

POLYMERS

1999 PROGRAMS

AND

ACCOMPLISHMENTS

**MATERIALS
SCIENCE AND
ENGINEERING
LABORATORY**

NISTIR 6435

UNITED STATES
DEPARTMENT OF
COMMERCE

TECHNOLOGY
ADMINISTRATION

NATIONAL
INSTITUTE OF
STANDARDS AND
TECHNOLOGY



**UNITED STATES
DEPARTMENT OF
COMMERCE**

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STANDARDS AND
TECHNOLOGY**

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MATERIALS SCIENCE AND ENGINEERING LABORATORY POLYMERS

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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 describes the fiscal year 1999 technical activities of the Polymers Division, organized according to the five major programs. For each program a concise summary is followed by a distillation of the major accomplishments during this fiscal year. These overviews are followed by descriptions of each project in terms of objective, technical approach, collaborations or teaming interactions, and a summary of accomplishments and outputs. The discussion in this report provides only a project summary of the Division's work during FY99 -- a year that resulted in over 160 scientific publications.

Just as it is impossible to include the extent of the year's technical output in a summary report such as this, it is also difficult to encompass the full significance of the accomplishments and impact of the work. During this year several projects from previous years have been recognized for major awards. For other projects the near term impact is already clear from the intensity of interactions with specific industrial collaborators. Although by definition an annual report presents a snapshot fixed in time, the most important goal of this report should be to convey the scope of our work and in doing so, make itself obsolete by facilitating even more effective future interactions with our customers.

The Polymers Division provides standards, measurement methods, and fundamental concepts in support of the measurement infrastructure for U.S. industries that produce or use polymers in essential parts of their business. The Division's programs are planned in response to and anticipation of measurement needs that support emerging markets for polymer materials as well as traditional industrial and technical communities. We rely heavily on advice gained during informal visits to and from our customers and from formal focused workshops as we plan our future directions. The current program areas are Electronic Packaging, Interconnections, and Assembly; Polymer Blends and Processing; Polymer Composites; Polymer Characterization; and Dental and Medical Materials.

Work in the Electronic Packaging, Interconnections, and Assembly program has led to development of new measurement capabilities in several areas. A unique combination of small-angle neutron scattering, high-resolution x-ray reflectivity, and ion scattering has been developed and applied to characterized critical parameters of thin film low dielectric nanoporous materials. The characterization includes average pore size, porosity, pore wall density, pore connectivity, film thickness, film composition, coefficient of thermal expansion, and moisture uptake. A test protocol and microstrip test specimen has also been developed for dielectric measurements of polymer composite films with dielectric constant up to 50 in a frequency range up to 5 GHz for applications as embedded passive components in wireless communication and high-speed electronics.

The Polymer Blends and Processing program has extended previous applications of on-line processing monitoring for multiphase polymer blends to systems which demonstrate a shear induced morphological transition from dispersed droplets to extended ribbons. Measurements have been applied to two phase immiscible blends, reactive systems, and polymers with inorganic fillers where processing is critical to the fabrication of high performance nanocomposites materials. Experiments focusing on the perturbation of phase separation by the presence of fillers in polymer blends have been tied to computer simulations performed in the Center for Theoretical and Computational Materials Science. In addition, large scale computer

simulations of homopolymer melts have identified signatures of dynamic heterogeneities that correspond to spatially correlated molecular motions in the vicinity of the glass transition.

Work in the Polymer Composites program has brought on line two critical measurement technologies for microstructural analysis of composites. The rate dependent behavior of fiber fragmentation tests has been linked to stress concentrations at the fiber fragment ends. The implications of this work are particularly significant for linking fiber-matrix interfacial chemistry to characterization of failure mechanisms. To further enhance the measurement capability for non-destructive evaluation of composite materials we have designed and constructed an optical coherence tomography system optimized for polymer composites.

The Polymer Characterization program is responsible for the majority of the Standard Reference Materials produced by the Division. Intrinsic viscosity and light scattering characterization is proceeding for three new polyethylene materials. At the same time, work in progressing on a potential replacement for these classical measurements as we continue to define and validate measurements of molecular mass and mass distribution using matrix assisted laser desorption/ionization time-of-flight mass spectrometry.

