foundation, and are now being modified for multiple fiber tests designed to provide realistic estimates of the interface performance in hybrid composite systems. Imaging technology based on both classical optical and SEM, as well as nondestructive tomographic techniques are being applied to measure the fiber architecture and the imperfections in hybrids. Such microstructural data obtained before, during and after testing carefully produced specimens is expected to provide the information necessary to develop the structure-property relationships necessary for model generation. There are currently six specific projects in this Task, including an international round-robin on interface testing and a collaboration with the Automotive Composites Consortium to determine the effects of processing conditions on the interface of polymer composites.

The Composites Program promotes knowledge dissemination by actively organizing and participating in meetings worldwide. For example, the 1999 Gordon Research Conference on Composites, scheduled for January 10-15, 1999, was organized by Richard Parnas, and includes the world's leading authorities on a number of topics including processing, interfaces, compression, nanocomposites, and ceramic composites. In addition, Composites Program staff helped the National Academy of Engineering organize materials oriented sessions at its Frontiers of Engineering meetings for the past three years, organized all the processing sessions at the 1998 American Society of Composites meeting, and serve as international advisory members for several European meetings.

Significant Accomplishments

- Successfully used optical coherence tomography to rapidly measure the porous structure of a high fiber volume fraction glass fiber reinforcement in sufficient detail to predict the permeability using a 3-D fluid flow simulation based on the lattice-Boltzmann method.

- Developed mathematical theory for lattice-Boltzmann formulation of viscoelastic flows in porous media and constructed a 2-D simulation to test the theoretical formulation.

- Released a database of permeability and other reinforcement properties in collaboration with the NIST Standard Reference Data Program.

- Developed a viscoelastic micromechanics model describing the single fiber fragmentation test for assessing the quality of interfaces in composites.

Developed facility and test procedures for assessing the effects of processing on interface performance, and demonstrated its use by showing a large reduction of interface quality in a rapidly cured e-glass / vinyl ester system, relative to the slowly cured material.

Co-sponsored a workshop with the Department of Energy, Advanced Light Source (UC Berkeley), North Carolina State University, Carnegie Institution of Washington, Dow Chemical, and General Electric, entitled *X-ray Microscopy of Synthetic and Natural Polymers: Towards Chemical Speciation at 10 nm Spatial Resolution. Assessment of Research Opportunities and the Need for X-ray Microscopy Facilities*, which was held at NIST on May 11-12, 1998. The workshop resulted in a successful DOE proposal for $500,000 to develop an X-ray imaging facility at the the Advanced Light Source devoted to the study of polymers.

Demonstrated the potential of the sandwich beam specimen for characterizing the mechanical properties of adhesives. The data highlighted the shortcomings of currently available analyses, but the simple testing geometry provides incentive for improving the analysis.

- Organized the Gordon Conference on Composites for January 10-15, 1999, in Ventura, CA. The conference includes sessions on the role of viscoelasticity, damage tolerance in ceramic matrix composites, ceramic matrix and carbon/carbon composite microstructure, fiber architecture effects, compressive failure, nanocompsites, processing and microstructure, new applications, and critical issues. The speakers were invited from Israel, England, Germany, and Belgium in addition to the United States.

Liquid Composite Molding: Development of Permeability Database

R. Parnas, K. Flynn, M. DalFavero[1], and H. Friedman[2]
[1]NIST, Standard Reference Data Program
[2]Textile Research Institute, Princeton, NJ

Objective

The objective is to establish a data base of permeability values for use as a design tool by the composites industry.

Technical Description

Permeability measurements conducted over several years at NIST are documented, collected, and placed into a Clipper based database. External sources of reliable data are identified and their measurements are being documented for inclusion in the database.

External Collaborations

Henry Friedman, Textile Research Institute - perform comparative measurements.
Raymond Gauvin, University of Montreal - provide data.
Christopher Rudd, University of Nottingham - provide data.
Staffan Lundström, Chalmers University, Sweden - perform comparative measurements.

Planned Outcomes

The database released in 1998 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

Version 1.0 of the Permeability Database, consisting of work done at NIST by NIST personnel, was released in collaboration with the NIST Standard Reference Data Division, and has resulted in the sale of 11 copies to date. Version 2.0 of the database is being developed by documenting data submitted by external collaborators, and the size of the database has been doubled.

Impacts

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, *Preform Permeability*, in RTM for Aerospace Applications, Chapman & Hall, NY, 1998, Ch. 8.

R. S. Parnas, K. M. Flynn and M. DalFavero, *A Permeability Database for Composites Manufacturing by Liquid Molding*, Polymer Composites **18(5)**, 623-33, 1997.

Liquid Composite Molding: Development of Permeability Measurement Techniques

R. S. Parnas, F. R. Phelan, R. C. Peterson, and H. Friedman[1]
[1]Textile Research Institute, Princeton, NJ

Objective

To develop new permeability measurement techniques for assessing flow behavior in deformed and model materials.

Technical Description

Permeability measurements are continuing at the Textile Research Institute with an emphasis on the permeability of fabrics deformed around curves, as would be found in molds of complex shape. Measurements conducted on a 3-D woven fabric were completed, and in the flat sections of the material the measurements agreed well with previous measurements conducted at NIST on the same material. Although difficult to quantitate precisely, the measurements in the curved regions of the 3-D fabric clearly indicated a substantial increase in flow resistance. Quantitation of the permeability measurements in the curved regions of the fabric was difficult due to nonuniform flows and an entrance effect. Partly to overcome these difficulties and partly to contrast the behavior with another material, experiments were conducted more recently with a continuous strand random mat (CSRM). The entrance effect is not present in the CSRM, as indicated by previous work at NIST, and the flow moves through the fabric more uniformly. We therefore expect the data analysis of the CSRM to be more straightforward than with the 3-D woven fabric, allowing quantitation of the permeability reduction in the curved region of the material.

Measurements are conducted with the 3-D woven fabric and with the CSRM at 3 different radii of curvature. A measurement system has been built to provide constant flows to L-shaped molds. The molds are designed to maintain constant channel thickness around the curves, and use 5.08 cm (2") thick plexiglas external sections to provide for flow visualization. A video capture system, controlled by a LabView software application, works in conjunction with the flow apparatus to permit detailed analysis of the progression of the flow front throughout the experiment.

A model porous medium measurement system was constructed at NIST to verify the microflow predictions of the Lattice-Boltzmann flow model. A specialized mold was designed and built to permit the anchoring of model media components in a variety of arrangements within the mold. Model media are then constructed by press-forming CSRM to desired fiber volume fractions, and stamping out circular or elliptical shapes of the pressformed material. These shapes are arranged and anchored in the mold in square or hexagonal arrays to model the arrangement of tows in a preform. Experiments are conducted by flowing aqueous corn syrup solutions through the array under constant injection pressures, recording the filling behavior on video tape and measuring steady state flows and pressures after the mold filled.

External Collaboration
Henry Friedman, Textile Research Institute - performing flow studies in deformed fabrics.

Planned Outcomes
Develop knowledge-based rules to guide process designers in controlling resin flows in complex molds. Verify a microflow simulation tool for predicting permeability and unsaturated flow behavior in porous media.

Accomplishments
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.

Void formation and depletion dynamics were successfully imaged in model porous media with enough resolution to permit direct comparison with model calculations.

Outputs

Publications
Henry L. Friedman, Alexander V. Neimark, David R. Salem, and Richard S. Parnas, *Visualization and Quantification of Forced In-Plane Flow Through Deformable Porous Media,* Proc. American Society of Composites Conference, Baltimore, MD, Sept. 21, 1998, in press.

R. C. Peterson, and F. R. Phelan Jr., *An Investigation of Void Formation Dynamics in Fiber Preform Materials*, Proc. American Society of Composites Conference, Baltimore, MD, Sept. 21, 1998, in press.

H. L. Friedman, R. A. Johnson, B. Miller, D. R. Salem, and R. S. Parnas, *Forced In-Plane Flow Through Complex Deformable Structures: Influence of an Imposed Curve*, Polymer Composites **18(5)**, 663-71, 1997.

H. L. Friedman, R. A. Johnson, V. Gusev, A. V. Neimark, D. Buvel, D. R. Salem, and R. S. Parnas, *Visualization and Quantification of Forced In-Plane Flow through Deformable Porous Media*, Polymer Composites, in press.

Presentations

Henry L. Friedman, Alexander V. Neimark, David R. Salem, and Richard S. Parnas, *Visualization and Quantification of Forced In-Plane Flow Through Deformable Porous Media,* American Society of Composites Conference, Baltimore, MD, Sept. 21, 1998.

R. C. Peterson, and F. R. Phelan Jr., *An Investigation of Void Formation Dynamics in Fiber Preform Materials,* " American Society of Composites Conference, Baltimore, MD, Sept. 21, 1998.

Liquid Composite Molding: Development and Verification of Process Simulation Models

F. R. Phelan Jr., K.M. Pillai[1], and C. L. Tucker III[1]
[1]University of Illinois, Urbana, IL

Objectives

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

Technical Description

LCM process optimization has typically been done with time-consuming and expensive trial and error methods on full scale equipment. Simulation models have the potential for greatly reducing the cost and increasing the speed of this task. In previous work, a simulation called CRIMSON which models the mold filling phase of LCM was developed. CRIMSON is based on a finite element/control volume numerical solution to the governing transport equations in which the momentum equation is expressed by Darcy's law. 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 current phase of this project, CRIMSON has been 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 satisfying their need to fabricate large structural parts in fast cycle times. Research has revealed that meeting the required process constraints with pure-injection LCM, results in excessively high injection pressures that induce undesirable fluid-structure interactions involving preform, foam core, or tool deformation. 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. During the initial injection stage of "open mold" I/CLCM there is a gap between the preform and the upper tool surface. The strategy 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. However, because there is some penetration of resin into the preform during the injection phase, during the compression step there is a combination of in-plane and through-thickness flow. Thus, a fully 3-D flow model is needed.

External Collaborations

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.
Kurt Schultz, Louisiana State University - RTM flow simulation.
Chuck Tucker and Krishna Pillai, University of Illinois - preform deformation modeling.

Planned Outcome

Provide the automotive industry and other interested organizations with simulation tools for design and optimization of the liquid molding process.

Accomplishments

This year, work was completed in cooperation with the University of Illinois at Urbana-Champaign (UIUC) to develop a numerical simulation of the open mold I/CLCM process. There are three main elements to the flow modeling algorithm, the preprocessor module, the preform compression module, and the flow module. The preprocessor and compression modules were developed in collaboration with UIUC. In the pre-processor, a 3-D flow mesh is constructed as input for the CRIMSON program. 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. From this information, a 3-D mesh of the final preform geometry and "spines" are constructed. "Spines" are vectors that run through groups of co-linear nodes from the lower surface to the upper surface of the FE mesh. The mechanical deformation module models the non-linear deformation of the fibrous preform during compression in three-dimensional geometries. Local 1-D mechanics with no shear deformation are assumed in the model for the sake of robustness. In response to compression, the preform deforms along the "spines" constructed in the preprocessing step as the spines rotate in response to the imposed deformation. Linking this module with CRIMSON enables CRIMSON to compute the volume changes that occurs in the elements during compression of the preform which is necessary in order to track the movement of the flow front.

In an effort to link the CRIMSON software with the user community, Structural Dynamics Research Corp. (SDRC) has developed a second generation graphical user interface to interface 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. Phase II of this effort includes Injection/Compression parameters.

Impact

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

Outputs

Publications

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

K. M. Pillai, C. L. Tucker III and F. R. Phelan Jr., *Numerical Simulation of Injection/Compression Liquid Composite Molding. Part 1: Mesh Generation*, Composites A, submitted.

K. M. Pillai, C. L. Tucker III and F. R. Phelan Jr., *Numerical Simulation of Injection/Compression Liquid Composite Molding. Part 2: Preform Compression*, Composites A, submitted.

K. M. Pillai, C. L. Tucker III, and F. R. Phelan Jr., *Injection/Compression Liquid Composite Molding 3-D Flow Analysis*, Proc. American Society of Composites Conference, Baltimore, MD, September, 1998, in press.

Presentations

F. R. Phelan Jr., K. M. Pillai, and C. L. Tucker III, *Injection/Compression Liquid Composite Molding 3-D Flow Analysis*, AIChE Annual Meeting, Los Angeles, CA, November, 1997.

K. M. Pillai, C. L. Tucker III, and F. R. Phelan Jr., *Injection/Compression Liquid Composite Molding 3-D Flow Analysis*, American Society of Composites Conference, Baltimore, MD, September 22, 1998.

Liquid Composite Molding: Development of Processing Models for Viscoelastic Flows

A. M. Reiff, and F. R. Phelan Jr.

Objectives

The objectives are to develop and apply numerical models to describe the flow of viscoelastic fluids in composites processing operations such as liquid molding, pultrusion and injection molding.

Technical Description

Due to the nonlinear rheological behavior of curing thermosets and of polymer melts, and the multi-phase nature of injection flows, the processing of composite materials is little understood and quite difficult to analyze. Lattice-Boltzmann (LB) methods have been shown to be quite powerful for modeling multi-phase flows, but have been limited to Newtonian fluids. In this project, a generalized Lattice-Boltzmann scheme is developed to simulate two dimensional viscoelastic flow of fluids. We solve the Navier-Stokes equations, representing the conservation of mass and momentum. Along with the conservation of mass and momentum, we use the upper Maxwell family of constitutive laws for the extra stress to describe the viscoelastic rheology of the fluid.

The basic approach in LB is to solve the discrete Boltzmann equation for the particle velocity distribution function on a lattice. Each particle velocity distribution function represents a packet of particles moving with a fixed velocity along the lattice. The evolution of these distribution functions is governed by the discrete Boltzmann equation which is approximated by a single relaxation time collision operator called the BGK approximation. This collision term forces particle distributions toward their local equilibrium value. The Boltzmann equation is discretized by permitting velocities of magnitude zero or one and directions determined by the spatial lattice geometry. For example, with a two dimensional hexagonal lattice, seven velocities are permitted including six of magnitude one connecting a given lattice point to its six nearest neighbors, and one velocity of magnitude zero.

The macroscopic flow quantities, density and velocity, are recovered by summing over the particle distribution function solution of the discrete Boltzmann equation.

Planned Outcome
To model multi-phase viscoelastic flow and provide the developed simulation tools to manufacturers for optimizing the production of composite materials.

Accomplishments
Within the LB framework, a second order accurate numerical scheme was derived for viscoelastic constitutive laws in the upper Maxwell family. The Lagrangian coordinate system used in the LB method proved to be convenient for discretizing the convected stress terms in the constitutive law. Assuming isotropic conditions along with the condition that the macroscopic stress matches the nodal stress, we derived the equilibrium distribution functions for the seven velocity vectors on the 2-D hexagonal lattice.

Using the LB method described, the conserved quantities mass and momentum can be found. Observing that the LB update is explicit, the new values for mass and velocity are utilized in the approximation of the stress tensor. From the dimensionless form of the upper Maxwell constitutive laws, we derive the second order approximation to the extra stress required in the LB calculation of the equilibrium distribution function.

At this time, the numerical model simulates flow in a square cavity with convex impermeable tows. We assume symmetric conditions at the walls parallel to the flow direction; at the walls perpendicular to the flow direction, we assume periodic velocity along with a constant pressure (or density) gradient. Along the boundary of the tow, we assume a no-slip condition, i.e. $U = 0$. The next phase of this project will be to alter the no-slip boundary conditions to allow for permeable tows.

Liquid Composite Molding: Process Monitoring and Control

J. P. Dunkers, R. S. Parnas, K. M. Flynn, C. Zimba, S. Keuh[1], and K. Murphy[2]
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[2]F&S Inc., Blacksburg, VA

Objectives

To develop measurement methods based on optical fibers for monitoring the flow and reaction processes that occur in composites manufacturing, and to begin commercialization efforts for such technology.

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 optical fiber trajectory in the mold to provide flow data most indicative of proper mold filling.

External Collaborations

Kent Murphy, F&S Inc. - developing a commercial sensor system.
Rob Bannerjee, EDX - developing quality control methods for sandwich panel products.
Dennis Sourlas, University of Missouri - developing process control algorithms.
Suresh Advani and Sylvia Kueh, University of Delaware -applying sensors to flow monitoring.

Planned Outcome

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

Accomplishments

An SBIR subtopic was announced and a proposal from F&S selected for phase I feasibility study. In this study the market for an optical fiber sensor system is being assessed in the composites industry. The technical design of such a system is being explored by designing fibers and electronics to multiplex multiple sensors on a single fiber.

The potential to use a well developed fiber optic cure sensor system for flow monitoring during mold filling has been demonstrated with simulations. Using a reasonable sensor response function, the ability of a single fiber sensor system to detect flow anomalies such as edge effects was demonstrated in simple edge filled molds as well as in complex molds containing inserts. This result leads to the intriguing possibility of a simple and fast system suitable for manufacturing that can provide real time information for controlling mold filling.

Outputs

Publications
Joy Dunkers, Kathleen Flynn, Mitchell Huang, and Walter McDonough, *Fourier Transform Near-Infrared Monitoring of Reacting Resins Using and Evanescent Wave High-Index Fiber-Optic Sensor*, Applied Spectroscopy **52(4)**, 552 (1998).

Richard Parnas, Joy Dunkers, and Raymond Neff, *Monitoring Composites with Optical Fiber Sensor Systems*, Proc. SPE ANTEC '98, Atlanta, GA, May, 1998.

Richard S. Parnas, *Process Monitoring and Control for High Speed Composites Manufacturing*, Proc. SPE Thermoset Regional Technical Conference 1998, Chicago, IL, March, 1998.

Dennis Sourlas, Susmito Naha, Gary Patterson, and Richard Parnas, *Study on the Estimation and Control of a Liquid Composite Molding Process*, Proc. Automatic Control Conference, Philadelphia, PA, June 24-26, 1998.

Sylvia R. M. Kueh, Suresh G. Advani, and Richard S. Parnas, *Virtual Sensor Simulation Study of Flow During Resin Transfer Molding Process*, Proc. American Society of Composites Meeting, Baltimore, MD, Sept. 22-25, 1998, in press.

Presentations
Richard S. Parnas, *Optical Fiber Sensors for Monitoring and Control of Composite Processing*, Second International Conference on Composite Materials for Offshore Operations, Houston, TX, October 29, 1997.

Richard S. Parnas, Optical Fiber Monitoring of Fast Systems, American Institute of Chemical Engineers 1997 Annual Meeting, Los Angeles, CA, November 19, 1997.

Richard S. Parnas, *Experiments with Evanescent Wave Optical Fiber Sensors*, 1997 International Mechanical Engineering Congress & Exposition, Dallas, TX, November 21, 1997.

Richard S. Parnas, *Mode Coupling Theory for Evanescent Wave Optical Fiber Sensors*, poster at Gordon Research Conference on Composites, Ventura, CA, January 6, 1998.

Richard Parnas, Joy Dunkers, and Raymond Neff, *Monitoring Composites with Optical Fiber Sensor Systems*, SPE ANTEC '98, Atlanta, GA, May, 1998. Best Paper Award.

Richard S. Parnas, *Process Monitoring and Control for High Speed Composites Manufacturing*, SPE Thermoset Regional Technical Conference 1998, Chicago, IL, March, 1998.

Dennis Sourlas, Susmito Naha, Gary Patterson, and Richard Parnas, *Study on the Estimation and Control of a Liquid Composite Molding Process*, Automatic Control Conference, Philadelphia, PA, June 24-26, 1998.

Sylvia R. M. Kueh, Suresh G. Advani, and Richard S. Parnas, *Virtual Sensor Simulation Study of Flow During Resin Transfer Molding Process*, American Society of Composites Meeting, Baltimore, MD, Sept. 22-25, 1998.

Liquid Composite Molding: Interface Sensitive Optical Fiber Sensor

J.P. Dunkers, R.S. Parnas, J. Lenhart[1], and J. VanZanten[1]
[1]The Johns Hopkins University, Baltimore, MD

Objective

Develop a method of measuring the chemical and physical behavior of the polymer matrix in the first 100 Å around glass fibers.

Technical Description

Fluorescence monitoring becomes more practical by grafting the fluorophore onto the glass fiber instead of dissolving the fluorophore into the resin. The fluorophore responds to its environment by undergoing a fluorescence shift to shorter wavelengths as the viscosity and polarity of the environment increases. A fluorescing silane coupling molecule, Robello siloxane (RBS), is being synthesized and grafted on model flat glass and silicon surfaces. The RBS is grafted onto the surfaces strongly diluted by other typical co-silane coupling agents to minimize fluorescence self quenching and to mimic the typical silane chemistry used in composites as closely as possible. The silane hydrolysis and deposition conditions are systematically varied with respect to hydrolysis and deposition time, solvent, and co-silane. The grafted layer is assessed using fluorescence and contact angle measurements, atomic force and scanning electron microscopy, and infrared spectroscopy.

External Collaborators

William Birch, Corning, France - silane deposition procedures.
Joe Lenhart and John VanZanten, The Johns Hopkins University - silane layer characterization.
Steve Pollack, Howard University - RBS synthesis.

Planned Outcome

To use the interface sensitive fiber optic sensor in conjunction with a commercial sensor system for quality control of industrial composites manufacturing.