Fiscal year 1999 marked successful completion of another round of intramural funding by the National Institutes of Health for the Dental and Medical Materials program. This program continues to be focused on a core collaboration with the American Dental Association in support of new materials developments for dental composites and polymer based remineralization. For example we have validated a new near-infrared method for analysis of degree of conversion during polymer curing. A collaborative project with the Polymer Composites group has also developed a new micro-shear bond test that greatly improves utilization of test surfaces and allows new investigations related to the effects of different regions of the tooth structure.

The items noted above reflect only a few highlighted activities and accomplishments for fiscal year 1999. By their nature these descriptions often neglect to emphasize the effort involved in program planning and ongoing discussions with collaborators. Workshops continue to play a major role in program planning, as do numerous industrial visits and visitors. Most of the work in the Division involves direct collaborations with industrial and academic partners. We are pleased to provide more details in the following program reports and invite inquiries to any of the project leaders.

Recognizing Leadership in Measurement Science **...providing technical leadership in measurements of materials properties**

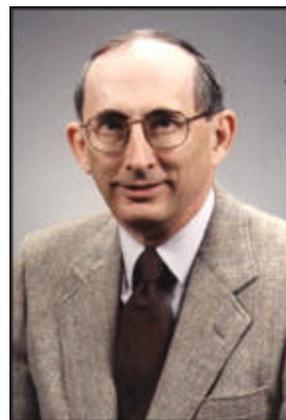
Charles Han receives High Polymer Physics Prize from APS

The American Physical Society (APS) has awarded its 1999 High Polymer Physics Prize to Charles Han of the Polymers Division. This prestigious prize was endowed by the Ford Motor Company in 1960 and is the highest APS award in recognition of outstanding accomplishment and contributions to the field of polymer physics research. The citation for Han reads: "For outstanding contributions in the application of light and neutron scattering to the physics of polymer phase separation." The Prize will be presented at the APS Centennial Meeting in March 1999 in Atlanta Georgia. At this meeting Han will present a lecture on his research in a special symposium organized in his honor. The award consists of \$10,000 and a certificate. Charles Han has been in the Polymers Division at NIST since 1974, and before becoming a NIST Fellow in 1995, he led the Polymer Blends and Processing Group for 10 years. He received the Bronze, Silver, and Gold Medals, and the Samuel Wesley Stratton Award from NIST and the Department of Commerce. In 1995 Han was awarded a Senior Research Fellowship from the Alexander von Humboldt Foundation in Germany. He is a Fellow of the American Physical Society and in 1984 he was the first recipient of the Dillon Medal, the only other award from the APS Division of High Polymer Physics, in recognition of his early achievements in polymer physics.



Donald Hunston Named Fellow of the Adhesion Society

Donald Hunston of the Polymers Division was named Fellow of the Adhesion Society at its 1999 Annual Technical Conference held in Panama City, Florida. Only 15 scientists, counting the 3 new inductees in 1999, have been given this prestigious status by the Society. Hunston was cited for fundamental scientific contributions to the mechanics of failure in adhesives and interfaces as well as for outstanding service to the Society. The award made special note of Donald Hunston's two terms as Vice President of the Society and his research on fracture. The latter was a ten-year effort in which he and his collaborators elucidated the mechanisms of toughening that make structural adhesives possible.



Recognizing Leadership in Standards Development **...providing leadership in standards development**

Polymers Division Scientist Receives ASTM Committee Award

ASTM Committee F04 on Medical and Surgical Materials and Devices presented its 1999 MOSES award to John Tesk of the Polymers Division during its standards meeting in Seattle, Washington. The MOSES medallion, so named as an acronym for Member of Science and Engineering with Sensitivity, was established to recognize the advantages of standards for the public good. The MOSES Award is awarded in one of the following categories: physician, engineer, consumer, general interest, special liaison, government, and research. It was presented to Tesk as the committee's Most Honored Government Representative, in recognition for many years of outstanding service and active participation in the work of the committee.



Leadership in Dental Standards

Officers of The American National Standards Institute Accredited Standards Committee MD 156, and of the U.S. TAG for the International Standards Organization (ISO) TC 106, Dentistry, presented a Certificate of Appreciation to John Tesk of the Polymers Division "For Outstanding and Dedicated Service" as chairman of those Committees from 1981 to 1986. During Tesk's tenure, the dental standards activity encompassed *ca* 100 national and 100 international standards; he also led the U.S. delegation to the meetings of the ISO. The award was presented during an ceremony at the annual meeting of those Committees on March 3, 1998 in Minneapolis, Minnesota. John Tesk was among the committee leaders recognized for their valuable contributions in this first ever presentation of the award.

TECHNICAL ACTIVITIES

ELECTRONIC PACKAGING, INTERCONNECTION AND ASSEMBLY PROGRAM

The objectives of this program are to help the U.S. microelectronics and supporting infrastructure industries by addressing their most pressing materials measurement and standards issues central to the development and utilization of advanced materials and material processes within new product technologies, as outlined within leading industry roadmaps¹. This program is part of a broad effort within the NIST Materials Science and Engineering Laboratory with a vision to be the 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 measurements and data.
- Develop and apply *in-situ* measurements on materials and material assemblies having micrometer- and submicrometer-scale dimensions.
- Quantify and record the divergence of material properties from their bulk values as dimensions are reduced and interfaces are approached.
- Develop fundamental understanding of materials needed for future packaging, interconnection and assembly schemes.

With these objectives in mind, the program currently consists of thirteen separate projects dealing in matters such as electrical, thermal, and mechanical characteristics of polymer thin films; interfaces and adhesion; and 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 (<http://www.msel.nist.gov/epia1996/contents.htm>). Copies may be obtained by contacting Wenli Wu at (301) 975-6839 or wenli@nist.gov.

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

² <http://www.eeel.nist.gov/810.01/index.html>

Significant Accomplishments

- Developed a successful methodology based on small-angle neutron scattering, high resolution x-ray reflectivity and ion scattering to determine the average pore size, porosity, pore wall density, pore connectivity, film thickness, film composition, coefficient of thermal expansion, and moisture uptake of porous thin films up to 1.4 μm thick supported on silicon wafers.
- Applied the above mentioned methodology to 19 different materials, including sol-gel materials, silsesquioxane-based materials, chemical vapor deposition (CVD) films, and high glass transition temperature (T_g) porous polymers in a joint project with SEMATECH. Three different data analysis schemes have been developed to accommodate the large variety of sample types. The measurement results have been disseminated to industries via reports to SEMATECH.
- Developed a microstrip test specimen and test protocol for dielectric measurements of polymer composite films. The technique is appropriate for films as thin as 10 μm with a dielectric constant up to 50 at frequencies of up to 5 GHz. This new capacity is essential for wireless communication and high-speed electronics where new polymer composites are being tailored for the applications as embedded passive components.
- Near-edge x-ray absorption fine structure (NEXAFS) measurements suggest that surface chains relax toward their unperturbed configuration faster than bulk chains in uniaxially-deformed polystyrene. This result is consistent with the notion of a lower glass transition temperature of material within 5 nm of the free surface.
- Demonstrated for the first time the applicability of sum-frequency generation (SFG) to determine the phenyl ring orientation on unoriented polystyrene surfaces.
- Measured the contact angles formed at solder/polymer/vapor triple junctions and applied data to validation of two different computer codes for flow of solder in wafer level underfill technology development. Technical representatives of Delco Electronics learned of this work through the Center for Theoretical and Computational Materials Science web site and expressed interest in a collaborative effort with NIST.
- Measured the hygrothermal expansion of thin films using a NIST-designed capacitance cell and supplied results to SEMATECH, a microelectronics consortium, and CINDAS, a materials database. A new capacitance cell for the measurement of conducting and semiconducting thin films has been designed, built, and is currently being calibrated.
- Showed, by dielectric spectroscopic studies on buckyballs in toluene, that the particle shape and degree of dispersion can be quantified in nanocomposite materials.
- Developed a new analytical technique to determine thermal properties of thin polymer films from thermal pulse data. The technique is based on an approximate theory for the diffusive heat transport that contains simpler equations than previously. These equations allow determining the thermal conductivity and interfacial thermal resistance by curve fitting data obtained from thermal pulse measurements.