Accomplishments

A room temperature deposition procedure of the RBS and co-silane upon glass was developed. The layer was shown to be strongly bonded to the glass by performing contact angle measurements before and after washing with solvent. The potential for the grafted RBS dye to be used as an interface sensitive cure monitoring sensor was demonstrated. Both fluorescence intensity changes and spectral shifts from the RBS can be followed when an epoxy resin cures over the mixed coupling agent layers. It was also shown that layer thickness had an effect on the emission shift upon cure. For the RBS/ isocyanopropyltrimethoxysilane system, a 1 µm layer underwent a blue shift of 17 nm whereas a 10 µm layer only underwent a 4 nm shift upon cure. A correlation was found between the polarity of the co-silane and the emission wavelength of the RBS. With the more polar co-silanes the emission is around 640 nm and with non-polar co-silanes the emission is near 540 nm. In addition, the polarity of the co-silane also influenced the emission intensity, with the polar co-silanes exhibiting an intrinsically lower fluorescence intensity than the non-polar silanes. Using atomic force microscopy, the roughness of the RBS/co-silane film on the glass surface was measured and was found to vary drastically with co-silane. Using these results, it is now possible to design a sensor that has the optimized properties for the interface sensor and the cure sensor.

Output

Publications

Joseph L. Lenhart, John VanZanten, Joy P. Dunkers, Carl G. Zimba, Steven K. Pollack, and Richard S. Parnas, *A Fiber Optic Sensor for Composite Cure Monitoring*, Proc. American Society of Composites Meeting, Baltimore, MD, Sept. 21-23, 1998, in press.

Presentations

J. L. Lenhart, J. VanZanten, J. P. Dunkers, C. G. Zimba, S. K. Pollack, and R. S. Parnas, *A Fiber Optic Sensor for Composite Cure Monitoring*, American Society of Composites Meeting, Baltimore, MD, Sept. 22, 1998.

Microstructure Studies: Chemical Imaging

C. G. Zimba, and R. S. Parnas

Objective

Apply chemical imaging techniques in the infrared and x-ray to measure the spatial distribution of individual chemical species in a variety of polymeric materials, including composites, blends, and other multi-component polymer systems.

Technical Description

In most cases, the polymer systems of interest are not homogeneous or single-components, but are blends, composites, or copolymers. To understand the nature of the molecular and physical processes in these heterogeneous systems, it is important to understand both the spatial distribution and the chemical behavior of the various components within the polymer matrix.

However, there is typically a trade-off between spatial resolution and chemical specificity. Techniques, such as transmission or scanning electron microscopies (TEM and SEM), have high spatial resolution but limited chemical information, while infrared microscopy has low spatial resolution and high chemical content.

While many chemical imaging tools exist, those that use photon probes offer the best combination of chemical identification with spatial resolution. Two such techniques have been the focus of this effort: infrared microspectroscopy and x-ray microscopy. The infrared technique allows spectra of areas as small as 10-20 microns to be acquired with conventional IR sources and microscopes. While this is still a relatively large size scale, the infrared spectrum affords one of the best probes of molecular structure and morphology of polymers. X-ray microscopy is a useful adjunct to infrared analysis, providing somewhat less chemical information but with a spatial resolution of 50 nm. Using Near Edge X-ray Absorption Fine Structure (NEXAFS) in the soft x-ray region as the spectroscopic probe, x-ray microscopy is sensitive to the hybridization and molecular bonding of carbon. Thus, different moieties of carbon, i.e., carbonyl, phenyl, nitrile, can easily be distinguished. When combined with an imaging capability, this spectroscopic sensitivity makes it possible to ascertain the spatial distribution of chemically different species. Using both infrared and x-ray microscopy, many systems, including laminates, blends, composites, and block copolymers, have been characterized.

External Collaborations
Nicolet Instrument Corporation and Spectra-Tech, Inc. - infrared array detectors.
Rina Dukor, Vysis, Inc. - infrared microspectroscopy of single cells in breast cancer biopsies.
Sanjeeva Murthy, Allied Signal - NEXAFS microscopy of nanocomposites.
E. L. Thomas (MIT) C. Ober (Cornell) - NEXAFS microscopy for block copolymers.
C. Jacobsen, SUNY Stoneybrook, - improved spatial resolution in NEXAFS microspectroscopy.

Internal Collaborations:
E. Heilweil (Physics) - infrared microspectroscopy using array detectors
N. Eidelman (ADAHF) - infrared and NEXAFS microscopy of calcified tissue

Planned Outcomes
Dedicated X-ray microscope for polymers at the Advanced Light Source, and improved infrared imaging equipment available commercially.

Accomplishments
The most noteworthy examples of the use of infrared and x-ray microscopy include the characterization of calcified tissue and the observation of molecular orientation in individual lamellae of a block-copolymer.

The calcified tissue sample was a cryo-microtomed cross-section taken from a larger piece of bovine pericardium which was pretreated with gluteraldehyde, implanted subdermally in a laboratory rat for 28 days, retrieved, washed with distilled water and lypholized to remove excess water. In these sections, it was observed by x-ray microscopy (Beamline X1A, NSLS) that the calcified growths were irregularly shaped nodules of 3 to 6 microns in size and that they were preferentially deposited on the side of the implanted pericardium away from the muscle tissue of the rat. Infrared analysis of the tissue, using the infrared microscope at Beamline U4IR at the NSLS with a Cu:Ge detector, showed that the calcified deposits were composed of biological apetite. This is an excellent example of the combined power of infrared and x-ray microscopy.

The block copolymer, p(S-b-HIC), having a styrene (S) block of 9K and a hexylisocyanate (HIC) block of 245 K molecular weight, respectively, spontaneously organizes into a lamellar structure. Previous analysis by TEM has shown that the styrene blocks form arrowhead like structures that alternate in orientation in adjacent lamellae. Electron diffraction from an area comprised of 10-20 lamellae shows that the HIC blocks form highly-crystalline regions which alternate in orientation between adjacent lamellae. X-ray microscopy of these thin cast films also shows the arrowhead morphology of the styrene blocks as seen with TEM. Moreover, the orientation of individual lamellae has been observed using dichroic imaging. This is the first time that orientation in block copolymers has been directly observed on a size scale significantly smaller that than the lamellar spacing.

Improvements in instrumentation and methodology have also been achieved. In x-ray microscopy, methods have been developed and used to obtain NEXAFS spectra of smaller sample areas, approaching the spatial resolution of the optics. Previously, it has not been possible to achieve this due to uncertainties in the position of the zone plate focus as the x-ray energy was changed. By obtaining images at finely spaced energies and then aligning them to account for any positional drift, spectra from single pixels can now be obtained. This has proven to be quite useful for the characterization of features that are close in size to the spatial resolution of the microscope. In infrared spectroscopy, an existing infrared microscope at NIST has been modified to accept a two-dimensional infrared array detector. By using an array for a detector, it is possible to simultaneously obtain infrared spectra from the sample area corresponding to each pixel, greatly reducing the time required to characterize large sample areas. While this experiment is still under development, the imaging and spectroscopic capability has been demonstrated for both transmission and reflection samples. Future work will emphasize time-dependent phenomena.

The Division of Materials Sciences in the Office of Basic Energy Science of the Department of Energy awarded a $450K grant to a multi-partner team, including NIST, to build a new x-ray microscope that will be dedicated to polymer science. This new facility, which will be built at the Advanced Light Source in Berkeley, CA, will greatly augment the amount of beam time available for the investigation of polymers and make possible more extensive and detailed studies which thus far have been impossible due to limited beam time. While this new x-ray microscope will use proven technology for the most part, improvements that have a high benefit/cost ratio, such as improved detectors, will also be pursued.

Outputs

Workshops
Infrared Spectroscopy Using Synchrotron User Facilities, 24th Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Providence, RI,

October 29, 1997. This was sponsored by the User Executive Committee of the National Synchrotron Light Source, and Carl Zimba helped organize and teach it.

X-ray Microscopy of Synthetic and Natural Polymers: Towards Chemical Speciation at 10 nm Spatial Resolution. Assessment of Research Opportunities and the Need for X-ray Microscopy Facilities, NIST, Gaithersburg, MD, May 11-12, 1998. This was co-sponsored by NIST, Department of Energy, Advanced Light Source, North Carolina State University, Carnegie Institution of Washington, Dow Chemical, and General Electric.

Publications

C. G. Zimba, P.A. Martoglio, and J. A. Reffner, *Infrared Microspectroscopy with Synchrotron Radiation Sources*, Applied Spectroscopy, submitted.

C. G. Zimba, *Application of Two-Dimensional Correlation Methods to Infrared Microspectroscopy*, Applied Spectroscopy, submitted.

Presentations

Carl G. Zimba, *Developments in Infrared Microspectroscopy Using Synchrotron Radiation*, 24th Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Providence, RI, October 30, 1997.

Carl G. Zimba, *Chemical Imaging in the Infrared and X-ray Regions*, Syracuse University, Department of Chemistry, Syracuse, NY, March 31, 1998

Carl G. Zimba, *Chemical Imaging in the Infrared and X-ray Regions*, Society of Applied Spectroscopy, Chicago, IL, April 14, 1998

Carl G. Zimba, *Chemical Imaging in the Infrared and X-ray Regions*, Society of Applied Spectroscopy, Reading, PA, April 15, 1998

Carl G. Zimba, *X-ray Microscopy: Introduction and Applications*, Workshop on X-ray microscopy of synthetic and natural polymers, NIST, Gaithersburg, MD, May 11-12, 1998.

Naomi Eidelman, Catheryn Jackson, and **Carl G. Zimba**, *Measuring and Mapping the Calcium in Calcified Bovine Pericardium Implants Retrieved from Rats by Scanning Transmission X-ray Microscopy*, poster at Workshop on X-ray Microscopy of Synthetic and Natural Polymers, NIST, Gaithersburg, MD, May 11-12, 1998.

Carl G. Zimba, *X-ray Microscopy of Multilayer Polymer Coatings*, poster at workshop X-ray Microscopy of Synthetic and Natural Polymers, NIST, Gaithersburg, MD, May 11-12, 1998.

Carl G. Zimba, and Chris Jacobsen, *NEXAFS Microspectroscopy Using STACK*, poster at workshop on X-ray Microscopy of Synthetic and Natural Polymers, NIST, Gaithersburg, MD, May 11-12, 1998.

Carl G. Zimba, *Chemical Imaging: Application to Polymers*, Bundesanstalt fur Materialforschung und -prufung (BAM), Berlin, Germany, June 29, 1998

Carl G. Zimba, *Chemical Imaging in the Infrared and X-ray Regions*, University of Heidelberg, Department of Chemistry, Heidelberg, Germany, July 1, 1998

Carl G. Zimba, *Microspectroscopy and Imaging of Polymers*, Max Planck Institut fur Polymerforschung, Mainz, Germany, July 2, 1998

Carl G. Zimba, *Application of 2D Correlation Techniques to Infrared and X-ray Microspectroscopy Data*, poster at International Symposium on Advanced Infrared and Raman Spectroscopy, Vienna, Austria, July 6-9, 1998

Carl G. Zimba, *Chemical Imaging in the Infrared and X-ray Regions*, Laboratoire pour l'Utilisation du Rayonnement Electromagnetique (LURE), Orsay, France, July 15, 1998

Carl G. Zimba, *Polymer Applications of X-ray Microspectroscopy and Imaging*, poster at Polymer Physics Gordon Research Conference, Newport, RI, August 16-21, 1998

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. Cheng[1]
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Objective

The objective in this project is to develop the tools required to obtain reliable measurements of the interfacial adhesion in composites having rheologically complex matrices.

Technical Description

Perhaps the single most important problem in the measurement of fiber-matrix interface strength is the lack of standardization. To address this issue, NIST and Michigan State University have organized an international program 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. The objectives are to establish consensus test procedures, to conduct round robins to verify these procedures, and to provide 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 may expand to other measurement methods if the program is successful. Participants include 15 laboratories in 8 countries.

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. The polymer matrix is rarely linear elastic or elastic-perfectly plastic. This project seeks to quantify the impact of non-ideal matrix behavior on the interfacial shear strength determined by the most widely used test method, 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 fiber fragmentation process with increasing strain, (3) investigating the impact of loading rate on the matrix modulus and fragmentation process, (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.

An important aspect of the work is to assess the durability of adhesion promoting silane coupling agents that are applied to the fiber surface before composite manufacturing. These coupling agents are designed to promote adhesion of the matrix to the embedded fiber and provide a protective barrier against moisture attack. Because moisture absorption alters the properties of the matrix material, traditional data analysis methods that do not account for matrix property changes cannot decouple the effects of moisture on the matrix from the effects of moisture on the interface. Hence, assessing the durability of a fiber coating requires decoupling the changes resulting from differences in matrix properties from the true changes in interfacial shear strength due to degradation of the chemical bonds formed between the silane coupling agent and the 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 the apparent 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

Eric Pohl, OSI is collaborating in the study of durability of industry coatings.
Larry Drzal, Michigan State University is cooperating test method development.
G. Mao, Wayne State University is using atomic force microscopy to study silane coatings.
John Nairn, University of Utah is investigating dynamics of debond region formation.
Leigh Phoenix, Cornell University is correlating NIST experimental data with theoretical models.
Graham Sims, Versailles Advanced Materials and Standards Program (VAMAS) and 14 other participating laboratories are participating in an effort to establish standardized tests for interfacial shear strength.

Planned Outcome

Establish international protocol for single fiber fragmentation test.

Accomplishments

VAMAS Program: During the past year, a consensus test procedure was developed, and a model material system was selected. A single batch of samples is now being prepared with this system, and specimens will be distribution to all participants. The round robin with these samples is scheduled for completion in December 1998.

Research on Fragmentation Test and Viscoelastic Characterization: An empirical nonlinear viscoelastic constitutive equation was developed to model the behavior of the resin during the single fiber fragmentation test. As a result of these modeling efforts, a nonlinear viscoelastic micromechanics model was developed to more accurately determine the interfacial shear stress transfer coefficient (I-STC). Noting that viscoelastic materials are history dependent, a reasonable estimate of the I-STC was obtained by using the stiffness of the matrix at the end of the test. This approach allows comparison of the I-STC from different resin systems.

Rate Effects: To assess the impact of strain rate on the single fiber fragmentation process, two sets of model E-glass composites were made from diglycidyl ether of bisphenol-A / m-phenylenediamine (DGEBA/m-PDA) epoxy resin and polyisocyanurate. When the effective strain rate of the test was decreased, the I-STC of the E-glass model composites made from DGEBA/m-PDA increased. This is opposite to what one might expect based solely on viscoelastic behavior. Similar tests on model composites composed of E-glass and polyisocyanurate, however, do not show dramatic changes in the I-STC with decreasing strain rate. These results indicate that the viscoelastic behavior of the matrix must be considered when establishing a single fiber fragmentation testing protocol.

Outputs

Publications

G. A. Holmes, R. C. Peterson, D. L. Hunston, W. G. McDonough, and C. L. Schutte, *Non-linear Viscoelasticity in a DGEBA/m-PDA Resin System and Its Impact on E-Glass Interfacial Shear Strength Measurements*, ASTM STP 1357, in press.

D. L. Hunston, G. A. Holmes, R. C. Peterson, *Viscoelastic Properties of a Resin Commonly used in the Single Fiber Fragmentation Test*, Proc. American Society of Composites Meeting, Baltimore, MD, Sept. 21-23, 1998, in press.

G. A. Holmes, R. C. Peterson, and D. L. Hunston, *Modeling of Multi-Step Nonlinear Stress Relaxation in DGEBA/m-PDA Epoxy Resins*, Proc. of the 2nd Int. Conference on Mechanics of Time Dependent Materials, Pasadena, CA, March, 1998, p. 26.

G. A. Holmes, R. C. Peterson, D. L. Hunston, and W. G. McDonough, *The Influence of the Matrix Modulus on the Interfacial Shear Strength Parameter*, Proc. of the 21st Annual Meeting of the Adhesion Society, Savannah, GA, February, 1998, p. 175.

Gale A. Holmes, Richard C. Peterson, Donald L. Hunston, Walter G. McDonough, *The Applicability of Nonlinear Melt Rheology Concepts to the Nonlinear Solid Rheology of DGEBA/m-PDA Epoxy Resin in the Glassy Region*, Proc. of NOBCChE '98, Dallas, TX, April 13, 1998, in press.

Presentations

D. L. Hunston, G. A. Holmes, R. C. Peterson, *Viscoelastic Properties of a Resin Commonly used in the Single Fiber Fragmentation Test*, American Society of Composites Meeting, Baltimore, MD, Sept. 21-23, 1998.

D. L. Hunston, G. A. Holmes, W. G. McDonough, *Standardization of Test Methods for Fiber-Matrix Interface Strength in Polymer Composites*, poster at NIST Assessment Panel Meeting, NIST, Gaithersburg, MD, March 19, 1998.

G. A. Holmes, *Debond Region Formation during Fiber Fracture*, Imperial College London, UK, June 10, 1998.

G.A. Holmes, *Effect of Strain Rate on Fiber Fracture in Single Fiber Fragmentation Test Specimens*, UMIST, Manchester, UK, June 11, 1998.

G. A. Holmes, *Modeling of Multi-Step Relaxation Behavior of DGEBA/m-PDA using Melt Rhelogy Concepts*, University of Leeds, Leeds, UK, June 12, 1998.

G. A. Holmes, *The Deformation Mechanics of the Single Fiber Fragmentation Test*, CIMTEC '98 Conference, Florence, Italy, June 14, 1998.

G. A. Holmes, R. C. Peterson, and D. L. Hunston, *Modeling of Multi-Step Nonlinear Stress Relaxation in DGEBA/m-PDA Epoxy Resins*, The 2nd Int. Conference on Mechanics of Time Dependent Materials, Pasadena, CA, March, 1998.

G. A. Holmes, R. C. Peterson, D. L. Hunston, and W. G. McDonough, *The Influence of the Matrix Modulus on the Interfacial Shear Strength Parameter*, The 21st Annual Meeting of the Adhesion Society, Savannah, GA, February, 1998.

Gale A. Holmes, Richard C. Peterson, Donald L. Hunston, Walter G. McDonough, *The Applicability of Nonlinear Melt Rheology Concepts to the Nonlinear Solid Rheology of DGEBA/m-PDA Epoxy Resin in the Glassy Region*, NOBCChE '98, Dallas, TX, April 13, 1998.

Hybrid Reinforced Polymer Composites

D. L. Hunston, K. M. Flynn, R. S. Peterson, J. P. Dunkers, G. A. Holmes, W. G. McDonough, and S. Zaghi

Objective

The objective is to formulate a scientific basis for testing the mechanical properties of hybrid composite materials by developing an understanding of the way that the microstructures of these materials influence the behavior and complicate the interpretation of test results.

Technical Description

There is a great deal of interest in composites which are reinforced with two or more different types of fibers. By combining the advantageous features of carbon, glass, and Kevlar fibers, the fabricator can achieve significantly better trade-offs between various properties and between cost and performance. Industries currently exploring the use of hybrids include off-shore oil, infrastructure, and alternate fuel vehicles. The challenge, however, is that the design methodology for hybrids is inadequate. For example, studies at the University of Houston have shown that some properties of hybrid tubes cannot be understood with current theories and some properties measured with tubes do not agree with equivalent properties obtained from plate experiments. The explanation seems to be that the failure modes and the interpretation of test results depend on details of the sample microstructure in ways that we do not understand. Moreover, characterizing this microstructure is a challenge since the available tools have not been applied to these types of systems. Because the variety of possible hybrid materials is almost unlimited, the work here will focus initially on the filament wound tubes of interest to the off-shore oil industry and the questions raised by the Houston study. The work will first develop/adapt tools to characterize the microstructure of these materials. A systematic effort will then measure the microstructure and mechanical properties of tubes and plates prepared with a model system. The project is a major collaboration with Drs. Wang and Williams at the University of Houston who will be conducting much of the large scale mechanical testing. Since the project must eventually extend to other types of hybrids as well, some selected experiments will be initiated immediately using the layered hybrids of interest for infrastructure applications and the fabric hybrids being considered for use in alternate fuel vehicles.

External Collaborations

Prof. S. S. Wang and Dr. J. Williams, University of Houston - testing of hybrid tubes.
Prof. Frank Ko, Advanced Product Development, Bristol, PA - providing hybrid fabrics for tests.
Guy Rossi, Solectria, Wilmington, MA - application of hybrids in electric vehicles.

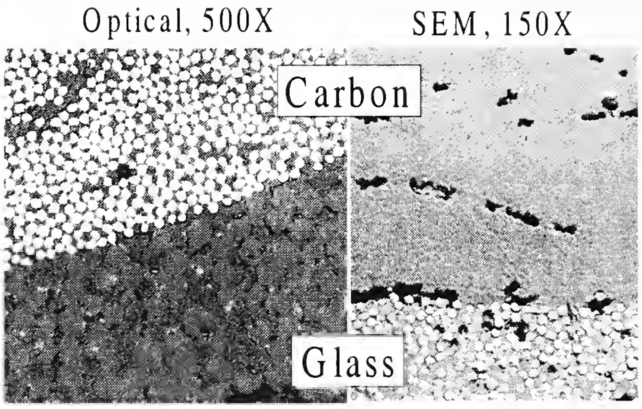
Planned Outcomes

- Guidelines for tests that will provide reliable information for materials evaluation and design of hybrid composites.
- Test methods for determining the microstructure in hybrid materials.