- Identified, by neutron scattering measurements, the crystalline transformations induced by electron irradiation in the dose range that produces a large electrostriction in copolymer of vinylidene fluoride and trifluoroethylene. The derived information about the crystalline dimensions of the several crystalline phases reduces the number of admissible theoretical descriptions of the electrostriction.
- Showed that single-phase inorganic/organic molecular hybrid materials, epoxy-functionalized octameric silsesquioxane cubes cured with different diamines, are promising candidates to replace current multi-phase and highly filled underfill formulations. These silsesquioxane-based materials show very low viscosities before cure, low coefficients of thermal expansion, and very high glass transition temperatures, properties critical for underfill applications.
- Determined, by x-ray reflectivity, that the glass transition temperatures of thin (60 nm or below) films of polystyrene and poly methyl-methacrylate (PMMA) increased with decreasing hydrophobicity of the substrate. Radiologically modified self assembled monolayers were used to provide substrates with systemically varied surface energy in our study of polymer/substrate interactions.
- Determined the crystalline morphology and dewetting characteristics of thin films (thickness < 100 nm) of deuterated isotactic polypropylene (iPP). The crystal structure was monoclinic with a strong orientation of the unit cell c-axis (chain backbone) in the plane of the film. X-ray reflectivity revealed a remaining surface layer of iPP after apparent dewetting by extended annealing of the film above the melt temperature. This persistent interfacial layer strongly suggests the presence of a highly oriented polymer interfacial layer from which the rest of the film auto-dewets.

Characterization of Low-k Dielectric Porous Silica Thin Films

Wen-li Wu, Eric K. Lin, William E. Wallace and Gary W. Lynn¹

¹ University of Tennessee, Knoxville, TN

Objective

The objective is to provide the semiconductor industry with unique on-wafer measurements of physical and structural properties of porous silica thin films important to their use as low-k dielectric materials. More specifically, we aim to develop a novel methodology to measure the average pore size, pore connectivity, film thickness, matrix material density, coefficient of thermal expansion, moisture uptake, and film composition. These properties are provided to aid industry in the selection of candidate materials and processes to be used in next generation integrated circuits.

Technical Description

Low-k dielectric materials have been identified by the microelectronics industry as a critical factor to enable deep submicron technology for improved performance of integrated circuits. With decreasing line widths, low-k materials are required to increase the signal propagation speed, decrease the energy needed to propagate a signal, and decrease the cross-talk between adjacent conducting lines. Nanoporous materials have been identified as an important class of

low-k dielectric materials because the incorporation of voids effectively reduces the dielectric constant of the film. Unlike traditional homogeneous dielectric materials, the structure of the porous network affects properties needed for their integration into current fabrication lines. It is critical to be able to measure the structural properties of these thin films to understand correlations between processing conditions and the resulting physical properties.

We have developed a novel combination of small angle neutron scattering (SANS), high-resolution x-ray reflectivity (HRXR), and ion scattering techniques to determine important structural information about the film. These measurements are performed directly on films supported on silicon substrates. HRXR is used to accurately measure the film thickness, electron density, and the coefficient of thermal expansion. SANS is used to determine the pore structure providing information such as the average pore size, pore connectivity, and moisture absorption. We have successfully determined the pore structure of films less than 0.5 μm thick. Ion scattering techniques are used to determine the elemental composition of the films. By combining information from all three of these techniques, we provide the first measurements of important quantities such as the porosity and the pore wall density. By providing measurement results on the properties of a wide range of materials and processing conditions, we help the U.S. microelectronics industry to develop the proper materials and processing conditions for low-k dielectrics needed for the commercial production of next generation integrated circuits.