Accomplishments

This project is new, and the first step was the design and purchase of test specimens made with a model material system. Based on the Houston results, both tubes and plates were included. The resin and curing chemistry were chosen to be acceptable to industry and commercial fabricators. Carbon and glass fibers were selected for the mix since this combination gives the best opportunity to balance high specific strength and stiffness with low cost -- the goal for many commercial applications. The mix pattern was selected to combine both fiber types within each ply. This avoids the weak planes that can occur when each ply is a single fiber type. Based on these choices, detailed specifications for the samples and the filament winding process were developed, and specimens were ordered.

The second step in the project was the development of microstructure characterization techniques. A number of methods were examined and proved useful. One of the most interesting was the combination of optical and electron microscopy (see Figure). The optical experiments easily distinguished the carbon fibers while the glass fibers stood out clearly in electron micrographs. These characterization methods provide the tools needed for the remainder of the program.



Micrographs from hybrids. Carbon tows are at the top of each picture while glass tows are at the bottom. Carbon fibers are clearly seen in the optical micrograph while glass fibers are visible in the SEM. Voids can also be seen within the glass tows and between adjacent carbon tows.

In a complimentary study, experiments were initiated on a hybrid system of interest for alternate fuel vehicles. Several reinforcement geometries are being considered including a hybrid fabric. Because such systems are totally new, there is a need to obtain basic mechanical property data.

Unfortunately, most existing test methods were designed to accommodate simple reinforcement geometries like unidirectional layers or random mat materials. Consequently, these tests must be examined and where necessary adapted for use with hybrids. During the past year, a matrix of desired properties was established and possible measurement methods were identified.

Microstructure Studies: Performance Relationships

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Objectives

The objectives are to develop and apply measurement tools to establish relationships between the microstructural features generated during processing and the performance properties of polymer composite systems. The work focuses on the role of the polymer-polymer, polymer-metal, and the polymer-fiber interfaces in performance of structural adhesives and composites.

Technical Description

The work in this project involves four areas: bulk resins, coatings, composites, and adhesives. The common thread is structure-property relationships. With bulk resins, toughened thermosets were studied. 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. Te 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 coatings is developing an ultrasonic technique to characterize non-destructively polymer layers of 1 mm or less bonded to a flat surface. Once developed, the technique will be used to monitor adhesives and coatings during polymer cure or attack of the cured polymer by water. The work on composites is examining the fatigue behavior of pultruded samples to develop test methods for durability and to generate data that explore degradation mechanisms. The final area of work is developing a new technique for characterizing the viscoelastic properties of adhesives. The specimen involves two strips of metal bonded together with the adhesive. This sandwich is subjected to three point bending perpendicular to the adhesive plane. The specimen is simple to make, disposable, and simulates the constrains and processing environment of an adhesive joint. In addition, there is a published elastic analysis which would permit the calculation of the shear modulus for the adhesive from the bending stiffness of the sandwich.

External Collaborations

Dwight Hoffman, Dow Chemical Co. - information on morphology of rubber-toughened epoxy.
David Dwight, Owens Corning - the relationship between fragmentation test and full composites.
Glen Barefoot and Daniel Witcher, Strongwell - materials for durability of pultruded composites.
Prof. Catherine Brinson, Northwestern University - durability for pultruded composites.
Prof. D. Raghavan, Howard University - structure-property relationships in toughened epoxies.
Prof. K. Liao, Nanyang Technological University, Singapore - fatigue of pultruded composites.

Planned Outcomes

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 adhesive and composite studies will provide guidelines and methodologies for testing the properties and durability of structural adhesives and composites.

Accomplishments

In the areas of toughening, ultrasonics, and environmental fatigue, the focus during the past year was publication of the results. In addition, an important question was addressed for the model toughened thermoset. The material used here is designed to produce samples where the size and size distribution of toughener particles remain constant while the concentration of toughener is varied over a wide range. Although all the previous data support with this assertion, the evidence was indirect. During the past year, transmission electron micrographs were taken of cryogenically sliced thin sections stained to reveal the acrylic rubber. Efforts to quantitatively analyze the micrographs is now underway, but simple visual inspection of the photographs confirm that the rubber remains phase separated as particle over the complete range of concentrations studied. Moreover, there is no indication of a major change in the size or size distribution of the particles. This is important because high concentration of toughener in other systems often produces phase inversion.

The behavior of adhesives in the new sandwich specimen is being explored by testing a model thermoset with a T_g of 30 °C over a range of temperatures from 5 °C to 55 °C, using both stress relaxation and dynamic mechanical experiments. The results clearly show the contribution of the adhesive can easily be measured so the technique has good sensitivity to the properties of the adhesive. Surprisingly, when the curves for different temperatures were shifted, they seemed to superimpose to form a master curve even though they represent stiffness of a structure and not a simple modulus. To test the elastic analysis which is available for the sandwich specimen, results at 5 °C and 55 °C were used since the adhesive behavior is approximately elastic at these temperatures. Unfortunately, the calculated values for the adhesive's shear modulus are completely unrealistic. Examination of the theory suggests that some of the assumptions made in the analysis may not be valid unless the adhesive is a very thin. Work on a new, viscoelastic analysis is now underway.

Outputs

Publications

J. He, D. Raghavan, D. Hoffman, and D. Hunston, *The Influence of Elastomer Concentration on Toughness in Dispersions Containing Preformed Acrylic Elastomeric Particles in an Epoxy Matrix*, Polymer, in press.

D. L. Hunston, J. He, R. Raghavan, and D. Hoffman, *Limits on toughening in Structural Adhesives*, Proc. Adhesion Society Meeting, Adhesion Society, Blacksburg, 1998, pp. 200-202.

D. L. Hunston, *Automated Monitoring of Thin Film Properties via Ultrasonics*, Proc. Adhesion Society Meeting, Adhesion Society, Blacksburg, 1998, pp. 440-442.

K. Liao, C. R. Schultheisz, D. L. Hunston, and L. C. Brinson, *The Effect of Water on the Fatigue Behavior for a Pultruded Glass-Reinforced Composite*, Proc. 56th Annual Technical Conference of Society of Plastics Engineers, ANTEC '98, SPE, Brookfield, 1998, pp. 2245-2250.

D. L. Hunston, *Performance Property Relationships*, in Micro-Mechanics Measurement Technologies for Fiber-Polymer Interfaces, ed. by McDonough, Parnas, Holmes, and Hunston, NISTIR-6102, NIST, Washington, DC, 1997, pp. 169-191.

D. Raghavan, D. L. Hunston, J. He, and D. Hoffman, *The Influence of Morphology and Concentration on Toughness in Dispersions Containing Preformed Acrylic Elastomer Particles in an Epoxy Matrix*, Polymeric Materials Science and Engineering Preprints, American Chemical Society, in press.

Presentations

D. L. Hunston, "Thermosets," Adhesion Short Course, Adhesion Society, Savannah, Feb. 21, 1998.

D. L. Hunston, J. He, R. Raghavan, D. Hoffman, "The Effect of Elastomer Concentration on Toughening in Rubber-Modified Thermosets," 49th ACS Southeast Regional meeting , Roanoke, October 20, 1997.

D. L. Hunston, J. He, R. Raghavan, and D. Hoffman, "Limits on toughening in Structural Adhesives," Adhesion Society Meeting, Savannah, Feb. 21-24, 1998.

K. Liao, C. R. Schultheisz, **D. L. Hunston**, and L. C. Brinson, "The Effect of Water on the Fatigue Behavior for a Pultruded Glass-Reinforced Composite," 56th Annual Technical Conference of Society of Plastics Engineers, ANTEC '98, Atlanta, April 16-May 1, 1998.

D. Raghavan, D. L. Hunston, J. He, and D. Hoffman, "Toughening of Epoxies - Dispersion of Preformed Acrylic Elastomeric Particles in an Epoxy Matrix," poster at poster at Gordon Conference on Composites, Ventura, Jan. 4-10, 1998.

D. L. Hunston, "Automated Monitoring of Thin Film Properties via Ultrasonics," poster at Adhesion Society Meeting, Savannah, Feb. 21-24, 1998.

D. Raghavan, D. L. Hunston, J. He, and D. Hoffman, "The Influence of Morphology and Concentration on Toughness in Dispersions Containing Preformed Acrylic Elastomer Particles in an Epoxy Matrix," poster at Symposium on Toughening of Plastics, Polymeric Materials Science and Engineering Division, American Chemical Society, Boston, August 23-27, 1998.

Z. Miyagi, M. Koike, and D. L. Hunston, "Development of Testing Method for in-situ Shear Modulus of Composites Material using Sandwich Beam," Symposium by National Research Laboratory of Metrology, Tsukuba, March 10, 1998.

Microstructure Studies: Measurement of Interface Strength after High Speed Processing of Polyurethanes

W. G. McDonough, Y. H. Kim[1], K. M. Flynn, and R. S. Parnas
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Objectives

The effects of processing on interfacial shear properties as measured by the single fiber fragmentation test (SFFT) will be determined. The materials to be evaluated are resins and reinforcements used in automotive applications. New processing procedures will also be developed to enable the preparation of fast curing (in the order of minutes) specimens that can be used in the microstructure program and which are equivalent to materials made in industry by structural reaction injection molding (SRIM).

Technical Description

Single fiber specimens for the SFFT are typically prepared by pouring premixed resin into an open rubber mold, and then curing the resin in an autoclave. This method cannot work with rapidly curing resins of interest to the auto industry. Consequently, an injection molding procedure has been 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. 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 and vinyl ester resins can gel in a few minutes.

External Collaboration

Thomas Dearlove, Automotive Composites Consortium - coordinating results with the automotive industry.

Planned Outcome

Provide the automotive industry methods for estimating the tradeoffs between processing speed and composite properties.

Accomplishments

A multi-cavity mold was designed and built to produce 8 single fiber dogbone specimens from a single injection. A specially designed injection system was made to simulate the SRIM process. Flow visualization experiments were 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, verifying that SFFT samples can be prepared in an SRIM-like process.

Vinyl ester/E-glass single fiber fragmentation specimens were made at different processing times. Initial results indicate changing the gel time changes the measured interfacial properties. A single formulation of vinyl-ester was either catalyzed with 2% or 10% catalyst to produce either a 45 minute or a 10 minute gelation time. The materials were processed to the same total level of cure. The fiber fragmentation patterns observed upon testing, and subsequent analysis, indicated that the interfacial shear strength was approximately 30% less in the more rapidly cured material.

Outputs

Publications

W. McDonough, R. Parnas, G. Holmes, D. Hunston, <u>Workshop on Micromechanics Measurement Technologies for Fiber-Polymer Interfaces</u>, NISTIR-6102, NIST, Washington, DC, 1997.

W. McDonough, G. Holmes, R. Peterson, *Interface Adhesion of E-glass Fibers in Model Polyisocyanurate Networks*, Proc. American Society of Composites Baltimore, MD, Sept. 21-23, 1998, in press.

Presentations

W. McDonough, G. Holmes, R. Peterson, *Interface Adhesion of E-glass Fibers in Model Polyisocyanurate Networks*, American Society of Composites Baltimore, MD, Sept. 21, 1998.

Microstructure Studies: Non-destructive Characterization by Optical Coherence Tomography

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Objective

The goal of this work is to image composite microstructure using a new technique, optical coherence tomography (OCT). Knowledge of tow position and orientation are applied to permeability prediction. Characterization of defects such as voids, wrinkles, cracking, delaminations, and crazing is important for optimizing processing parameters and evaluation of composite health.

Technical Description

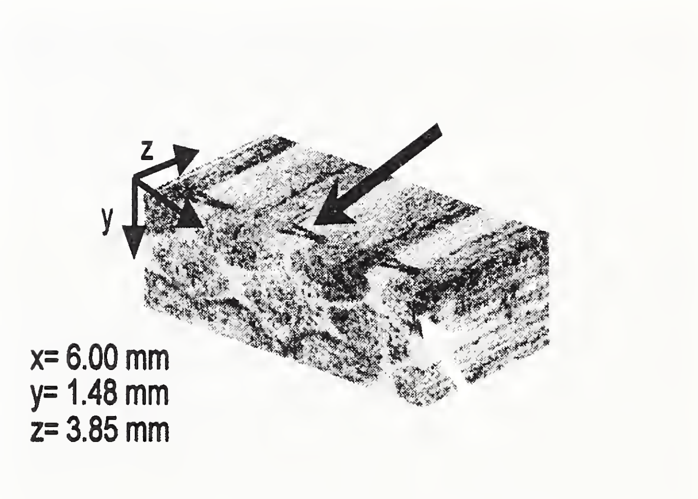
OCT will be applied to a variety of composites systems to determine its potential for characterizing microstructure and damage. OCT is a non-invasive, non-contact optical imaging technique that allows the visualization of microstructure within scattering media. OCT uses light in a manner analogous to the way ultrasound imaging uses sound and, while typically affording shallower penetration depth, provides significantly higher resolution (5-30 µm). To perform OCT imaging, broad-spectrum laser light (20 - 200 nm bandwidth) is transmitted using a single mode fiber and coupled into a 50/50 fiber optic splitter that illuminates the sample and a linearly translating, constant velocity reference mirror. The fiber optic splitter, fixed sample and constant velocity reference mirror can be thought of as a Michelson interferometer. Light back-reflected from each interferometer arm is recombined at the fiber optic splitter. Interference fringes are registered at the detector only when the optical path length of the reference arm matches that of the sample arm to within the coherence length of the light source. The axial resolution with which this ranging can be performed is therefore determined by the coherence length or inverse spectral width of the source. Therefore, the axial resolution can be as low as 5 µm. Low coherence sources such as mode-locked solid-state pumped lasers or superluminescent diodes are used. Transverse resolution in OCT is determined by the focal spot size of the probing beam, which is usually 10-30 µm. Higher numerical aperture optics provide superior transverse resolution, but at the expense of a diminished depth-of-field.

Planned Outcome

To provide the composites community a versatile and low cost non-destructive technique for the study of composite microstructure.

Accomplishments

Reinforcement permeability was calculated using OCT images and the lattice-Boltzman fluid flow program. Images from OCT that show tow location, size, and shape of a unidirectional epoxy/unidirectional E-glass composite (see Figure) were used in these permeability calculations. Before the permeability calculation could be run, the low contrast grayscale image had to be converted into a binary image through an automated and robust image processing program that used various techniques to enhance the contrast between the tows and resin, and then automatically identify the tows. There was good agreement between the axial permeability values calculated using the OCT images and the experimental permeability. In addition, the calculated permeabilities from two different regions in the sample were almost identical. By comparing automatically and manually processed images, it was determined that the tow roughness had a large influence on the calculated permeability.



Three dimensional reconstruction of OCT images from an epoxy/ unidirectional E-glass composite. The black arrow shows the polyester stitching while the white arrow indicates the voids within the tows.

The versatility of OCT was demonstrated by imaging a variety of defects. A three dimensional tomographic reconstruction of the data enabled visualization of the defect within the composite along any plane. A re-slicing along the fiber length revealed voids that are oriented in the direction of the fiber tows. Analysis of a 0-90° woven reinforcement showed the relative position and orientation of layers to one another and a wrinkle in one of the interior layers.

It was also demonstrated that OCT could image cracks and delaminations in composite. The epoxy/unidirectional E-glass composite was subjected to impact damage. OCT was then performed along a selected surface crack. OCT revealed the crack penetrating through a tow in the top layer. When the crack reached 575 mm, a rectangular delamination zone that was 2.9 mm by 660 mm was revealed. The 575 mm corresponded to the epoxy rich area between the first and second layer of composite.

External Collaborations

R. Prasankumar and J. Fujimoto, MIT - Hardware and expertise in OCT Imaging.

Outputs

Publications

Joy P. Dunkers, Richard S. Parnas, Carl G. Zimba, Richard C. Peterson, Kathleen M. Flynn, James C. Fujimoto, and Brett E. Bouma, *Optical Coherence Tomography of Glass Reinforced Polymer Composites*, Composites A, in press.

J. P. Dunkers, C. G. Zimba, K. M. Flynn, R. S. Parnas, D. L. Hunston, J. G. Fujimoto, B. Bouma, and R. Prasakumar, *Optical Coherence Tomography of Polymer Composites*, Proc. of the American Society of Composites Conference, Baltimore, MD, Sept. 21-23, 1998, in press.

Joy P. Dunkers, Carl G. Zimba, Frederick R. Phelan, Richard S. Parnas, and James Fujimoto, *Real Structure Determination for Permeability Prediction*, Proc. of 8th US-Japan Conference on Composite Materials, Baltimore, MD, Sept. 24-25, 1998, in press.

Presentations

J. P. Dunkers, R. S. Parnas, R. C. Peterson, C. G. Zimba, K. Flynn, B. Bouma and J. G. Fujimoto, *Optical Coherence Tomography of Composites*, Fall Meeting of the Materials Research Society, Boston, MA, December 4, 1997.

J. P. Dunkers, C. G. Zimba, K. M. Flynn, R. S. Parnas, D. L. Hunston, J. G. Fujimoto, B. Bouma, and R. Prasakumar, *Optical Coherence Tomography of Polymer Composites*, American Society of Composites Conference, Baltimore, MD, Sept. 21, 1998.

Joy P. Dunkers, Carl G. Zimba, Frederick R. Phelan, **Richard S. Parnas**, and James Fujimoto, *Real Structure Determination for Permeability Prediction*, 8th US-Japan Conference on Composite Materials, Baltimore, MD, Sept. 24, 1998.

POLYMER CHARACTERIZATION PROGRAM

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.

Complete 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

- Overcame a major obstacle to the use of mass spectrometry to determine the molecular mass distribution of synthetic polymers through improvements in sample preparation methods that reduced variation of signal intensity from 42% on samples prepared by conventional techniques to below 5% on samples prepared by the new procedures.

- Showed that mass spectrometry is capable of determining the three dimensional molecular structure of polysilsesquioxanes and its dependence on molecular mass. For polymethacryloxypropyltrimethoxysilane it was found that the number of closed intramolecular loops (ladder steps) scaled directly with the number of repeat units.

- Determined by optical and electron microscopy that crystallization into spherulites can either distort or completely destroy microphase separated morphologies exhibited by tri- and diblock polymers containing one crystallizable component.

- Chemical shift calculations for the ethylene defect in isotactic polypropylene confirmed assignments of experimental NMR data used to establish relationships between molecular defects and crystallinity.

- Completed research to identify material for a new Nonlinear Fluid Standard and organized an inter-laboratory comparison of fluid involving 35 researchers from industry (instrument makers and material suppliers) and academe.

- Recommendations for standards for estimation of statistical errors in SAS data sets were made to the Commission on Small-Angle Scattering of the International Union of Crystallography

- Successful application of a model for time dependent surface concentration to the non-Fickian moisture uptake in a commercial epoxy adhesive. The model accurately described both absorption and reabsorption behaviors.

- Confirmed, with a 95 % confidence limit, the existence of an expansion gap in volume recovery data from polymer glasses through analysis of literature data and unpublished data from the Institut Charles Sadron in Strasbourg, France.

- In a collaboration with Eastman Kodak Company, poly(ethylene naphthalate) (PEN) was shown to be "thermo-rheologically complex" because the α and β relaxations showed different temperature and aging time dependencies in classical aging time experiments.

- Successfully described volumetric and mechanical responses of an epoxy glass to jumps in relative humidity.

- In a collaboration with General Electric Company and the University of Pittsburgh, the evolution of the viscoelastic response of a commercial epoxy thermoset during cure was successfully modeled.

- Showed that an approximate method proposed in the literature for the determination of the thermal conductivity using Temperature Modulated DSC can lead to significant (≈30 %) errors in the determination of the thermal conductivity.

- Successfully described, within approximately 20%, the stress response of polyurethane elastomers to multiple step and trapezoidal deformation histories through application of a hybrid VL-BKZ model developed in this laboratory.

- Showed that the glass transition temperature of semi-dilute polystyrene solutions, when confined to small pores having sizes from approximately 10 nm to 50 nm, decreases below that of the bulk.

- Demonstrated that structural recovery in polymeric glasses can dramatically affect the heat flow signal in temperature modulated DSC measurements. This leads to nonlinear responses that cannot be analyzed by simple linear response theory.

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 markets. 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 masss 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 (SRMP) at NIST.

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: SRM 2885, the lowest polyethylene molecular mass standard, and SRM 2886, the middle polyethylene molecular mass standard, have been blended and bottled by SRMP. The bottled materials have been evaluated for homogeneity. No bottle-to-bottle variation was found. A glass rod was calibrated against benzene at room temperature and then used to obtain the V_v, the absolute scattering intensity, of 1,4 trichlorobenzene at 130 °C. As a check on the alignment and the calibration, the M_w of SRM 1483 was measured and found to be 33.4 ku in close agreement with the certificate value. Calibration measurements have commenced on SRM 2886.

Mass Spectrometry of Polymers

Charles Guttman, William Blair, William Wallace and Bruno Fanconi

Objective

The objective is to improve reliability of calibration standards for size exclusion chromatography (SEC), widely used by the polymer industry for characterizing the molecular mass distribution (MMD) and the moments of the MMD of synthetic polymers. Mass spectrometry (MS) is developed as a reliable 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) allow determination of the mass spectrum of whole undegraded polymer molecules with molecular masses up to 300,000 g/mol. As part of an effort to explore the usefulness of this technique for the production of molecular mass SRM's , research was initiated to determine the limits of applicability for the measurement of the absolute molecular mass of a polymer molecule. Research in FY 98 were focused on the following three activities.

i. Sample Preparation Methods: Development of sample preparation techniques that yield consistent repeatable signals in the MS was undertaken to improve on the conventional random crystallization of a matrix and polymer sample on a MALDI target that produces an inhomogeneous surface and large fluctuations in polymer signal intensity. For SRM certification of polymer properties, valid statistical sampling of a target surface does not permit searching for regions that produce the most intense polymer signals. Statistically random sampling must be used. New sample preparation techniques are investigated in an effort to produce a homogenous sample surface with a uniform signal intensity.

ii. Data Analysis methodology: Methodology is developed to analyze the mass spectral data of synthetic polymers in collaboration with staff in the NIST Statistical Engineering Division. Other absolute methods (light scattering or membrane osmometry) yield only one moment of the molecular mass distribution (MMD) of synthetic polymers. To obtain 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 n-mer peaks can be analyzed. In addition, autocorrelation function analysis was applied to mass spectra to resolve polymer architecture and copolymer composition in some samples.

iii. Molecular Structure of Polysilsequioxanes: Polysilsesquioxanes have silicon coordinated with three bridging oxygen atoms in the form of [RSiO3/2] and as a result are generally complex three-dimensional structures. The typically highly-branched silsesquioxane reacts with itself to form intramolecular, closed topographic loops. Specifically, two -SiOH groups within the molecule may react to eliminate water (mass of 18 u) and form a new Si-O-Si bridge. The number of -Si-O-Si- bridges has a profound effect of the solubility and rheology of the polymer. Counting the number of closed loops in the molecule (or, conversely, determining the number of -SiOH groups) is not possible by techniques other than high-resolution time-of-flight mass spectrometry.

iv. Polymer Fragmentation: Under MALDI TOF MS, some polymers will fragment, breakup as a result of the MALDI process. Fragmentation results in a degradation of the signal of the MS and thus possibly an incorrect MMD. Fragmentation of a polyethylene glycol was investigated by post source decay to understand how this fragmentation may affect the measured MMD.

External Collaborations

A collaboration with S. Samal of Revenshaw College, Cuttack, India , seeks to develop matrix materials that are compatible with synthetic polymers.

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

In collaboration with Paul Kowalski of Bruker Instruments fragmentation processes that occur in MALDI-TOF- MS are investigated.

Accomplishments

- Variation in signal intensity was reduced from 42 % on samples prepared by conventional techniques to below 5 % by using a combination of electrospray sample deposition, specially synthesized matrix compounds and very thick deposits of matrix/polymer material.

- Of the approximately 12 polysilsesquioxanes studied, polymethacryloxypropyltrimethoxy-silane was investigated in greatest detail. This polymer when synthesized in the bulk was found by mass spectrometry to occur mainly as a ladder-like structure. Such structural information could not be inferred from other characterization studies, such as NMR or FTIR. It was found for this polymer that the number of closed intramolecular loops (ladder steps) scaled directly with the number of repeat units. This indicates that as the molecule grows the likelihood of it reacting with itself does not increase, or that locally the molecule looks the same and can be said to be self-affine.

- Fragmentation studies on polyethylene oxide revealed that preferential cleavage occurs at the carbon-oxygen bond.

Outputs

Publications
C.M. Guttman, W.R. Blair, and P.O. Danis, *Comparison of Molecular Weight Moments from MALDI-TOF-MS with other Absolute Methods on Standard Reference Polymer*, Conference Proceedings at ANTEC ‘98, Atlanta, GA, April 1998, p. 2109.

W.E. Wallace, C.M. Guttman and J.M. Antonucci, *MALDI-TOF Mass Spectrometry of Polysilsesquioxanes*, Proceedings of the 46th Annual Conference On Mass Spectrometry and Allied Topics, 1998, p. 1076.

W.E. Wallace, C.M. Guttman and J.M. Antonucci, *Molecular Structure of Silsesquioxanes Determined by Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry*, Journal of the American Society for Mass Spectrometry, submitted.

W.R. Blair, C.M. Guttman and W.E. Wallace, *Comparison Investigation of Chemical and Mechanical Modifications of MALDI Sample Preparation techniques for Synthetic Polymers*, Proceedings of the 46th ASMS Conference on Mass Spectrometry and Allied Topics, 1998, p. 1059.

P. Kowalski , W.E. Wallace, and C.M. Guttman, *PSD analysis of Polymers by MALDI TOF MS*, Proceeding of the 46th ASMS Conference on Mass Spectrometry and Allied Topics, 1998, p. 1060.

Presentations
C.M. Guttman, W.R. Blair, and P.O. Danis, *Comparison of Moments from MALDI-TOF-MS with other Absolute Methods on a Standard Reference Polymer*, ANTEC ‘98, Atlanta, GA, April, 1998.

C.M. Guttman, W.E. Wallace, and W.R. Blair, *Statistical Analysis of Polymer Molecular Weight Distribution and its Moments from MALDI TOF MS* , The 45th ASMS Conference on Mass Spectrometry and Allied Topics,Orlando, FL, June, 1998.

W.E. Wallace, C.M. Guttman, and J.M. Antonucci, *MALDI-TOF Mass Spectrometry of Polysilsequioxanes,* The 46th ASMS Conference on Mass Spectrometry and Allied Topics, Orlando, FL, June, 1998.

W.R. Blair, C.M. Guttman and W.E. Wallace, *Comparison Investigation of Chemical and Mechanical Modifications of MALDI Sample Preparation techniques for Synthetic Polymers,* The 46th ASMS Conference on Mass Spectrometry and Allied Topics, Orlando, FL, June, 1998.

P. Kowalski , W.E. Wallace, and C.M. Guttman, *PSD analysis of Polymers by MALDI TOF MS,* The 46th ASMS Conference on Mass Spectrometry and Allied Topics, Orlando, FL, June, 1998.

Characterization of Polymer Morphology by Microscopy Techniques

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[1] Stevens Institute of Technology

Objectives

The objectives are to use 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 microscopy. Cryo-TEM, a relatively new technique in which polymers such as colloids, polymer micelles, gels and dendrimers in solvent are vitrified and imaged at low temperature, is especially useful because the native structure can be imaged without drying or staining.

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), optical and atomic force microscopy. The combination of microscopy techniques with other methods such as scattering, diffraction or spectroscopic measurements 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 C NRS in Grenoble, France, morphology of dendrimers.
Dr. Frank Booy of the Laboratory of Structural Biology, NIAMS, NIH, Betheda, MD, morphology of dendrimers.

Dr. Kenncorwin Gardner, DuPont Company, Wilmington, DE, morphology of spider silk.
Dr. Jonathan Coddington, National Museum of Natural History, Smithsonian, Washington D. C., morphology of spider silk.
Professor Reimund Stadler, University of Bayreuth, Bayreuth, Germany, morphology of semi-crystalline block copolymers.
Dr. Donald Tomalia, Michigan Molecular Institute, Midland, MI, morphology of dendrimers.
Professor Matthew Libera, Stevens Institute of Technology, morphology of semi-crystalline block copolymers.

Accomplishments

- Various thermal conditions were used to prepare thick films (5-10 µm) and bulk specimens of polystyrene(S)-polybutadiene(B)-polycaprolactone(C) (SBC) triblock and SC and BC diblock copolymers with or without spherulitic crystalline morphology. A comparison of the macroscopic crystalline superstructure (optical range 4-1000 µm) and microphase separated morphology (TEM range 5-100 nm) showed that crystallization into spherulites can either distort or completely destroy the microphase separated morphology. Long range crystallization of the C block can be suppressed in the SBC triblock, however, by appropriate annealing conditions. In this case, the microphase separated structure resembles that seen for ABC type amorphous block copolymers; for $S_{35}B_{15}C_{50}$ a lamellar microstructure with B cylinders at the interphase boundaries is observed. The competition between microphase separation and crystallization of the C block depends strongly on the rubbery or glassy character of the amorphous blocks and the overall composition.

- Previously, 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. More recent results on dendrimer blends show that PAMAM dendrimers (G-11) can be uniformly dispersed in interpenetrating polymer networks (IPN's) of hydroxyethylmethacrylate (B. Bauer, D. Liu) at 10 % by mass. Characterization by small angle x-ray scattering (Prosa et al.) measures the R_g to be 6 nm, corresponding to a diameter of 16 nm, assuming a uniform dense sphere. The TEM of thin sections showed that the dendrimers were well dispersed and visible as individual molecules, in good agreement with the SAXS results.

- A small amount of fumed silica (1 %) added to blends of polystyrene/ polybutadiene (PS/PB) (2K/3K) shifts the upper critical solution temperature (UCST) upward about 5 °C (Nakatani et al.). Optical microscopy shows that the fumed silica is aggregated and suggests that the PB preferentially wets the filler particles during the phase separation process (Hobbie et al.). TEM has been used to show that the silica is preferentially wetted by the PB phase, which is stained with OsO_4. The destabilization of the blend by filler is unexpected, and suggests interactions between the filler and PB phase are strong.

Outputs

Publications

C. L. Jackson, H. D. Chanzy, F. P. Booy, B. Drake, D. A. Tomalia, B. J. Bauer and E. J. Amis, *Visualization of Dendrimer Molecules by Transmission Electron Microscopy (TEM): Staining Methods and Cryo-TEM of Vitrified Solutions*, Macromolecules, in press.

G. Kim, C. L. Jackson, F. V. Gyldenfeldt, V. Balsamo, M. Libera, R. Stadler and C. C. Han, *Morphology Study of Polystyrene-Polybutadiene-Polycaprolactone (PS-b-PB-b-PCL) and Polybutadiene-Polycaprolactone (PB-b-PCL) and Polystyrene-Polycaprolactone (PS-b-PCL) Semicrystalline Block Copolymers*, *MSA Proc.*, **806** (1998).

B. J. Bauer, A. Topp, T. J. Prosa, D-W. Liu, C. L. Jackson and E. J. Amis, *Small Angle Scattering Studies of Dendrimer Blends and Interpenetrating Polymer Networks*, *SPE ANTEC*, 2065, (1998).

Presentations

B. J. Bauer, A. Topp, T. J. Prosa, D-W. Liu, C. L. Jackson and E. J. Amis, *Small Angle Scattering Studies of Dendrimer Blends and Interpenetrating Polymer Networks*, Society of Plastics Engineers, Atlanta, GA, April, 1998.

G. Kim et al., *Morphologies of Semicrystalline Block Copolymers Based on Polycaprolactone (PCL)* (poster) and **N. Eidelman**, C. Zimba and C. L. Jackson, *Measuring and Mapping the Calcium in Calcified Bovine Pericardium Implants Retrieved from Rats by Scanning Transmission X-ray Microscopy (STXM)*, X-ray Microscopy Workshop, NIST, Gaithersburg, MD, May, 1998.

J. A. Coddington, H. Chanzy, C. L. Jackson, G. Raty, **K. H. Gardner**, *Structure and Morphology of Major Ampullate Silk System From Recluse Spiders*, University of Virginia, VA, June, 1998.

C. L. Jackson, H. D. Chanzy and F. P. Booy, *Characterization of Polymer Micellar Suspensions and Dendrimer Solutions by Cryo-electron Microscopy* (poster), Workshop on Properties and Applications of Dendritic Polymers, NIST, Gaithersburg, MD, July, 1998.

G. Kim, C. L. Jackson, F. V. Gyldenfeldt, V. Balsamo, M. Libera, R. Stadler and C. C. Han, *Morphology Study of Polystyrene-Polybutadiene-Polycaprolactone (PS-b-PB-b-PCL) and Polybutadiene-Polycaprolactone (PB-b-PCL) and Polystyrene-Polycaprolactone (PS-b-PCL) Semicrystalline Block Copolymers*, Microscopy Society of America, Atlanta, GA, July, 1998.

C. L. Jackson, *Characterization of the Structure of Dendrimer Molecules by Transmission Electron Microscopy and Scattering Techniques,* North Carolina State University, Materials Science and Engineering Department, Raleigh, NC, October, 1997.

Characterization of Polymers by Spectroscopic Techniques

David VanderHart, Bruno Fanconi and Hanqiao Feng[1]
[1]Chinese Academy of Sciences

Objectives

The objectives are to: *i.* develop and use Nuclear Magnetic Resonance (NMR) techniques for characterization of molecular and microstructural level features that control properties of polymers, *ii.* establish capability to employ rapid phase shifts, amplitude changes and frequency shifts within pulse sequences, *iii.* quantify two-pulse phase modulation techniques for improving resolution in strongly coupled spin systems, *iv.* develop solid state NMR characterization methods at 7.05 T, particularly for the morphological locating of defect structures in olefins synthesized by metallocene catalysts and *v.* develop a modest capability for solution-state microstructural characterization of polymers.

Technical Description

Various NMR phenomena and experimental approaches to solid-state characterization are employed; the most useful being:

- **Proton spin diffusion** is characteristic of an extended network of dipolar-coupled protons. Spin diffusion is evidenced by the flow of proton polarization in the presence of an imposed polarization gradient and in the direction that restores spin equilibrium. Thus, properly designed proton spin diffusion experiments yield information about spatial relationships and domain size (typically for the 3 - 50 nm range) 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 (hence the opportunity for chemical identification) for protons in solids.
- **^{13}C spectra**, obtained using MAS, offer the best chemical resolution for organic solids. Also, NMR signals arising from the same chemical species in different states of order, e.g. crystal or non-crystal, can be distinguished. There is a continuing effort 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.

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 (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, branched vinyl polymers and copolymers)
M. Pursch (working with Lane Sander),Analytical Chemistry Division, NIST (Silica gels with organic coatings for high pressure chromatography)

Planned Outcomes

- Establish mechanisms whereby different molecular defect structures in isotactic polypropylene (iPP) dictate properties such as crystallinity, modulus and melting point. Here, “defect” refers to propylene insertions having stereo or regio irregularities or to the presence of various 1-alkene comonomers at low concentrations. The role of the catalyst, e.g. Ziegler-Natta or metallocene type, in determining defect distribution is also expected to reveal itself qualitatively in these studies.

- Develop a better understanding of morphology in polymer blends when one blend component is decorated with a few groups which strongly interact with the other component.

- Develop a better understanding of crystallization and its relation to tacticity in 1-alkene homopolymers, like poly(octadecene) or poly(dodecene), having 16- or 18-carbon branches on every other backbone carbon.

- Develop a better understanding of what controls spectral resolution in the ^{13}C MAS spectra of strongly-dipolar-coupled, crystalline polymers to aid NMR spectroscopists improve spectral resolution in organic solids.

- In connection with derivatized (coated) silica gels that are used for inverse-phase, high-pressure, liquid chromatography (HPLC), develop insight into the relationship between molecular order in the organic coating and molecular-shape selectivity for component molecules in the analyzed mixture.

- Assess the effectiveness of strategies whereby high-strength, high-temperature-stable fibers like poly (benzo-bis-thiazole) are chemically modified so that their compressive strengths can be improved via lateral crosslinking.

Accomplishments

- In iPP, the most common stereo and regio (2,1) defects are incorporated into the crystalline regions at 40 % and 30 %, respectively, of the overall content. Comonomer defects, like ethylene, have corresponding concentration levels near 37 %. Other 1-alkene defects have lower concentrations. Theoretical chemical shift calculations for the ethylene defect have successfully matched experimental spectral positions under the reasonable assumption that the backbone 3_1 helix is preserved.

- Several blend systems were characterized using proton spin diffusion and proton longitudinal relaxation (T_1^H) measurements. The systems include: **I**: a 10/90 PAMAM-dendrimer/poly(hydroxyethylmethacrylate) (PHEMA); **II**: blends of OH-decorated polystyrene (PSOH) with poly(methylmethacrylate) (PMMA) (both isotactic (i-) and atactic (a-) PMMA) or with poly(butylmethacrylate) (PBMA).

- Backbone crystallization was correlated with iso-tacticity in poly(dodecene) and inferred the backbone conformation of the crystal.

- A comprehensive paper was published in the Journal of Magnetic Resonance on spectral resolution in ^{13}C spectra with magic angle spinning.

- Derivatized silica gels (candidates for HPLC) coated with mixtures of silane-bonded benzene and n-C-30-alkanes were characterized.

Outputs

Publications

D.L. VanderHart and G.C. Campbell *Off-Resonance Proton Decoupling On-Resonance and Near Resonance: A Close Look at ^{13}C CPMAS Linewidths in Solids for Rigid, Strongly-Coupled Carbons Under CW Proton Decoupling*, Journal of Magnetic Resonance, in press.

E. Pérez, M.L. Cerrada and D.L. VanderHart, *Rapid Determination of Comonomer Content, Crystallinity, and Long Spacing by Multiple Pulse Proton NMR in Ethylene-Vinyl-Alcohol Copolymers*, J. Polym. Sci. B, Polym. Physics, **36**, 2103, (1998).

X. Hu, S. Kumar, M.B. Polk and D.L. VanderHart, *Tetramethylbiphenyl Substituted Poly(benzobisthiazole) 2. Synthesis and Characterization of Polymers*, J. Polym. Sci. A, Polymer Chemistry, **36**, 1407 (1998).

Presentations

D.L. VanderHart, *Morphological Study of an Ionomer/poly(amide) Blend Using Proton Spin Diffusion*, Federation of Analytical Chemistry and Spectroscopy Societies, Providence, RI, October 26, 1997.

D.L. VanderHart, *Partitioning of Various Defects Within the Semicrystalline Morphology of Isotactic Poly(propylene)*, American Physical Society, Los Angeles, CA, March 17, 1998.

D.L. VanderHart, *C^{13} NMR Study of the Inclusion of Stereo and Regio Defects in the Crystalline Region of Isotactic Poly(propylene)*, Rocky Mountain Conference on Analytical Chemistry, Denver, CO, July 26, 1998.

Structural Characterization of Polymers by Small Angle X-Ray Scattering

J.D. Barnes and T.J. Prosa[1]

[1]Kutztown University of Pennsylvania

Objectives

The objectives are: *i.* to maintain an up-to-date, 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, and *ii.* to use the SAXS Facility as a user facility for outside industrial clients and to support research within the Polymers Division.

Technical Description

By maintaining a fully capable 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. As a result, the NIST SAXS camera is an attractive research tool. Test and analysis capabilities are constantly upgraded and implemented as the need or opportunity arise. Projects using the facility are either external, with outside collaborators, or internal with NIST staff.

Internal NIST Research

Past work on matrix effects in semicrystalline polymers has been extended to studies of poly(4-methylpentene-1) (P4MP), polychlorotrifluorethylene, and a copolymer of tetrafluroethylene and hexafluoropropylene. P4MP, in particular, has demonstrated a striking temperature effect that parallels the one seen earlier in syndiotactic polystyrene. The formalism for resolving scattering patterns into lamellar and matrix components involves using both the temperature effect and the anisotropy in the scattering pattern from oriented materials. A variety of polymers are investigated to elucidate the role of molecular architecture. Studies of crystallization kinetics and the effect of crystallization temperature on long period provide background data needed to control the processing of these materials.

Improved tools for analyzing SAXS data, culminating in a set of recommendations for the proper treatment of noise and systematic errors, resulted from a detailed study of the statistical properties of the SAXS area detector. Data reduction algorithms should be designed to propagate properly both kinds of errors through the entire process and to present standard deviations arising from both sources of noise in the output data sets. These insights are being applied to standardization activities currently under way within the worldwide SAS community.

A lack of methods for describing the morphology of anisotropic scatterers has been a major difficulty for industrial users of SAS. This project has attempted to address this need by carrying out Monte Carlo simulations combined with SAXS experiments on track-etched membranes. The analysis of these results has shown how to construct basis functions to jointly describe the orientation texture and the distribution of particle size parameters in this model system. Work is currently underway to devise procedures for using these basis functions in fitting procedures designed to provide numerical descriptions of the morphology of the model system. Future work is expected to extend these methods to the description of morphology in semicrystalline polymers that are important for commercial applications.

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 Air Products and Chemicals Company (microstructure of high performance polyurethanes) and Exxon Corp (characterization of matrix effects in lamellar microstructures). Proprietary measurements in which the industrial client is interested in protecting sensitive data were performed by Zimmer Corporation. A continuing collaboration with the University of Maryland examines processing methods for producing oriented block copolymers as starting materials for nano-engineered polymer products.

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

- Proprietary usage beam time was provided to Zimmer Corporation.

- In collaboration with University of Maryland researchers, it was demonstrated 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 depending on cooling history.

- Recommended standards for inclusion of statistical errors in SAS data sets were provided to task groups of the Commission on Small-Angle Scattering of the International Union of Crystallography.

Outputs

Publications

J.D. Barnes, *Small-Angle Scattering for the Industrial Plastics Laboratory - An Overview*, ANTEC 98, Proceedings of the Society of Plastics Engineers, Annual Technical Conference, **II**, 2048-2051 (1998).

S. Musselmman, T. Santusosso, J. D. Barnes, and L. E. Sperling, *Domain Structure and Interphase Dimensions in Poly(urethaneurea) Elastomers using DSC and SAXS,* J. Polym Sci, Physics Edition, submitted.

Presentations

J.D. Barnes and T. J. Prosa *Statistics in Area Detector Data Analysis*, New opportunities for Better User Group Software workshop, Argonne Natl. Lab, Argonne, IL, November, 1997.

J.D. Barnes and T. J. Prosa, *Statistics in Area Detector Data Analysis*, Collective Aid for Nomadic Small-Angle Scatterers workshop, ILL/ESREF, Grenoble, France, Februar,y 1998.