External Collaborations

- E. T. Ryan and H. M. Ho, SEMATECH – collaboration and supply of samples for measurement. Supervise contract work to help develop comprehensive database of potential porous low-k materials developed by many materials suppliers for the semiconductor industry.
- W. Chen, Dow Corning – collaboration and supply of samples for measurement of proprietary porous low-k materials.
- M. O’Neill, Air Products – supply of porous polymer materials.
- N. Rutherford, AlliedSignal – supply of porous low-k dielectric materials.
- J. N. Cox, Intel - collaboration on thin film density and coefficient of thermal expansion measurements.

Planned Outcome

The unique measurement of properties such as the average pore size, porosity, and pore wall density are expected to be used by the semiconductor industry to guide their development of porous interlevel dielectrics as well as the integration process for next-generation chips.

Accomplishments

- A methodology was successfully developed using the combination of small-angle neutron scattering, high resolution x-ray reflectivity, and ion scattering to determine the average pore size, porosity, pore wall density, pore connectivity, film thickness, film composition, coefficient of thermal expansion, and moisture uptake of porous thin films up to 1.4 μm thick supported on silicon wafers.
- The experimental methodology was first demonstrated on a porous silica thin film, Allied Signal Nanoglass, prepared from spin-coating and sol-gel methods. This film was determined to have an average pore size of $(65 \pm 1) \text{ \AA}$, a pore wall density of (1.16 ± 0.05)

g/cm³, and a porosity of (53 ± 1) %. The pore size results were confirmed by positron life-time measurements.

- Under a contract from SEMATECH, this methodology was applied to 19 different samples including sol-gel materials, silsesquioxane-based materials, CVD films, and high Tg porous polymers as well as varying processing conditions. Three different data analysis schemes have been developed to accommodate the large variety of sample types.

Impacts

SEMATECH uses the structural information generated by this methodology in developing correlations with mechanical properties and processing conditions for the rapid development of porous materials as low-k dielectrics.

Outputs

Publication

W.L. Wu, W.E. Wallace, E.K. Lin, G.W. Lynn, C.J. Glinka, E.T. Ryan, and H.M. Ho, *Properties of Nanoporous Silica Thin Films Determined by High Resolution X-ray Reflectivity and Small-angle Neutron Scattering*, Journal of Applied Physics, Feb. 2000.

Presentations

W.L. Wu, W.E. Wallace, E.K. Lin and G.W. Lynn, *Low K Dielectric Film Characterization*, Dielectrics/Metallization/Module Integration PTAB Meeting, Austin, TX, 10/22/98.

W.L. Wu, W.E. Wallace, E.K. Lin and G.W. Lynn, *Characterization of Nano-Porous Thin Films*, Lucent Technologies, Murray Hill, NJ 11/13/98.

W.L. Wu, W.E. Wallace, E.K. Lin and G.W. Lynn, *Structure of Nano-Porous Dielectric Films*, AlliedSignal, Inc., Sunnyvale, CA, 1/25/99.

W.L. Wu, W.E. Wallace, E.K. Lin and G.W. Lynn, *Structure of Nano-Porous Dielectric Films*, Xerox Corporation PARC, Palo Alto, CA, 1/21/99.

W.L. Wu, W.E. Wallace, E.K. Lin and G.W. Lynn, *Structure of Nano-Porous Dielectric Films*, INTEL, Santa Clara, CA, 1/22/99.

W.L. Wu, W.E. Wallace, E.K. Lin and G.W. Lynn, *Ultra-Thin Polymer Films on Solid Substrates*, University of Akron, OH, 2/4/99.

W.L. Wu, W.E. Wallace, E.K. Li and G.W. Lynn, *Structure Characterization of Low k Films*, SEMATECH Ultra-Low k Workshop, Orlando, FL, 3/16/99.

W.L. Wu, W.E. Wallace, E.K. Lin and G.W. Lynn, *Comparison of CVD and Spin-on Films for Low k Interlevel Dielectrics*, Applied Materials, Santa Clara, CA, 10/99.

Dielectric Properties of Thin Polymer Films and Composites

Jan Obrzut and Chwan K. Chiang

Objectives

The objectives are to provide the U.S. electronic industry with a standard test method for dielectric permittivity of polymer composite films in the microwave frequency range and to identify the key structural and molecular attributes that control their dielectric properties.

Technical Description

Polymer-based high dielectric constant films can be used to construct embedded, discrete RLC circuits and de-coupling power planes for wireless communication and high-speed electronics. The permittivity of the prospective materials should be high and tailorable precisely for operation at microwave frequencies. In order to develop such materials, the industry needs a suitable test method to measure dielectric properties of thin films at high frequencies and a fundamental framework for modeling and predicting these properties.

Most of the difficulties in measuring the dielectric constant of thin films at higher frequencies arise from the fact that the dielectric thickness of the specimen is much smaller than the wavelength of the propagating electromagnetic wave. The characteristic impedance of the thin film specimen becomes very low, which causes the reflection coefficient to approach its maximum value, $\Gamma \approx 1$. For such low impedance, the usual calibration standards (coaxial shorts, opens and loads) become unreliable. To solve this problem, we designed a test pattern which consists of co-planar microstrip resonators and the corresponding non-coaxial terminations. This new approach allows for improvement of the dynamic range of the measurements necessary for thin dielectric films.

Experimental verification was performed on several test specimens with fine dimensions fabricated using photolithography. In comparison to the currently available test methods, which are applicable to dielectrics thicker than 1.2 mm with the dielectric constant lower than 12, the new test pattern is appropriate for films as thin as 10 μm having dielectric constant of 50 at frequencies of up to 5 GHz. Using this test specimen the microwave permittivity of several commercially developed high dielectric constant research formulations was accurately determined for the first time. For example, we evaluated the dielectric constant of the newest high dielectric constant composite from 3M that was only 3 μm thick, at frequencies from 100 MHz to 5 GHz.

In order to identify the key materials structural attributes that control dielectric properties of polymer composites, we formulated high dielectric constant composites using model polymer resins filled with ceramic BaTiO_3 ($\epsilon \approx 1000$, $f > 1$ GHz) and organic Emeraldine Salt ($\epsilon \approx 400$, $f > 1$ GHz) powders. To analyze the effect of polarizability, we have implemented a theoretical model according to which the resulting dielectric constant, ϵ_m , of the composite material depends on volume fraction of the constituents, v_i , their dielectric constant, ϵ_i , dipole moment, and interfacial polarization. The model is innovative in the sense that it assumes a parallel coupling between the organic and ceramic phases which is moderated by an internally induced electric field. This makes it applicable to composites of practical importance with higher volume fraction above the percolation point. The model predicts a considerable increase in ϵ_m of the composite when ϵ_1 of the polymer matrix increases.

The experimental data confirm the model predictions and indicate that composites of model polymer resins ($\epsilon_1 < 4$ above 1 GHz), filled with high dielectric constant components exhibit only 2 % to 4 % of the dielectric constant of the filler for the range of practically achievable loading levels. In addition, it has been determined that one of the key factors that control the dielectric properties of the composite is the dielectric constant of the polymer matrix. Thus, for polymer/BaTiO₃ composites for which the maximum achievable loading level is about 50 volume %, the highest predicted dielectric constant is about 50. This result compares reasonably well with the experimental value of 40 obtained for one of the best industrial research sample, PolyClad, which was formulated with an epoxy resin ($\epsilon_1 = 3.8$) filled with ferroelectric powder ($\epsilon_2=5000$) at the loading level of 46 %.

Functional analysis of generic devices for wireless communication indicates that both the RLC and decoupling functions of the thin film capacitors will ultimately require materials with a dielectric constant higher than 50. According to the results obtained, this requirement may be satisfied by composites based on polymers having the dielectric constants in the range of 15-20 at frequencies above 1 GHz. Since such polymers are not currently available, we will attempt to identify an organic molecular structure that might possibly exhibit high dielectric constant at microwave frequencies.