J. D. Barnes, *Small Angle Scattering in the NIST Polymers Division*, University of Hamburg/EMBL, Risoe Natl Lab, ESRF, Hamburg, Germany, January, 1998.

J. D. Barnes, *SAS Characterization of Polymers - An Overview*, University of Maryland Materials and Nuclear Engineering Departmental Seminar, College Park, MD, March, 1998.

J. D. Barnes, *Small-Angle Scattering for the Industrial Plastics Laboratory - An Overview*, Society of Plastics Engineers ANTEC 1998, Atlanta, GA, April, 1998.

J. D. Barnes, *Data handling for Small-Angle Scattering*, American Crystallographic Assn workshop, Arlington, VA, July 18, 1998.

T. J. Prosa and **J. D. Barnes**, *Lamellar vs.. Supramolecular Structure in Semicrystalline Polymers*, American Crystallographic Assn, Arlington, VA, July 19, 1998.

J. D. Barnes, *Small Angle Scattering in Polymer Processing and Characterization* American Chemical Society Division of Polymeric Materials Science and Engineering Workshop, Boston, MA, August, 1998.

J. D. Barnes, *Lamellar vs. Supramolecular Structure in Semicrystalline Polymers*, ACS PMSE Symposium on Scattering in Polymers, Boston, MA, August, 1998.

T. J. Prosa and J. D. Barnes, *SAXS Characterization of Anisotropic Microstructures: Polycarbonate Track-Etched Films*, American Crystallographic Assn, Arlington, VA, July 19, 1998.

Standardization and Organizational Activities
J. D. Barnes - Chair, Commission on Small-Angle Scattering of the International Union of Crystallogrpahy

J. D. Barnes - Member, International Advisory Committee for XIth World Congress on Small-Angle Scattering, Brookhaven Natl Lab, May 16-20 1999.

Nonlinear Viscoelasticity of Solid Polymers

G. B. McKenna and P. A. O'Connell[1]
[1]University of Leeds, U.K.

Objectives

The objectives are: *i.* develop measurement methods to characterize the nonlinear viscoelastic response of solid polymers and *ii.* 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.

- The range of validity of reduced time based nonlinear viscoelastic constitutive laws to the behavior of solid, glassy polymers will be established.

- Fundamental knowledge of the nonlinear viscoelastic response of glassy polymers will be provided.

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

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

Objective

The objective is to test the applicability of time-temperature, time-aging time and time-strain superposition principles to polymer glasses below the glass transition temperature.

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.

Accomplishments

- Time-temperature superposition was shown to be 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. Time-strain superposition at each temperature appears to be valid. However, it is found that the stress relaxation master curves obtained from time-strain superposition are not the same as those obtained from time-temperature superposition.

- Aging of polycarbonate into equilibrium below the glass transition temperature results in the appearance of a non-WLF regime in the shift factor-temperature relationship. This result is in agreement with the recent DiMarzio-Yang theory expectation of a transition from Vogel to Arrhenius behavior in the transport properties; hence no singularity in viscosity is expected near the Kauzmann temperature.

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 **41**, 929 (1997).

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.

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 **37**, 1469 (1997).

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 **37**, 1485 (1997).

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

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, p. 420.

P.A. O'Connell and G.B. McKenna, *Temperature Shift Factors for the Segmental Relaxation of Polycarbonate below the Glass Transition*, Society of Plastics Engineers, ANTEC 98 **II**, 2152-2157 (1998).

Presentations

P.A. O'Connell and G.B. McKenna, *Sub* T_g *Response of Polycarbonate: Deviations of the Equilibrium Response from WLF Expectations*, 69th Annual Meeting of the Society of Rheology, Columbus, OH, October, 1997.

G.B. McKenna, *Physical Aging in Engineering Plastics," and "Time Dependent Properties of Polymers: Long Term Performance and A Framework for Accelerated Testing*, GE Plastics, Mount Vernon, IN, November, 1997.

P.A. O'Connell and **G.B. McKenna**, *Sub-Glass Temperature Dependence of the Segmental Shift Factor for Polycarbonate: Evidence for Arrhenius Behavior*, American Physical Society, Los Angeles, CA, March, 1998.

G.B. McKenna, *Torque and Normal Force Measurements to Characterize the Non-Linear Viscoelastic Response of Solid Polymers*, 2nd International Conference on Mechanics of Time Dependent Materials, Pasadena, CA, March, 1998.

G.B. McKenna and P.A. O'Connell, *Temperature Shift Factors For The Segmental Relaxation of Polycarbonate Below The Glass Transition*, SPE Annual Technical Conference, Atlanta, GA, May, 1998.

Physical Aging and Structural Recovery in Polymers

G.B. McKenna, C.R. Schultheisz, P.A. O'Connell, M. L. Cerrada[1], S.L. Simon[2], M. Vangel[3], A. Rukhin[3], S.D. Leigh[3], B. Lotz[4], C. Straupe[4]
[1]Instituto de Ciencia Y Technologia de Polimieros, Madrid Spain
[2]University of Pittsburgh, Pittsburgh, Pennsylvania
[3]Statistical Engineering Division, NIST
[4]Institute Charles Sadron, Strasbourg, France

Objectives

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

Planned Outcomes

- Provide the scientific and industrial communities with fundamental data and model parameters that describe the physical aging and structural recovery responses of polymeric glasses.

Task 1. Dilatometric Investigation of the Structural Recovery of Polymer Glasses

G.B. McKenna, C.R. Schultheisz, M. Vangel, S.D. Leigh, A. Rukhin, C. Straupe and B. Lotz

Objectives

The objectives are: *i.* to 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. *ii.* to 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 and *iii.* to 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.

Technical Description

i. Kovacs' volume recovery data are fundamental to our understanding of the dynamics of glass formation and polymeric material behavior for considerations of dimensional stability and long term performance. The original Kovacs (1964) dilatometric data were re-analyzed using modern correlation of errors methods to determine if the expansion gap in asymmetry of approach experiments is supported by the data. The existence of the expansion gap is fundamental to the development of models of glassy kinetics.

ii. For an amorphous polymer below its glass transition temperature, rapid temperature changes result in a material that is not in thermodynamic equilibrium, but that evolves (slowly) into equilibrium. This equilibration process can be followed through measurements of a number of properties of the material, such as the volume, enthalpy, birefringence or mechanical stiffness. Previous research in this laboratory and elsewhere suggested different time scales for equilibration of the different properties. If true, it suggests that different properties depend on different aspects of the structure of the polymer, and it also means that mathematical models of the material must be fairly complex (requiring a different "clock" for each property). Direct comparisons of these properties are difficult, because the measurements are typically made on separate samples, leading to questions of homogeneity and equality of thermal histories between samples. The NIST Torsional Dilatometer instrument allows simultaneous measurement of volume recovery and mechanical response to a torsional deformation on the same sample, making direct comparisons possible. The torsional deformation also induces small volume changes and forces along the axis of the cylinder, which are also recorded by the torsional dilatometer.

iii. The time-scale issue for different material response functions has been identified as an important problem in glass dynamics at an international meeting held in Vigo, Spain in the summer of 1997. It was decided at that time to create a research material from the polycarbonate available to NIST through the GM/GE Thermoplastic Engineering Design Project supported by the ATP. NIST agreed to share responsibility for the program with Dr. J.M. Hutchinson of Aberdeen University (UK). The material is to be machined into standard shapes and distributed to laboratories around the world.

Accomplishments

- It was shown that the Kovacs volume recovery data in T-jump experiments to 40 °C exhibit the expansion gap, as originally claimed by Kovacs. The analysis provided a 95 % confidence limit for the values of volume at which the expansion gap exists. However, the data taken at 35 °C were shown to have been taken at time intervals that were larger than at 40 °C. This resulted in very weak correlation of errors for the 35 °C data and a larger uncertainty in the data for the expansion gap. Hence, the 35 °C data could not be used to support the claim for the existence of an expansion gap.

- Replication of previous measurements on a model epoxy system indicates that the volume recovery and the mechanical response to the torsional deformation equilibrate at roughly the same time, as does the axial force on the cylinder. Interestingly, the volumetric response to the torsion is somewhat different from the relaxational behavior of either the torsional or the axial stresses. These experiments have also shown chemical aging of the sample over its 3-year lifetime, as reflected by an order-of-magnitude increase in the time scale for stress relaxation. The chemical aging may be caused by additional curing or by a decrease in the moisture content of the material.

- Polycarbonate material was sent to Aberdeen for sample preparation (Dielectric and calorimetric geometries). NIST samples were successfully prepared (mechanical testing geometries, reserve material). As a back-up, NIST is now preparing the sample geometries originally tasked to Aberdeen.

Outputs

Publications

G.B. McKenna, M.G. Vangel, A.L. Rukhin, S.D. Leigh, B. Lotz and C. Straupe, *The τ-Effective Paradox Revisited: An Extended Analysis of Kovacs' Volume Recovery Data on Poly(vinyl Acetate)*, Polymer, in press.

C.R. Schultheisz and G.B. McKenna, *Volume Recovery, Physical Aging and the Tau-Effective Paradox in Glassy Polycarbonate Following Temperature Jumps*, Proc. NATAS 25th Annual Conference, September, 1997, p. 366.

P. A. O'Connell, C.R. Schultheisz, and G.B. McKenna, *The Physics of Glassy Polycarbonate: Superposability and Volume Recovery*, in <u>The Physics of Glassy Polymers</u>, ed. by A. Hill and M. Tant, ACS books, 1998, in press.

Presentations

G.B. McKenna, M.G. Vangel, A.L. Rukhin, S.D. Leigh, B. Lotz and C. Straupe, *The Expansion Gap in Volume Recovery of PVAc Glass: Kovacs' Data Revisited*, American Physical Society March Meeting, Los Angeles, CA, March, 1998.

C.R. Schultheisz and G.B. McKenna, *Investigations of Nonlinear Material Behavior Using Simultaneous Measurements of Volume Recovery and Physical Aging*, Symposium on Time-Dependent and Nonlinear Effects in Polymers and Composites, American Society for Testing and Materials, Atlanta, GA, May 4-5, 1998.

C.R. Schultheisz and G.B. McKenna, *Investigations of Nonlinear Material Behavior Using Simultaneous Measurements of Volume Recovery and Physical Aging*, 70th Annual Meeting of the Society of Rheology, Monterey, CA, October 4-8, 1998.

G.B. McKenna, *New Perspectives on Glass Forming Systems: Isochoric Behavior," Mini-Symposium on Spin Glass and Structural Glass Dynamics*, University of California, Riverside, Riverside, CA, March, 1998.

D.M. Colucci and **G.B. McKenna**, *Path Dependence of the Viscosity-Temperature Relationship in Polymer Melts: Fragility and Time-Pressure-Temperature Equivalence*, 69th Annual Meeting of the Society of Rheology, Columbus, OH, October, 1997.

Task 2. The Viscoelastic Response of Industrial Materials

G.B. McKenna, M.L. Cerrada, W.H. Han[1], J.M. O'Reilly[2], J. Greener[2], J. R. Gilmore[2], O. Sindt[3], S.L. Simon[3], E. Liang[4]
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[2]Eastman Kodak, Rochester, New York
[3]University of Pittsburgh
[4]General Electric Corporation Research and Development

Objectives

The objectives are *i.* to develop methods of analysis of the aging response of industrial materials that do not follow classical time-aging time and time-temperature superposition, *ii.* to perform experiments to characterize the aging response of industrial polymers, and *iii.* to investigate the impact of state of cure and moisture on the viscoelastic response of thermosets.

Technical Approach

Creep and stress relaxation measurements are been used to study the physical aging response of industrial materials subjected to temperature-jumps and moisture jumps. Experimental techniques are developed to perform experiments on films as thin as 50 μm to assure that diffusion times are short relative to the aging times of interest. Experiments are also performed in torsion for studies of an epoxy during cure and in the fully cured state. The Tool-Narayanaswamy-Moynihan model of structural recovery is extended to consider humidity or moisture impact on aging. Classical time-aging time superposition is used to characterize thermal histories. A model extending time-temperature superposition principles to the case of curing epoxies are also developed.

Accomplishments

- In a collaboration with Eastman Kodak Company, Poly(ethylene naphthalate) (PEN) was shown to be "thermo-rheologically complex" because the α and β relaxations showed different temperature and aging time dependencies in classical aging time experiments. This was true for both amorphous and semi-crystalline materials.

- In conjunction with the collaborative work with Eastman Kodak Company, a new experimental protocol to perform physical aging experiments in "iso-structural" conditions was used to study PEN. It was discovered that, in these conditions, time-temperature superposition is applicable to describe the viscoelastic response of amorphous PEN. Different "structures", however, exhibit different time-temperature master curves.

- The Tool-Narayanaswamy-Moynihan model was successfully extended to describe relative humidity jump experiments in an epoxy glass. Both volumetric and mechanical responses could be described with the model.

- In a collaboration with General Electric Company and the University of Pittsburgh, the evolution of the viscoelastic response of a commercial epoxy thermoset during cure was successfully modeled.

Outputs

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

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

M. L. Cerrada, G.B. McKenna, J.M. O'Reilly, J. Greener and J.R. Gillmor, *Physical Aging Behavior in Amorphous PEN as Measured by Creep*, Society of Plastics Engineers, ANTEC 98 **II**, 2198 (1998).

M.L. Cerrada and G.B. McKenna (1998) *Creep Behavior in Amorphous and Semi-crystalline PEN*, in Time Dependent and Nonlinear Effects in Polymers and Composites, ed. by R.A. Schapery, American Society of Testing and Materials, Special Technical Publication, STP 1357 submitted.

O. Sindt, S.L. Simon, G.B. McKenna, and E. Liang, *Cure, Shrinkage and Properties of an Epoxy Material*, Society of Plastics Engineers, ANTEC 98 **II**, 1658-1662 (1998).

Presentations
W.H. Han and G.B. McKenna, *Structural Recovery in Plasticized Epoxy: First Evidence of a Moisture Induced Memory Effect*, 69th Annual Meeting of the Society of Rheology, Columbus, OH, October, 1997.

M.L. Cerrada and G.B. McKenna, *Viscoelastic and Physical Aging Responses in Amorphous PEN Films*, 69th Annual Meeting of the Society of Rheology, Columbus, OH, October, 1997.

M.L. Cerrada and **G.B. McKenna**, J.M. O'Reilly, J. Greener and J.R. Gillmor, *Physical Aging Behavior in Amorphous PEN as Measured by Creep*, Society of Plastics Engineers, ANTEC, Atlanta, GA, May, 1998.

M.L. Cerrada and G.B. McKenna, *Creep Behavior in Amorphous and Semi-crystalline PEN,* Special Symposium on "Time Dependent and Nonlinear Effects in Polymers and Composites," American Society for Testing and Materials, Atlanta, GA, May, 1998.

O. Sindt, S.L. Simon, G.B. McKenna, and E. Liang *Cure, Shrinkage and Properties of an Epoxy Material*, Society of Plastics Engineers, ANTEC, Atlanta, GA, May, 1998.

G.B. McKenna, *Kinetics in Glass-Forming Liquids*, Phase Transitions in Polymers: Special Symposium Honoring E.A. DiMarzio, NIST, Gaithersburg, MD, November, 1997.

G.B. McKenna, *Kinetic and Viscoelastic Behaviors of Glass Forming Systems*, Polytechnic University of New York, Department of Chemical Engineering, Brooklyn, NY, November, 1997.

G.B. McKenna, *Kinetic and Viscoelastic Behaviors of Glass Forming Systems*, University of Massachusetts Amherst, Department of Polymer Science and Engineering, Amherst, MA, December, 1997.

G.B. McKenna, *Kinetic and Viscoelastic Behaviors of Polymers and Other Glass Forming Systems*, American Chemical Society, Pittsburgh Polymer Group, Pittsburgh, PA, February, 1998.

G.B. McKenna, *Time Dependent Properties of Polymers: Physical Aging, Viscoelasticity, and Their Implications for Long Term Use*, Gemfire Corporation, Palo Alto, CA, March, 1998.

G.B. McKenna, *Kinetic and Viscoelastic Behaviors of Glass Forming Systems*, University of California at Berkeley, Department of Mechanical Engineering, Berkeley, CA, March, 1998.

G.B. McKenna, *Glass Forming Materials: Fundamental Physics and Mechanical Properties*, California Institute of Technology, Materials Science Department, Pasadena, CA, May, 1998.

G.B. McKenna, *The Physics of Nonlinear Viscoelasticity and other Time Dependent Properties of Polymeric Glasses*, Xerox Research Center, Missassagua, CN, July, 1998.

G.B. McKenna, *Time Dependent Properties in Polymeric Glass Formers: Structural Recovery and Its Effect on Mechanical Performance*, University of Guelph, Department of Physics, Guelph, CN, July, 1998.

Task 3. Effects of Structural Recovery and Thermal Lag on Modulated and Dynamic Thermal Measurements

G.B. McKenna and S.L. Simon

Objectives

The objectives are to model the response of polymers to oscillatory thermal signals and to investigate the impact of physical parameters, such as structural recovery, thermal lag, etc. on the interpretation of signals from instruments in which such measurements are made.

Technical Approach

The Tool-Narayanaswamy-Moynihan (TNM) model of structural recovery has been solved for oscillatory thermal histories to address problems in the thermal analysis of glass forming materials. One issue is the impact of structural recovery on the thermal signal obtained in modulated DSC experiments. This problem 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 was solved for typical thermal histories that would be encountered in the thermal analysis laboratory using material parameters for polystyrene (PS) and poly(vinyl chloride) (PVC). By using a Lissajous loop analysis in which heat flow is plotted against the time derivative of temperature (HF vs dT/dt) it was 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 in the analysis that thermal lag in the samples due to simple thermal conductivity can have a significant effect on the data analysis, even for relatively small samples (thickness≈0.2 cm).

The boundary value problem for heat flow between a sample pan and the sample, the important parameter being the heat transfer coefficient, was solved. The impact of a non-infinite heat transfer coefficient on estimates of the thermal conductivity of large samples was then investigated using an approximate solution published in the literature.

Accomplishments

- Model calculations demonstrated that structural recovery in polymeric glasses can dramatically affect the heat flow signal in modulated DSC measurements leading to nonlinear responses that cannot be analyzed by simple linear response theory.

- The Tool-Narayanaswamy-Moynihan model of strucutural recovery was used with values for the material parameters obtained from the literature to predict quantitatively the dynamic heat spectroscopy results on glycerol and poly(vinyl acetate). This demonstrates that the dynamic heat spectroscopy results are a simple manifestation of structural recovery in a high fictive temperature glass.

- It was shown that a published approximate method for the determination of the thermal conductivity using Temperature Modulated DSC can lead to significant (>30 %) errors in the determination of the thermal conductivity.

Outputs

Publications

S.L. Simon and G.B. McKenna, *Interpretation of the Dynamic Heat Capacity Observed in Glass-Forming Liquids*, J. Chem. Phys. **107**, 8678 (1997).

S.L. Simon and G.B. McKenna, *The Effects of Structural Recovery and Thermal Lag in MDSC*, Thermochimica Acta **307**, 1-10 (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, pp. 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, pp. 677-684.

S.L. Simon and G.B. McKenna, *Measurement of Thermal Conductivity using Temperature-Modulated Differential Scanning Calorimetry: Solution to the Heat Flow Problem*, Society of Plastics Engineers, ANTEC 98 **II**, 2042 (1998).

S.L. Simon and G.B. McKenna, *Measurement of Thermal Conductivity using Temperature-Modulated Differential Scanning Calorimetry: Solution to the Heat Flow Problem*, J. Reinforced Plastics and Composites, submitted.

G.B. McKenna and S.L. Simon, *Time Dependent Volume and Enthalpy Responses in Polymers*, in Time Dependent and Nonlinear Effects in Polymers and Composites, ed. by R.A. Schapery, American Society of Testing and Materials, Special Technical Publication, STP 1357, submitted.

G.B. McKenna and S.L. Simon, *The Glass Transition: Its Measurement and Underlying Physics*," in Handbook of Thermal Analysis and Calorimetry, Vol. **3**, ed. by S.Z.D. Cheng, Elsevier, submitted.

Presentations

G.B. McKenna and S.L. Simon, *Time Dependent Volume and Enthalpy Responses in Polymers*, ASTM Symposium on "Time Dependent and Nonlinear Effects in Polymers and Composites," Atlanta, GA, May, 1998.

G.B. McKenna, *Everything (Or Almost) You Always Wanted to Know about the Glass Transition, but Were Afraid to Ask*, Carnegie-Mellon University/University of Pittsburgh Polymer Mini-Symposium, Pittsburgh, PA, March, 1998.

Failure in Polymers and Adhesives

M.Y.M. Chiang, H. Chai[1] and M. Fernandez-Garcia
[1]Tel Aviv University, Israel

Objectives

Develop numerical models of adhesive behavior and validate these with experimental observation. Investigate the effects of aging and environment on the failure and pre-failure behavior of polymers and adhesives.

Planned Outcomes

- Experiments and finite element analyses conducted to demonstrate that mode II fracture can be described by a criterion in which the local strain at the crack tip determines failure.

- Methods of testing and evaluation developed that impact on long term performance evaluation and predictability in polymers, composites and adhesives.

- Correlations established between long term moisture exposure and the mechanical response of commercial adhesives to support ATP focus program on Composites.

- Theoretical models of craze initiation and growth tested by using structural recovery (physical aging) to vary the material's viscoelastic response.

Task 1. The Effect of Strain Rate on the Mechanical Properties of Adhesive Bonds

M.Y.M. Chiang, H. Chai

Objectives

The objectives are to study the effect of strain rates on yielding and failure processes in a commercial adhesive and to correlate the results of this study to those of previous work from this laboratory in which strain rate effects on the crack propagation and interfacial fracture were analyzed within a fracture mechanics framework.

Technical Description

Based on past experience in this laboratory, the "napkin ring" shear test was chosen for the purpose of this task. The specimen for this test is composed of two tubular adherends butted coaxially and joined with the adhesive. Loading is applied with a remote torque. By making the tube wall sufficiently thin, radial variations are minimized. This leads to a state of virtually simple shear within the bond layer. The experimental procedure includes the preparation of napkin ring specimens with controlled bond thicknesses, testing, and then interpretation of the results. Once the adherents are bonded with the adhesive, the specimens are milled in the area of bond. The milled surfaces are then polished, and bond thicknesses measured with an optical microscope. Specimens are tested under torsion at room temperature in dry condition. The adherends were 5086 aluminum alloy while the adhesive was a toughened epoxy (BP-907). The bondline thickness varied from 25 micrometers up to 120 micrometers, with most of the bonds being fairly close to 60 micrometers. The straining rate (loading rate) was varied from 0.001/sec. to 0.25/sec. The specimens were tested in a MTS servo hydraulic testing machine. The shear stress and the shear strain were recorded during the tests.

Accomplishments

- A test fixture to hold the test specimens was prepared. This includes a specimen housing unit, a loading arm and an attachment to adapt the extensometer which is used for establishing a *truly* controlled shear strain in the bond.

- The preliminary results showed that the stress-strain behavior of the material greatly depends on the loading rate, both in the small and in the large deformation regimes.

Outputs

Publications
Chiang, M.Y.M. and Chai, H., *Nonlinear Computational Analysis of Experimentally Measured Crack Growth Along a Polymer-Metal Interface*, the Proceedings of Sixth Pan American Congress of Applied Mechanics (PACAM VI), Rio de Janeiro, Brazil, January, 1999.

Chiang, M.Y.M., Kuo, A. and Chen,W., *Stress Intensity Solutions for Plastic IC Package Delamination*, ASME Journal of Electronic Packaging, submitted.

Presentations
M.Y.M. Chiang and H. Chai, *Finite Element Analysis and Experimental Monitoring of Strain Localization and Failure Processing of Thin Adhesive Bonds* International Conference on Polymer Characterization, Denton, TX, January, 1998.

M.Y.M. Chiang and H. Chai, *Stable Interfacial Crack Extension in Polymeric Adhesive Bonds Under Shear,* AIChE 1997 Annual Meeting, Los Angeles, CA, November, 1997.

Task 2. Hygrothermal Aging Studies of a Commercial Structural Adhesive

M.Y.M. Chiang, M. Fernandez-Garcia

Objectives

The objectives are to characterize the hygrothermal aging of a commercial epoxy-based adhesive in adhesive joints with different bond thicknesses and to identify the failure mechanisms induced by the hygrothermal aging of the adhesive.

Technical Description

Increased use of adhesive bonding in structural components has renewed interest in the analysis of adhesive joints, taking into account the diffusion of moisture in the adhesive layer. Diffusion of moisture or solvent into the adhesive can significantly change the stress field and hence the reliability of the bond joints. Therefore, this research involves the disciplines of polymer science and applied mechanics, where the former addresses effect on the micro-level and latter is related to macro-response. A further goal of this project is to examine the effect of moisture on the failure behavior of highly constrained thin adhesive layers.

The adhesive used in this study is an epoxy-based structural adhesive supplied by 3M Corporation (3M 5024). Free-standing films of adhesive, 300 μm thick, have been produced by curing the epoxy between Teflon sticks in a pressure vessel at 130 °C and 1.38 MPa (200 psi) for 13 h. DSC experiments have demonstrated that the curing time, being much longer than recommended by the manufacturer, does not cause any alteration such as degradation or aging. After curing, the film is cut to dimensions of *ca.* 40 mm x 6 mm x 0.3 mm. Specimens are hygrothermally exposed in distilled water baths at constant temperatures of 30 °C, 35 °C, 40 °C, 45 °C, 50 °C and 70 °C. The specimens are taken from the baths at different times, water on the surface of specimens is removed by using a dry, clean paper towel, specimens are weighed and the mass uptake is determined.

Accomplishments

- Preliminary results of absorption and reabsorption at the temperatures studied showed that the water uptake did not follow Fickian diffusion which can be represented by a time-dependent mathematical model. The time scale for the mechanical relaxation at higher temperature is similar to that for water uptake. Consequently, their interaction significantly extends the time scale to reach the equilibrium.

- The observed increase in the rate of sorption in the previously absorbed specimens (reabsorption process) compared with dry specimens (absorption process) reflects the effect of this time-dependent reconfiguration of the polymeric molecules.

Outputs

Publications
M. Fernandez-Garcia and M.Y.M. Chiang, *Hygrothermal Aging Studies of A Commercial Structural Adhesive*, Proceedings of the Adhesion Society 21st Annual Meeting, February, 1998.

Presentations
M.Y.M. Chiang and M. Fernandez-Garcia, *Water Absorption and Desorption in a Structural Adhesive*, The Adhesion Society's 21st Annual Meeting, Savannah, GA, February, 1998.

Task 3. Measurement of Craze Initiation and Growth in Polymers

G.B. McKenna, M. Delin[1]
[1]Chalmers University of Technology, Goteborg, Sweden

Objectives

The objectives are *i.* to develop instrumentation and methods to investigate the craze initiation and growth responses during physical aging and *ii.* to determine the impact of physical aging on crazing in polymeric glasses.

Technical Approach

This project is based on the premise that crazing is a process that depends very strongly on the viscoelastic response of the glassy polymer under study. It is already known that temperature can have large effects on craze initiation and growth. Here the viscoelastic response will be altered by changing both temperature and aging time. Altering the aging time permits isothermal changes in the 'glassy structure'. Craze initiation and growth can be studied using special fixtures to provide equibiaxial and uniaxial loading in creep conditions and uniaxial loading in stress relaxation conditions.

Accomplishments

- A transition in craze growth rate (in logarithmic time) was discovered in stress relaxation conditions for a styrene-acrylonitrile copolymer. The logarithmic craze growth rate was found to decrease dramatically over a very narrow range of aging times. The magnitude of the logarithmic growth rate decreases by approximately a factor of five in going from below to above the transition aging time. It was also found that the aging time at the transition decreases as the temperature increases.

- The transition in craze growth rates was predicted, approximately, using the modified meniscus instability model developed originally by Kramer.

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 **37**, 1442 (1997).

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, p. 436.

M. Delin and G.B. McKenna, *Craze Growth in Stress Relaxation Conditions: Effects of Physical Aging*, SPE ANTEC, 1668 (1998).

Presentations

M. Delin and **G.B. McKenna**, *Craze Growth in Stress Relaxation Conditions: Effects of Physical Aging*, Society of Plastics Engineers ANTEC, Atlanta, GA, April, 1998.

M. Delin and G.B. McKenna, *Impact of Physical Aging on Craze Growth under Stress Relaxation Conditions*, 69th Annual Meeting of the Society of Rheology, Columbus, OH, October, 1997.

M. Delin and G.B. McKenna, *The Craze Growth Response in Stress Relaxation Conditions for a Styrene-Acrylonitrile Copolymer During Physical Aging*, ASTM Symposium on "Time Dependent and Nonlinear Effects in Polymers and Composites," Atlanta, GA, May, 1998.

Rheological Characterization of Polymer Dynamics

G.B. McKenna, C.R. Schultheisz, V. Rouiller[1], and V. Soulivong[2]
[1]NIST Guest Researchers from Houdemont, France
[2]Universite Louis Pasteur, France

Objectives

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

Task 1. Develop a Nonlinear Fluid Standard

G.B. McKenna and C.R. Schultheisz

Objective

The objective is to develop and thoroughly characterize a non-Newtonian fluid that can be used as a benchmark to measure the performance of rheometers in situations involving complex fluids.

Technical Description

Polymeric fluids, such as polymer melts and solutions, often do not follow the simple Newtonian ideal in their flow behavior. Such fluids are found in numerous applications 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 (SRM 2490) will provide a means for comparing the performance of different instruments, as well as a tool for research into better methods of measuring the rheological properties of polymeric fluids. 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-rate viscosity.

The new fluid supersedes the previous Standard Reference Material 1490 Nonlinear Fluid Standard, which was composed of a high-molecular- mass polyisobutylene dissolved in normal 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 hexadecane, which has a melting point of 18 °C (64 °F). The new fluid will consist of a high-molecular- mass polyisobutylene dissolved in 2,6,10,14-tetramethylpentadecane (pristane). The pristane is a branched alkane of a slightly higher molecular mass than the normal hexadecane; the branching prevents crystallization or vitrification down to -60 °C, while the higher molecular mass reduces the rate of evaporation of the pristane as compared to the normal hexadecane.

This project will 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 properties are acceptable to the community, and will provide information regarding the laboratory-to-laboratory variability in the measurements. The Statistical Engineering Division at NIST will be involved in evaluating the results of the round robin.

External Collaborations

Instrument Manufacturers

- ATS RheoSystems
- Bohlin Instruments
- Brookfield Engineering Laboratories
- Paar Physica
- Rheometric Scientific
- TA Instruments

Capillary Rheometer
Goettfert
Haake
TherMold Partners
Vilastic Scientific

Industrial Users

DuPont
Fluid Dynamics
National Starch and Chemical
Procter and Gamble

Universities

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 produced, and the process to produce and package the material for sale is underway. A new rheometer, with improved normal force measurement capability, has been acquired. Industry interest in the new fluid and expressed interest in participation in the round robin has been high.

Outputs

Publications

C.R. Schultheisz and G.B. McKenna, (1998) *A Nonlinear Fluid Standard Reference Material: Progress Report*, Society of Plastics Engineers, ANTEC 98 **II**, 2162-2166, (1998).

Presentations

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

C.R. Schultheisz and G.B. McKenna, *A Nonlinear Fluid Standard Reference Material: Progress Report*, SPE ANTEC, Atlanta, GA, April, 1998.

C.R. Schultheisz and G.B. McKenna, *A Nonlinear Fluid Standard Reference Material: Progress Report*, 70th Annual Meeting of the Society of Rheology, Monterey, CA, October, 1998.

C.R. Schultheisz and G.B. McKenna, *Thermal Expansion of the Force Rebalance Transducer in a Rheometric Scientific ARES Rotary Rheometer*, 70th Annual Meeting of the Society of Rheology, Monterey, CA, October, 1998.

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

G.B. McKenna and V. Rouiller

Objectives

The objectives are to apply the hybrid-VL-BKZ theory to the viscoelastic response of polyurethane foams, and to measure and model the behavior of the polyurethane materials as a function of temperature and moisture content.

Technical Approach

In the past, a hybrid VL-BKZ model has been successfully used in our laboratory to describe the nonlinear viscoelastic response of polymeric melts. The same approach is applied to investigate and model the nonlinear response of polyurethane elastomers.

Accomplishments

- The hybrid VL-BKZ model has been implemented such that the stress response to multiple step and trapezoidal deformation histories can be described within approximately 20 %. In addition, a computer program has been developed to calculate creep loading histories. Comparison with experimental results provides good agreement for complicated loading histories.

Outputs

Publications

V. Rouiller and G.B. McKenna, *A Viscoelastic Constitutive Model for the Creep Response of Polyurethane Rubber.* (Progress Report for the Period September, 1996 to December, 1997), NISTIR 6177, August, 1998.

V. Rouiller and G.B. McKenna, *A Hybrid Nonlinear Constitutive Model: Comparisons with Multiple Step Data for a Polyurethane Rubber*, Society of Plastics Engineers, ANTEC 98 **II**, 2138-2143, (1998).

J.M. Niemiec, V. Rouiller, G.B. McKenna, J. Sweeney, and I.M. Ward, *Prediction of Uniaxial Extension, Pure Shear, and Equibiaxial Responses in Constant Deformation Rate Experiments from Single Step Stress Relaxation Experiments in Uniaxial Extension*, J. Rheology, submitted.

Presentations

V. Rouiller and G.B. McKenna, *A Hybrid Nonlinear Constitutive Model: Comparisons with Multiple Step Data for a Polyurethane Rubber*, Society of Plastics Engineers, ANTEC, Atlanta, GA, May, 1998.

V. Rouiller and G.B. McKenna, *Viscoelastic Response of Polyurethane Elastomers*, 69th Annual Meeting of the Society of Rheology, Columbus, OH, October, 1997.

G.B. McKenna, *A Hybrid Valanis-Landel/BKZ Constitutive Model for Rubber and Polymer Melts*, Carnegie Mellon University, Department of Chemical Engineering, Pittsburgh, PA, February, 1998.

Task 3. Melt and Solution Nonlinear Rheology

G.B. McKenna, C.R. Schultheisz, V. Soulivong

Objective

The objective is to characterize the dependences of viscosity and first normal stress difference for model polyisobutylene and polystyrene systems as functions of concentration and temperature.

Technical Approach

Molecular rheology has been well investigated over the years in the domain of the linear viscoelastic response. In particular, the reptation theory has proven highly successful in dealing with many aspects of polymer melt dynamics. On the other hand, the nonlinear response of materials and, especially, the concentration dependence of the polymer solute is less well investigated. Here soluitions of polyisobutylene dissolved in 2,6,10,14-tetramethylpentadecane (the material to be used as the nonlinear fluid standard) will be made and the effects of concentration on the material functions will be examined. Second, solutions of monodisperse polystyrene in ortho-terphenyl will be used to investigate the impact of concentration and molecular mass on the time-dependent strain potential function (BKZ theory) and the damping function (Doi-Edwards theory).

Accomplishments

- Methods have been established for producing solutions of polystyrene in ortho-terphenyl and preliminary tests have been performed.

- The rheometer to be used for the polyisobutylene solutions has been shown to have a vibrational problem when high viscosity samples are placed in the cone and plate and narrow gap parallel plate geometries. The problem is being fixed by the manufacturer.

General Outputs in Rheology

Publications

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, in press.

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. **107,** 3645-3655 (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 Behavior*, SPE ANTEC **II**, 1027 (1997).

Calorimetric Measurement of the Glass Transition in Nano-scale Confined Geometries

McKenna, G.B. and Park, J.Y.[1]
[1]Korea Advanced Institute of Science and Technology

Objectives

The objective is to make the first calorimetric measurements of the effect of size and confinement on the glass transition of polymer chains imbibed into nano-meter scale porous glasses.

Technical Approach

The glass transition in confined geometries in films and porous materials is currently of great interest both scientifically and industrially. The approach adapted follows that developed previously in this laboratory; fluids were imbibed into control pore glasses to investigate the effect of size and confinement on phase transitions. The prior work was performed with organic, small molecules. The large size of polymer chains and their high viscosity makes it difficult to get the chains into the (10-50) nm size pores of interest. Consequently, the experiments are performed in solution where known concentrations of polystyrene in ortho-terphenyl are imbibed into the porous glasses. The glass transition is measured using conventional differential scanning calorimetric approaches.

Planned Outcomes

- Measurements will show the impact of size and confinement at the nano-meter scale on the calorimetric glass transition of polymer solutions.

- Concentration and molecular architecture effects on the glass transition of polymer solutions in nano-meter size pores will be established.

- The effect of pore size on the structural (enthalpy) recovery of vitrified polymer solutions will be established.

Accomplishments

- Measurements of the glass transition for solutions of a 100,000 molecular mass polystyrene in ortho-terphenyl imbibed into pores having sizes from approximately 10 nm to 50 nm have been made. Concentrations ranged from c* to 4 c*.

Outputs

Presentations

G.B. McKenna, *Kinetics in the Vicinity of the Glass Transition: Some Old Results and Some New Perspectives*, Canadian Association of Physicists, Annual Meeting, Waterloo, CN, July, 1998.

Theory and Modeling of the Ten Polymer Phase Transitions

E. A. Di Marzio

Objectives

The objectives are *i.* to discover, classify and understand all the polymer phase transitions, *ii.* to determine how these couple to one another, *iii.* to use polymer phase transitions as models for self-assembly, and *iv.* to investigate the coupled phase transitions as technology opportunities.

Technical Description

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.

Planned Outcomes

- Methodology will be developed for classifying phase transitions in polymers.

Accomplishments

- A tenth polymer phase transition, a polymer molecule threading a membrane separating two solutions, has been discovered. The transition is first-order. In addition, an important insight was obtained which shows why linear macromolecules display phase transitions in abundance. Other transitions are: The polymer adsorption transition (2nd-order); the helix to random coil transition (diffuse-order for polypeptides, 2nd-order for DNA, 1st-order for Collagen); the collapse transition (1st and 2nd-order); equilibrium polymerization (2nd-order).

- The number of coupled phase transitions was determined. The 10 classes of polymeric phase transitions result in 1013 *a priori* possible coupled phase transitions.

- The extent to which self-assembly in polymeric systems can be viewed as thermodynamic phase transition phenomena was investigated . 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).

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DENTAL AND MEDICAL MATERIALS PROGRAM

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 objective of this program is the development of improved dental and medical materials that have greater durability, wear resistance and clinical acceptability, with the main program focus on dental restorative materials.

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

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

The occupational and environmental hazards associated with the use of mercury-containing dental alloys are a recurring source of public concern. Since dental amalgams have performed exceedingly well over more than one hundred years, the development of a direct filling material still based on the common constituents of dental amalgams, other than mercury, is desirable. 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.

Besides the dental materials projects, efforts are directed toward the development of improved bone fixation materials and the evaluation of biomaterials. A project, carried out in collaboration with the American Dental Association and the National Institute of Dental Research, is directed at enhancing the biocompatibility and mechanical properties of composite bone cements. The biomaterials evaluation effort centers on the NIST Orthopedic Wear Consortium which consists of four companies to develop accelerated wear test procedures for rapid screening of materials used in hip and knee replacements. This will accelerate the introduction of new biomaterials into practice.

Dental and medical research directions in support of the goals are established in collaboration with the American Dental Association (ADA), the National Institute of Dental Research, the National Heart, Lung and Blood Institute, the US Food and Drug Administration, 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 30 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 series of highly fluorinated dimethacrylate monomers were prepared and evaluated in homopolymerization studies. Dental composites with enhanced durability and color stability may result from several of the new fluoropolymers that combine excellent mechanical strength with extreme hydrophobicity.

- A near-infrared analytical technique was developed to allow the determination of bulk polymerization conversion on dental resin and composite specimens. This provides a nondestructive method to analyze conversion directly on a variety of test specimens such as flexural strength bars or water sorption disks.

- An effective dental bonding system for both enamel and dentin was developed based on mineral acid-modified phenyliminodiacetic acid. In addition, it was demonstrated that methoxy ring substitution significantly enhanced the polymerization-initiating properties of phenyliminodiacetic acid without adversely affecting its self-etching and priming abilities. The ability to enhance both the etching and polymerization-initiating ability of phenyliminodiacetic acid permits the development of simplified, highly effective adhesive systems for the entire tooth structure.

- Further modification in the microbond test has led to the successful development of a micro-shear bond test for studying dental adhesion of extremely small bonded areas. This new test facilitates surface and depth profile mapping of tooth structure, and reduces the need for extracted teeth in the evaluation of dental adhesive systems.

- Fluorescent probes were successfully used for cure monitoring of dental bonding resins and bone cements. Improved products will result from the addition of one of the probes to dental bonding resins or bone cements.

- A new accelerated wear resistance machine was developed in collaboration with the Ceramics Division and the University of Maryland under a NIST research consortium formed by CRADAs with four orthopaedic companies: Biomet Inc. and Zimmer Inc, both of Warsaw, Ind.; Johnson & Johnson Professional Inc., Raynham, Mass.; and Oesteonics Inc., Allendale, New Jersey. The new test machine allows for evaluation of new orthopaedic joint materials in five days or less, under a variety of loads, load-cycle and motion conditions promises to hasten the introduction of longer lasting hip, knee, and other orthopaedic joint implants to the market. As a result of this successful development, the four companies elected to seek extension of their CRADAs to September 30, 2000.

Dental Resins Based on Fluorinated Monomers and Oligomers

Jeffrey W. Stansbury

Objective

The objective of this project 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, more hydrolytically stable polymers and interfacial layers to enhance the resistance of composite restoratives to the challenging oral environment.

The use of ring-opening spiro orthocarbonate (SOC) monomers, which can produce expansion during polymerization, and monomers with bulky spacer groups that limit the density of reactive groups can provide photocurable resins that offer low shrinkage and good mechanical strength properties. The introduction of organofluorine substituents in the monomers allows the formation of inert polymers that repel not only water, but a wide range of chemicals that can potentially degrade or stain polymer-based dental restorations. Structural alterations to increase the hydrophobicity of the 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, who had been working under a NIDR-supported contract between NIST and the University of California, Irvine, completed her portion of the project to develop new fluorinated resins and composites.

Dr. Chetan Khatri is presently working on urethane-containing methacrylate monomers under a contract between NIST and the University of Massachusetts.

Professor Chris Bowman of the Chemical Engineering Department at the University of Colorado in Boulder is collaborating on projects involving photopolymerization cure kinetics and development of new methacrylate monomers.

Dr. Hidekazu Takahashi of Tokyo Medical and Dental University is involved with durability studies of fluorinated resins and composites.

Planned Outcomes

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

- Development of organofluorine-containing dental composites with less than 1/10th the water uptake of conventional materials. Expect more durable composites that retain their excellent initial properties during prolonged exposure to challenging environments.

- Improve understanding of structural factors of methacrylate monomers that control their photopolymerization kinetics, comonomer interactions and network development.

Accomplishments

Fluorinated resins and composites: New fluorinated monomers were prepared and evaluated in homopolymerization studies. Amorphous dimethacrylate monomers with perfluoroalkane segments of C_4 to C_{10} had viscosities suitable for use as hydrophobic diluent comonomers but with low mechanical strength properties. Novel fluorinated dimethacrylates with aromatic core groups produced photocured homopolymers with high flexural strengths as well as low levels of water uptake. Unlike prior examples of fluorinated oligomers, which showed significant mechanical reinforcement due to urethane group hydrogen bonding interactions, the addition of urethane functionality in fluorinated dimethacrylate monomers did not provide significant mechanical property improvements. Further, the presence of the polar urethane groups led to unacceptable levels of water uptake in the polymers.

Photopolymerization kinetics of methacrylate resins: Resin viscosities and hydrogen bonding interactions were examined using rheometric and FT-IR analyses. The photopolymerization reaction rate shows a clear dependence on resin viscosity, which originates primarily from hydrogen bonding interactions. In addition, structural variations among the different methacrylate monomers examined influence other factors, such as diffusion, cross-linking potential and possibly polymerization reaction pathways. These factors combine to provide significantly different kinetic profiles for the various dental resins studied.

Variations in coreactivity of dental monomers: A study of Bis-GMA/TEGDMA and urethane dimethacrylate/TEGDMA resins was conducted to determine the compositional drift that occurs during the photo-activated, cross-linking copolymerization of these widely used materials. The photopolymerization of unfilled resins was controlled by varying the irradiation time to give polymers with conversions ranging from 20 % to 80 %. The extraction residues from the resulting polymers were analyzed by FT-IR and NMR to determine the composition of the sol fraction (and by difference the composition of the gel fraction). The results show that at all stages of the copolymerization, TEGDMA is more reactive than either Bis-GMA or UDMA but that the reactivity bias with Bis-GMA, which has a more limited diffusion potential than UDMA, is particularly pronounced. This has implications as to the network structures of the resulting cross-linked polymers. It is also critical information for evaluation of data concerned with the evolution of physical properties during the course of the polymerization. This extraction technique can provide useful information on the coreactivity of fluorinated monomers with conventional dimethacrylate comonomers.

Near-infrared analyses of dental resins: A near-infrared (NIR) analytical technique was developed to determine bulk polymerization conversion of dental resins and composites with specimen geometries of approximately 0.5 mm to >5 mm rather than the typical thin film or KBr pellet sampling approaches. There is a significant exotherm that accompanies the rapid photopolymerization of methacrylates in bulk samples that is not accounted for in the thin film conversion measurements dictated by the traditional mid-IR technique. The NIR technique can be applied to samples with dimensions that are practical as models for actual dental restorations. This approach offers a new method for direct study of the influence of filler on conversion in composites. At the same time, a separate region of the near-IR spectrum provides valuable information about the water content and the hydrogen bonding interactions of water within the polymeric network.

Polymerization kinetics of urethane-based methacrylate monomers and oligomers: Photo-differential calorimetry was used to examine the polymerization kinetics of resins based on either a commercially available urethane dimethacrylate monomer (UDMA) or a series of experimental urethane-containing monomers and oligomers. The results demonstrated that the smaller UDMA monomer had slightly higher polymerization reactivity than the experimental monomers with the bulky aliphatic core urethane group based on the high molecular mass diisocyanate DDI. Addition of an aromatic substituent near the terminal methacrylate groups did not decrease reactivity. Resins from the experimental urethane monomers had significantly greater degrees of conversion than UDMA resins. The resins based on a multifunctional urethane oligomer had similar reactivities to those of the urethane monomers. This is preliminary work that can be applied to the fluorinated urethane monomers and oligomers in our NIDR proposal.

Impact

The provisional patent filed in 1996 on the new fluorinated resins was converted to a full patent filing in November 1997. A dental materials producer has expressed interest in the fluorinated monomers as alternatives to Bis-GMA based dental resins. This same company is currently conducting internal evaluations of some spiro orthocarbonate oligomers for low shrinking dental resins. The work on the coreactivity of dimethacrylate monomers in cross-linking polymerizations is the first in this area.

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J. M. Antonucci, J. W. Stansbury, and B. O. Fowler, *Novel methods and compositions for the preparation of silyl derivatives of resins.* Provisional patent application filed December 1997.

Dental Composites with Improved Interfaces

Joseph M. Antonucci, Walter G. McDonough, and Joy P. Dunkers

Objective

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

Technical Description

Microbond Test: It is anticipated that improvements in the quality of the interfacial phase, along with similar improvements in the polymer matrix and filler phases will result in dental composites of improved performance and service life. In addition to the use of traditional mechanical tests as a means of measuring interfacial strength, two single fiber tests, the microbond test and the single fiber fragmentation test, have also been used to assess interfacial behavior. Previously it was shown that the microbond test can 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 adapted to assess the interfacial shear strength between dental polymers and flat substrates such as quartz slides and sliced specimens of dentin and enamel.

Development of a Micro-Shear Test for the Study of Dental Adhesion: It is common in many dental adhesion studies to employ a shear bond test as a method of assessing the strength of the interfacial bond between enamel or dentin and adhesive dental materials. In these tests, bonding areas of about 12-14 mm^2 are typically used. With the modified microbond test, bonded areas of 1.5-3.2 mm^2 can be studied. Recent experiments with both commercial and experimental adhesive materials have shown that it is feasible to employ the microbond test apparatus to study bonding at multiple sites on one flat tooth specimen of enamel and dentin. Such adhesive studies are difficult, if not impossible, with conventional shear adhesion tests. The ability of the micro-shear test to perform adhesive mapping of heterogeneous substrates such as dentin has obvious advantages. It can also be used to study adhesion in small, less accessible regions of tooth structure, e.g., proximal areas. The micro-shear bond test also is expected to facilitate depth profile and durability adhesion studies. A major advantage of the micro-shear bond test is that it reduces significantly the need for extracted teeth to conduct *in vitro* adhesion studies. Future studies are planned with more homogeneously characterized substrates (e.g., metals, porcelain) and to explore the relationship between the size of the bonding area and interfacial strength. Surface analysis studies of debonded surfaces using scanning electron microscopy and FT-IR microscopy also are planned.

Single-Fiber Fragmentation Test: 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 suggest that this approach may obviate this problem.

Synthesis of Oligomeric Organosilsesquioxanes: There has been increasing interest in organosilsesquioxanes, especially those that are oligomeric or polymeric, and those that can be further polymerized. The generic structure of organosilsesquioxanes can be represented by the empirical formula $(RSiO_{1.5})_x$, where R is an organic substituent and x designates the number of repeat units in what is often a complex molecular structure. In previous studies, controlled hydrolysis-condensation reactions of trialkoxysilanes such as 3-methacryloxypropyltrimethoxysilane were used to synthesize reactive oligomers having basically $(RSiO_{1.5})_x$ structures. These oligomers were characterized by FT-IR and nuclear magnetic resonance (NMR) and also shown by gas permeation chromatography (GPC) to have a broad distribution of molecular weights (polydispersity = 3.51) and $M_w \sim 7000$. Recently, the complex, three dimensional structure of a methacrylic organosilsesquioxane has been studied by MALDI (Matrix Assisted Laser Desorption Ionization) time-of-flight (TOF) mass spectroscopy. Analysis of the mass spectral data suggest that this $(RSiO_{1.5})_x$ has significant elements of ladder structure with some linear branched and polyhedral structure as well (see Mass Spectrometry of Polymers, Charles Guttman et al.) The methacrylic functionalized oligo-silsesquioxanes are readily polymerized by free radical methods to yield clear, hard, cross-linked polymers and are undergoing evaluation in dental resin systems and composites.

In an effort to understand the influence of the organic substituent, R, on the molecular structure and properties of $(RSiO_{1.5})_x$, several types of organosilsesquioxanes have been synthesized and characterized by FT-IR and ^{1}HNMR spectroscopies. MALDI TOF mass spectrometric analysis of these new $(RSiO_{1.5})_x$ are planned. Of especial interest has been the synthesis of oligomeric organofluorosilsesquioxanes from commercially available fluoroorganosilane agents. By co-oligomerization of fluoroorganosilanes with methacrylic silane agents, it appears feasible to synthesize methacrylic organofluorosilsesquioxanes.

Synthesis of Silylated Resins: In a related research initiative, it was demonstrated that simple exchange (transetherification) reactions between hydroxylated monomers such as BIS-GMA and organotrialkoxysilanes such as 3-methacryloxypropyltrimethoxysilane were feasible routes to silylated resins. Characterization by FT-IR and ^{1}HNMR spectroscopies indicate that a significant number of hydroxyl groups of BIS-GMA have been converted to silyl ether groups. The extent of the transetherification appears to be amenable to control by proper selection of reactant composition and reaction conditions. This facile silylation technique can be adapted for the preparation of new types of silane coupling agents. Other applications include self-adhesive sealants, coatings and matrix resins. An invention disclosure has been submitted.

External Collaboration

B. O. Fowler, a Guest Scientist from the Craniofacial and Skeletal Diseases Branch of the National Institute of Dental Research is assisting in the characterization of the silsesquioxanes and silylated resins.

Dr. Hidekazu Takahashi of the Department of Dental Technology of the Tokyo Medical and Dental University is assisting in the mechanical property evaluation of experimental composites.

Dr. Yasushi Shimada of the Department of Operative Dentistry of the Tokyo Medical and Dental University is actively assisting in the evaluation of new dental adhesive systems and the development of a microshear bonding test.

Accomplishments

By further refinements of the microbond test, a micro shear bond test capable of studying dental adhesion of extremely small bonded areas, and that permits surface and depth profile mapping of mineralized tissue substrates has been developed.

Facile syntheses of organofluorosilsesquioxanes and methacrylic organo-fluorosilsesquioxanes from readily available silane coupling agents were developed. These reactive oligomers are readily polymerized by free radical methods and have potential for use in dental composites, coatings, sealants and adhesives. These fast curing resins are expected to yield polymers with low dielectric properties and high resistance to aggressive chemical environments. Polymers with these properties also may be suitable for electronic packaging applications.

Facile silylation techniques for converting hydroxylated monomers to their silyl derivatives were developed. There novel resins are expected to have self-adhesive properties and be suitable for potential applications in composites, coatings, sealants and adhesives.

Impact

An invention disclosure based on the synthesis of silylated resins has been submitted. These novel resins have potential as self-adhesive matrices for use in composites, coatings and sealants. This technology also permits the facile preparation of improved types of silane coupling agents.

Outputs

Publications

W. G. McDonough, J. M. Antonucci, and J. P. Dunkers, *Evaluation of Dental Adhesion and Durability by Means of the Microbond Test*, Proceedings of the 21st Meeting of the Adhesion Society, Savannah, GA, Feb. 22-25, 1998, pp. 129-131.

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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

Previously it was shown that the application of aqueous acetone solutions of N-phenyliminodiacetic acid (PIDAA) to dentin both etches and activates the dentinal surface for subsequent polymerization of photoactivated adhesive resins. With this simple two-step bonding protocol strong composite-to-dentin 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 order to make the PIDAA bonding system applicable to enamel as well as dentin, a study was initiated to determine the effect of adding mineral acids to this self-etching primer. With phosphoric acid-modified PIDAA, relatively poor bonding to both enamel and dentin occurred. By contrast, nitric acid-modified PIDAA gave excellent bonding to both enamel and dentin. Other types of acid-modified PIDAA systems are currently under study. In addition, in order to gain further insight into the etching, priming and polymerization-initiating properties of PIDAA, several analogs of PIDAA have been synthesized and characterized. It was found that methoxy ring substituents enhanced the polymerization-initiating properties of PIDAA without adversely affecting its self-etching and priming properties. Presumably the electron-donating-methoxy group enhances the electron density of the nitrogen of the substituted PIDAA thereby enhancing its initiating potential.

External Collaborations

Dr. Eichmiller, Dr. Farahani and Dr. G. E. Schumacher, Guest Scientists from Paffenbarger Research Center are assisting in the evaluation of new adhesive systems for dentin and enamel.

Dr. T. Nikaido a guest scientist from the Tokyo Medical and Dental University is assisting in the evaluation of new dental adhesive systems.

Dr. Chetan A. Khatri, a Guest Scientist from the University of Massachusetts, is actively advancing the synthetic aspects of the adhesion studies under an NIDR supported contract between NIST and the University of Massachusetts.

Accomplishments

N-phenliminodiacetic acid (PIDAA), modified with dilute nitric acid, was shown to be a multi-functional dental primer with the ability to etch effectively not only dentin but also enamel at the same time. In addition, PIDAA with methoxy ring substituents demonstrated enhanced polymerization-initiating properties compared to PIDAA, probably due to the electron-donating effect of the methoxy group.

Impact

Two patents (U.S. Patent 5,498,643 and U. S. Patent 5,690,840) have 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. A new patent based on acid-modified PIDAA has been applied for in conjunction with the ADA.

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

Joseph M. Antonucci

Objective

The objective is to develop improved polymeric composities 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. Composite sealants were effective in remineralizing caries-like lesions in extracted bovine enamel.

In the present study, potentially adhesive composites made of pyrophosphate-stabilized ACP and various new photocurable resin mixtures containing carboxylic acid monomers are being screened for their ion releasing potential. It is thought that the presence of the carboxylic acid functional group in the resin will confer adhesive properties on these composites. Those that exhibit adequate ion release will be further tested for mechanical and adhesive strength. Of the composites examined to date, those containing triethylene glycol dimethacrylate and the adhesive monomer PMGDM released Ca and PO_4 at rates exceeding those of previously examined non-adhesive Bis-GMA resin mixtures.

External Collaborations

Dr. E.D. Eanes and Mr. A. W. Hailer of NIDR and Dr. D. Skrtic of the American Dental Association Health Foundation's Paffenbarger Research Center are actively assisting in the further development of bioactive polymeric composites utilizing ACP as a remineralizing filler.

Accomplishment

The results of this study demonstrated that experimental, visible-light curable ACP resin composites with remineralizing properties and potentially good adhesive properties can be prepared with certain carboxylic acid monomers as components of the resin phase.

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

J. M. Antonucci, E.D. Eanes, and D. Skrtic, *Bioactive Polymeric Composites Based on Hybrid Amorphous Calcium Phosphates*, Polymer Preprints **39(2),** 236-237 (1998).

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Cure Monitoring of Dental and Medical Resins by Fluorescence Spectroscopy

Francis W. Wang

Objective

The objective is to monitor the cure of resins by fluorescence spectroscopy, to establish correlations between fluorescence properties and performance properties for curing resins, and to transfer technology in photo-physics of fluorescent probes to manufacturers of resins for dental and medical applications.

Technical Description

Cure Monitoring of Bonding Resin: The durability and the physical properties of resin-infiltrated demineralized dentin depend primarily on the completeness of the cure of the primer and the bonding resin that infiltrate the demineralized dentin. It is therefore important to develop a technique to determine the degree of cure of the resin in resin-infiltrated demineralized dentin. Fluorescence techniques are particularly useful for cure monitoring because they are sensitive and adaptable to nondestructive, *in-situ* monitoring. Furthermore, with the use of fluorescence microscopy, the depth dependence of the degree of cure can be observed.

A wavelength-shift fluorescent probe, whose peak fluorescence wavelength changes with the polarity and the mobility of the probe's environment, is used in this project to monitor the degree of cure of the bonding resin. In this method, a trace amount of the wavelength-shift fluorescent probe was dissolved in a bonding resin, and the fluorescence spectrum of the probe was recorded as a function of cure time during the photo-initiated cure of the bonding resin. Because the polarity and the mobility of the bonding resin change during the cure, the peak fluorescence wavelength of the fluorescent probe decreases with the cure time. The change in the peak fluorescence wavelength of the probe can be correlated the degree of cure of the bonding resin. This correlation is established by relating the change in the peak fluorescence wavelength with the degree of cure determined by FTIR. An absolute value for the degree of cure can then be obtained from the change in the peak fluorescence wavelength.

Cure Monitoring of Bone Cement: The ultimate success of methyl methacrylate bone cements in surgical arenas requires application at an appropriate viscosity. Long term durability could be compromised by the empirical nature of the approach now used to determine the setting of a particular sample. The literature from one manufacturer states that, in addition to the concentration effects one would expect in a bi-phasic free-radical system, ambient temperature and humidity can substantially affect the setting time of a sample. It suggests that "..the working time ....is best determined by the experience of the surgeon..." In this project, a trace amount of a fluorescent probe is used as an *in situ* indicator of the viscosity of a bone cement sample and its suitability for surgical application. In addition, the project capitalizes on a novel technique- the impedance of quenching- for monitoring the increase in local viscosity accompanying polymerization.

A bone cement is made by mixing its liquid component [97% by volume methyl methacrylate and 3% by volume *N,N*- dimethyl- *p*-toluidine] and its solid component [15% by mass poly(methyl methacrylate), 75% by mass styrene-methyl methacrylate copolymer, 10% by mass $BaSO_4$, and 2% by mass benzoyl peroxide], often at a powder to liquid ratio of 2 to 1 by mass. After the mixing, the viscosity of the bone cement increases as the polymers dissolve in the liquid and methyl methacrylate polymerizes. If a trace amount of a fluorescent probe is dissolved in the liquid component, the probe initially fluoresces faintly because *N,N*- dimethyl- *p*-toluidine from the liquid component quenches the fluorescence. However, the fluorescence intensity of the probe increases as the increase in the viscosity of the cement suppresses the diffusion-controlled fluorescence quenching. Consequently, the increase in the fluorescence intensity of the probe is a measure of the viscosity of the bone cement. Once a correlation is established between the increase in the fluorescence intensity and the viscosity, an absolute value for the viscosity can be obtained from the change in the fluorescence intensity.

External Collaborations

Dr. Deborah G. Sauder, a Guest Scientist from Hood College, Frederick, MD, and Dr. Koichi Komatsu, a Guest Scientist from Nihon University, School of Dentistry at Matsudo, Matsudo, Chiba, Japan, are actively advancing the efforts to monitor curing of dental and medical resins by fluorescence spectroscopy.

Planned Outcome

Technology transfer, to manufacturers of dentin bonding resins and bone cements, of quality control methods for the development of bone cements and dentin bonding resins.

Accomplishments

A fluorescent probe, 4-(*N,N*-dibutylanilino)hexatrienyl-4'-pyridinium butylsulfonate (AHPBS), has been evaluated for cure monitoring of a bonding resin. The peak fluorescence wavelength of the fluorescent probe was shown to decrease with the cure time. A correlation was established between the peak fluorescence wavelength and the Vickers hardness of the bonding resin.

It was demonstrated that anthracene or $Re(CO)_3ClL$, (where L=4,7-diphenyl-1,10-phenanthroline) can be used as a fluorescent probe in a bone cement. The decrease of fluorescence quenching by *N,N*- dimethyl- *p*-toluidine (DMT) was measured to monitor the change in cement viscosity. With anthracene as a probe, the ratio of the fluorescence intensity from anthracene-DMT exciplex to that from anthracene decreased linearly with time until it leveled off at 40 min while, with $Re(CO)_3ClL$, the probe's fluorescence intensity, initially quenched, increased linearly from 5 min to 10 min after which the intensity leveled off. Since, for these probes, the linear change in the intensity ratio or the probe's intensity occurred over the working time of a bone cement, they are suitable as *in-situ* indicators of the viscosity of the bone cement.

Outputs

Publications
F. W. Wang, and D. G. Sauder, *Application of Fluorescent Molecules As In Situ Probes of Bone Cement Cure,* Polymer Preprints **39(2),** 256 (1998).

K. Komatsu, and F. W. Wang, *Fluorescent Probe for Cure Monitoring of Bonding Agent on Surface,* Proceedings of the Dental Materials Group, International Association for Dental Research Meeting, #1410, June, 1998.

F. W. Wang and D. G. Sauder, *Cure Monitoring of Bone Cement by Fluorescence Spectroscopy,* Proceedings of the Dental Materials Group, International Association for Dental Research Meeting, #64, June, 1998.

Presentations
F. W. Wang, *Fluorescence monitoring of polymerization,* 3M Engineering Systems and Technology, St. Paul, MN, November 20, 1997.

F. W. Wang, *Collaborative research on dental and medical materials at Dental and Medical Materials Group, Polymers Division,* Dental Products Division, 3M Pharmaceutical and Dental Products Group, St. Paul, MN, November 20, 1997.

F. W. Wang, and **D. G. Sauder**, *Application of Fluorescent Molecules As In Situ Probes of Bone Cement Cure,* American Chemical Society Meeting, Boston, MA, August 25, 1998.

K. Komatsu, and F. W. Wang, *Fluorescent Probe for Cure Monitoring of Bonding Agent on Surface,* Dental Materials Group, International Association for Dental Research Meeting, Nice, France, June, 1998.

F. W. Wang, and D. G. Sauder, *Cure Monitoring of Bone Cement by Fluorescence Spectroscopy,* Dental Materials Group, International Association for Dental Research Meeting, Nice, France, June, 1998.

Patent:
F. W. Wang, and D. G. Sauder, *Non-destructive method for determining the extent of cure of a polymerizing material and the solidification of a thermoplastic polymer based on quenching of fluorescence.* Provisional patent filed November 19, 1997.

Support for the Biomaterials Integrated Products Industries

J. A. Tesk, Steve Hsu[1], C. Johnson[2], Jeffrey Stansbury, Ming Tung[3], Drago Skrtic[3], and Alan Litsky[4]
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Objective

The objective is to provide support for the American biomedical industry via development of test methods and standards needed by industry, provision of reference materials, 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 and denture base applications, and metallic glasses for coatings of orthopaedic implants for bearing surfaces or boney fixation.

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 workshops, developing CRADAs and other agreements, and actively supporting standards related activities. New materials and needed property data will be explored within NIST, and with universities and industry.

External Collaborations

Biomet Inc. (Warsaw Ind.), Johnson & Johnson Professional, Inc. (Raynham, Mass.), Ostenoics Inc. (Allendale, N.J.), and Zimmer, Inc., (Warsaw, Ind.), are members of the Cooperative Research and Development Agreement (CRADA) Consortium, established to develop a new wear test machine and test for accelerating the evaluation of the wear properties on orthopaedic joint implant materials and to provide partial support.

Poly Hi Solidur (Fort Wayne, Ind), and Teledyne Allvac/Vasco (Monroe, NC) have or will be contributing materials to the consortium.

Professor Alan Litsky (Ohio State University) is contributing to research on use of cyclopolmerizable monomers as acrylic biomaterials.

American Association of Orthopaedic Surgeons, Hip and Knee Society is contributing to release of public information of the CRADA Research.

National Institutes of Health (Member,Biomaterials Implant Science Coordinating Committee) & Food and Drug Administration helped plan two industry workshops, one on Biomedical Reference Materials and the other on Heart Valves with Carbomedics Inc., Carbon Research Inc., Medtronic, Inc., St. Jude Medical, Inc., Baxter , Inc., and Alliance, Inc.

Planned Outcomes

- Development of a test machine and methodologies for accelerating evaluations of the wear of orthopaedic joint materials.
- Identification of health-care industry needs for reference materials for implant materials and devices (implanted and explanted).
- Identification of materials and test-methods needed by industry to help NIST plan resources to accommodate those needs.
- 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.
- Through standards and test methods development, foreshortened acceptance time of device submissions to the FDA, with benefits to industry and patients.
- More timely introduction of improved biomedical materials devices through research and standards, and the identification of resources needed for NIST to provide technical support for the biomaterials integrated products industries.

Accomplishments

An accelerated-wear tester and test methodology was developed to evaluate the wear properties of orthopaedic joint materials, developed during year two of Cooperative Research & Development Agreements (CRADAs). Four (4) orthopaedic companies joined together as a CRADA-formed consortium and based on the successful development of the test machine these four companies requested extension of the CRADAS (to September 30, 2000) to support research on evaluation of new materials. They have opened the opportunity for research to others who may wish to join the consortium as the benefits are perceived useful to the industry as a whole for standards and regulatory purposes and in the development of basic understanding of the wear resistance of implant joint materials.

Through its standards and reference materials effort, this program facilitated a NIST-NIH-FDA-Industry collaboration for NIST dissemination of Industry Developed Polyetherurethane, low density polyethylene, and silica free poly(dimethylsiloxane) reference materials, useful for development of cardiovascular and other devices. A workshop on Biomedical Reference Materials was planned for November 13, 1998, with cooperation of the NIH, FDA, Industry, and the Society for Biomaterials.

A workshop on Carbon Heart Valves was held on February 23 with the heart valve industry and a follow-up workshop is scheduled for December 2, 1998.

An ASTM Workshop on Standards for Tissue-Engineered Medical Products was held at NIST on December 16, 1997.

A method was found for using poly(methyl methacrylate) powders with co-monomers of cyclopolymerizable and methylacrylate types to produce doughs and heat curing in times comparable to those used for dental denture base (DB) formulations, but which can persist for a over one day. Extended-time dough state could be expected to be labor saving as a DB material. Other potential benefits include reduced polymerization shrinkage (Bone Cement, DB, & DB reline); for improved fits and, due to low vapor pressure, elimination of noxious odor. In the heat cured condition (105 °C) the fraction of double bonds converted was 96 %.

Outputs

Publications
J. A. Tesk, and Christian E. Johnson, *Glassy Alloys as Potential Coatings for Orthopaedic Applications*, Program Abstract for ASTM Symposium on Alternative Bearings for Orthopaedic Joints, San Diego, November, 1997, P. 25.

J. A. Tesk, Jeffrey W. Stansbury, and Alan Litsky *Cyclopolymerizable Monomers as Acrylic Biomaterials,* Transactions of the Society for Biomaterials, Vol 21, Abstr, 373, San Diego, CA., Apr. 22-26,1998.

G. L. Picciolo, K. B. Hellman, J. A. Tesk, R. Valentini, A. Coury, and P.C. Johnson, *Living Standards*, Biomaterials FORUM, Vol 20, #2, March-April, 1998, pp. 17-18..

G. L. Picciolo, J. Tesk, R. Valentini, A. Coury, and P. C. Johnson, *Tissue Engineering Products Standards: Living Standards for Living Tissue*, on Web at www.pittsburgh-tissue.net/brochure/Outreach/TEMPS.html.

J. A. Tesk, and Christian E. Johnson, *Glassy Alloys as Potential Coatings for Orthopaedic Applications*, ASTM Special Symposium Publication Alternative Bearings for Orthopaedic Joints, in press.

J. A. Tesk, S Hsu, and M. Shen, Quarterly Reports (confidential) to Orthopaedic CRADA Research Consortium, September, December, March, June, FY 1998.

Presentations
J. A. Tesk, and Christian E. Johnson, *Glassy Alloys as Potential Coatings for Orthopaedic Applications*, ASTM Symposium on Alternative Bearing Surfaces in Total Joint Replacement, Sheraton Harbor Hotel, San Diego, CA., November 11-12, 1998.

J. A. Tesk, Jeffrey W. Stansbury, and Alan Litsky *Cyclopolymerizable Monomers as Acrylic Biomaterials,* Annual meeting of the Society for Biomaterials, San Diego, CA., Apr. 22-26,1998.

J. A. Tesk, Jeffrey W. Stansbury, and Alan Litsky *Cyclopolymerizable Monomers as Acrylic Biomaterials,* Johns Hopkins University Symposium, Biological Response to Orthopaedic Implants, Renaissance Harborplace Hotel, Baltimore, MD., May 1 -2, 1998.

J. A. Tesk, *Traditional Methods by which The Laboratories of The National Institute of Standards & Technology may help meet the needs of the Biomedical Devices Industry,* presented to the Board of the Alliance for Medicine and Biology in Engineering, Washington Marriot Hotel, Washington DC, May 2, 1998.

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. During the past year, work has been conducted on one such project for the Bureau of consular Affairs, U.S. Department of State.

Development and Utilization of Test Methods for Qualification of Passport Laminates

W.G. McDonough, and D.L. Hunston

Objective

The objective is to perform testing and to provide consultation to assist the Bureau of Consular Affairs at the U.S. Department of State in selecting and purchasing the plastic laminate that is used to protect the photograph and descriptive information on the U.S. Passport.

Technical Description

NIST has been under contract for the past ten years to test and evaluate the laminate security film that is used to cover the data page in the U.S. Passport. This laminate protects the data page from fraud and counterfeiting attempts as well as protecting the data page from dirt, abrasion and accidental damage. Prior testing and evaluations performed at NIST on the passport laminates revealed limitations in the current technology's ability to protect the data page. This finding prompted the Department of State to investigate and develop alternatives to the processing and design of the U.S. Passport. The role of NIST has been to evaluate proposed products and to identify areas of vulnerability and strength. In fact, NIST has been and continues to be the primary agency to evaluate new products.

External Collaborations

John Mercer, and Richard McClevey of the U.S. Department of State

Accomplishments

The NIST part of the Next Generation U. S. Passport project was successfully commpleted. Future passports shall incorporate digital imaging and a new high security laminate to protect against tampering or forgery. The production method for this new passport shall be made in a "one-step" process that shall greatly reduce production times and costs. The work done at NIST to assess the quality of submitted products and to evaluate the test results was a critical factor in deciding the winning proposal. In fact, it was work at NIST examining the level of security in the current passport system that led to the decision to pursue the novel approach of digital imaging.

Impact

The procurement was a $63 million award over the next five years, and the implementation of this one-step, digitized image passport is the first of its kind for a large country. Several countries are following the United States' technical lead in this field and are planning to issue similar passports. It is expected that the technology incorporated into the new U.S. Passport shall eventually become an international standard.

Outputs

Report on the test results for the technical evaluation of submitted products was sent to the Department of State.

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Meredith, J. Carson	o Biodegradable polymer blends o Phase-separation and mechanical properties of blends o thin-films of biodegradable polymer blends
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 Shear induced two phase structures
Mischenko, Mykola I.[+] mykola.mischenko@nist.gov	o Neutron and x-ray scattering o Dendrimers o Polyelectrolytes o Physical gels
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. frederick.mopsik@nist.gov	o Dielectric measurements and behavior o Automated measurement design o Computerized data analysis and programming o Electrical properties of polymers

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Mueller, Herbert J. * herb.mueller@nist.gov	o Dental Biomaterials o Interfacial interactions via electrochemical and infrared spectroscopics o Chevron notch fracture toughness o Mechanical properties via nondestructive methods
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 o Filled polymers o Rheo-optical behavior of polymers
Nisato, Giovanni+ giovanni.nisato@nist.gov	o Polymer gels o Polyelectrolytes o Dynamic light scattering o Dendrimers
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 acqusition o Patent process (in electronic packaging)
Park, Joon-Yang+ jypark@nist.gov	o Glass transition o Molecular rheology
Parnas, Richard S. richard.parnas@nist.gov	o Flow through porous media with heterogeneous structure o Surface rheology o Polymer dynamics o Evancescent 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

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Phelan, Jr., Frederick R. frederick.phelan@nist.gov	o Resin transfer molding: modeling and processing studies o Viscoelastic flow modeling o Flow in porous media o Lattice Boltzmann methods
Pochan, Darrin darrin.pochan@nist.gov	o SEM & TEM of polymeric materials o Wide-angle and small-angle x-ray scattering o Block copolymer phase behavior
Qiao, Fang[+]	o Polymer mixing and compounding o Liquid crystalline polymer/thermal plastic polymer mixing
Raghavan, Dharmaraj T.[+] Dharmaraj.Raghavan@nist.gov	o Rubber recycling o Interface chemistry o Mechanical properties of concrete
Ramzi, Aissa[+]	o Dendrimers o Neutron scattering
Reiff, Andrea andrea.reiff@nist.gov	o Viscoelastic flow modeling o Hyperbolic systems o Numerical modeling
Rolnick, Robert A.	o Network administrator (Blends Group) o Computer maintenance
Roth, Steven C. steven.roth@nist.gov	o Piezoelectric polymer transducers-fabrication and applications o Vacuum deposition of metals o Calibration of polymer transducers o Microcomputer interfacing o Fluorescence measurements
Rupp, Nelson W.[*]	o Clinical dentistry o Amalgams o Direct golds o Composites o Microleakage o Dentin adhesives

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Schen, Michael A. michael.schen@nist.gov	o Non-linear optical polymer o Optical spectroscopy o Micoelectronics packaging materials o Photonics o Coefficient of thermal expansion o National technology roadmaps in electronics
Schultheisz, Carl R. carl.schultheisz@nist.gov	o Failure of composites o Experimental mechanics o Torsional dilatometry o Physics of polymer glasses o Polymer rheology
Schumacher, Gary E.* gary.schumacher@nist.gov	o Clinical dentistry o Composites o Dentin adhesives
Sieck, Barbara A.* barbara.sieck@nist.gov	o Calcium phosphate compounds o Chemical analysis o Remineralization
Skrtic, Drago* drago.skrtic@nist.gov	o Calcium phosphates as dental materials o Liposome studies
Snyder, Chad chad.snyder@nist.gov	o Polymer crystallization o WAXD and SAXS of polymeric materials o Thermal expansion measurements o Thermal analysis of polymers
Soulivong, Vannarong+ soulivon@nist.gov	o Polymer rheology o Polymer mechanics
Stansbury, Jeffrey W. jeffrey.stansbury@nist.gov	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

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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 Wear testing, orthopaedic materials o Reference biomaterials
Topp, Andreas[+]	o Small angle neutron scattering o Dendrimers
Tung, Ming S.[*] 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.[*] gerald.vogel@nist.gov	o Dental plaque chemistry, chemistry of calcium phosphates o Microanalytical techniques
Waldron, William K.[+] william.waldron@nist.gov	o Nonlinear viscoelasticity o Mechanics and thermodynamics of rubber
Wallace, William E. william.wallace@nist.gov	o Surface and interface behavior o Ion beam and electron spectroscopies o X-ray and neutron reflectivity o MALDI mass spectrometry

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Wang, Francis W. francis.wang@nist.gov	o Photophysics and photochemistry of polymers o Fluorescence spectroscopy o Cure monitoring of polymerization
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 Fiber and whisker reinforcement
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
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

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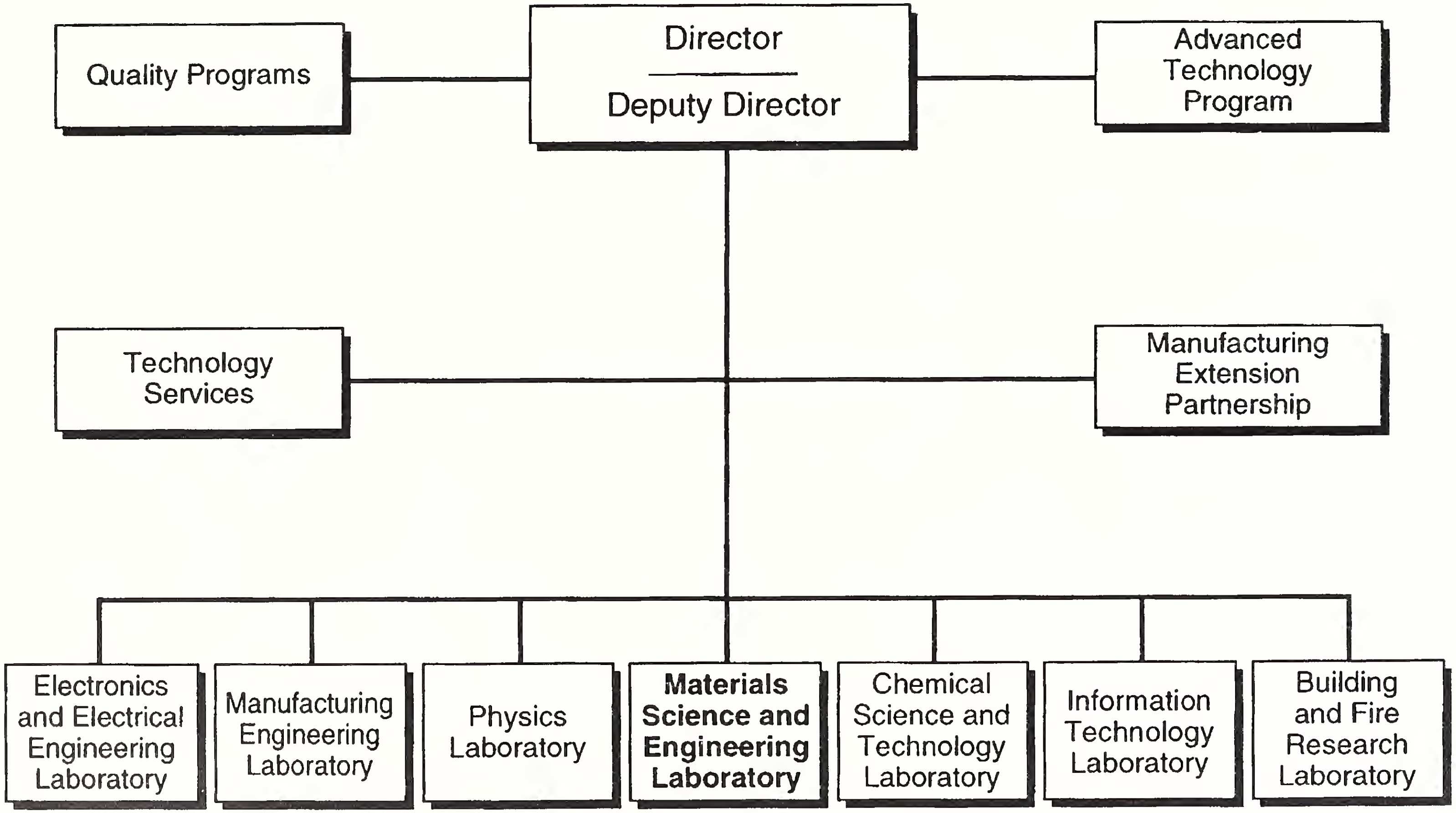
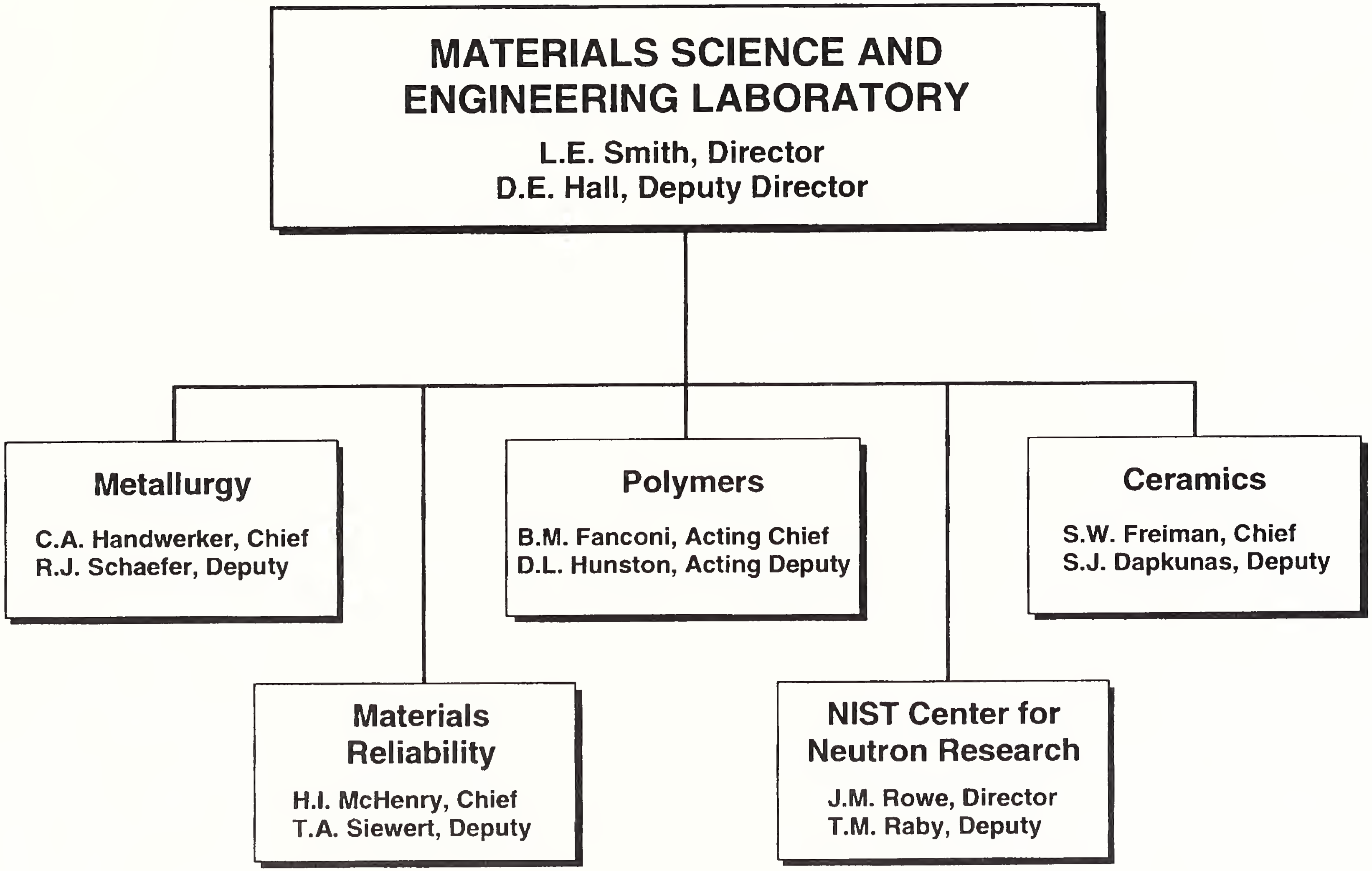
Organizational Chart




MATERIALS SCIENCE AND ENGINEERING LABORATORY
L.E. Smith, Director
D.E. Hall, Deputy Director
Metallurgy
C.A. Handwerker, Chief
R.J. Schaefer, Deputy
Materials Reliability
H.I. McHenry, Chief
T.A. Siewert, Deputy
Polymers
B.M. Fanconi, Acting Chief
D.L. Hunston, Acting Deputy
NIST Center for Neutron Research
J.M. Rowe, Director
T.M. Raby, Deputy
Ceramics
S.W. Freiman, Chief
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