External Collaborations

- Joel Peiffer, 3M, - developing a polymer composite film with the highest capacitance density among the industrial formulations.
- Dale Murry, Litton Advanced Circuitry– developing an artwork of the microstrip test pattern and fabrication of the test specimen with several high dielectric constant composite films.
- Yueh-Ling Lee, DuPont – member of the team that has developed a polyimide – based composite for embedded thin film capacitors.
- Rick Charbonneau, Storage Technologies – manufacturing of functional prototype boards with embedded thin film capacitors.
- Lee Patch, National Center for Manufacture Science (NCMS) - coordinator of the Thin Film Capacitance Project. Interfacing the project team members with AlliedSignal and PolyClad.
- Philip Bowles, Delphi-Delco Electronics – environmental stress analysis, coordinator of the Thin Film Capacitance Project.
- Mark Poliks, IBM – environmental stress test.
- Joe Dougherty, University of Pennsylvania – low frequency materials analysis of thin film capacitors.
- Todd Hubbing, University of Missouri – functional analysis of the distributed capacitance.

Planned Outcome

It is expected that the effort of this research program will result in a new standard test method for high frequency permittivity measurements of thin dielectric films. The industry needs such a method to test materials and devices used by the wireless communication technologies. This work is also aimed at exploiting a fundamental mechanism which controls the dielectric properties of polymer composites. The outcome will help improve fundamental understanding of the limitations and capabilities of polymer composites and will facilitate formulation of materials with desirable dielectric characteristics.

Accomplishments

- A microstrip test specimen and test protocol has been developed for dielectric measurements of polymer composite films. The technique is appropriate for films as thin as 10 μm having dielectric constant of 50 at frequencies of up to 5 GHz. This new capacity is essential for wireless communication and high-speed electronics where new polymer composites are being used to make embedded passive components.
- Using the new microstrip test specimen the microwave permittivity of several commercially developed high dielectric constant research formulations was accurately determined for the first time.
- It has been determined that one of the key factors controlling the dielectric properties of the composite is the dielectric constant of the polymer matrix. To satisfy requirements of future electronic technologies new polymers are needed that exhibit at microwave frequencies dielectric constant value in the range of 15-20.

Impacts

A test pattern for standardized measurements of high dielectric constant films in the microwave range has been used by members of the Embedded Capacitance Project as a common test vehicle. The list of participants include major manufacturers of electronics such as Delco-Delphi Electronics, 3M, DuPont, Raytheon, TI and several other companies. The implemented testing technique has helped in the manufacture of materials for thin film embedded capacitors with improved quality. U.S. sales of experimental boards with embedded capacitance jumped in 1998 from 0 % to 3 % of all boards sales, indicating increasing confidence in the embedded passive technologies that utilize polymer composites.

Outputs

Publication

J. Obrzut and C.K. Chiang, *Microwave Dielectric Characterization of Polyaniline Composites*, Proceedings of the MRS, Organic / Inorganic Hybrid Materials II, 576 (1999).

Presentation

J. Obrzut, *Dielectric characterization of polymer composite films for decoupling capacitance*, NCMS, April 13-15, Boulder Co (1999).

Optical Polarization Dependent Performance of Photonic Devices

Jan Obrzut

Objectives

The objectives are to determine the effects of polarization on the performance of commercial photonic high-speed switches and to evaluate applicability of nonlinear optical (NLO) organic crystals and polymers for photonic switch functions.

Technical Description

Photonic devices utilizing electro-optic crystals are sensitive to the polarization state, which affects the modulation speed and the ON/OFF voltage contrast. A number of approaches have been proposed to circumvent the polarization dependence problem. Typically, a polarization controller is placed between the fiber and the electro-optic crystal to convert any input polarization into a preferred linear polarization state. However, the performance of such devices becomes unstable when coupled to single-mode input-output fibers with random polarization. An improvement in performance can be achieved when the input light is decomposed into two orthogonal, linearly polarized modes and processed independently by two separate electro-optic crystals.

We have examined a commercial electro-optic modulator built by Cleveland Crystals, Inc., which uses the newest dual crystal Pockels cell technology. The modulator employs high quality beta-Barium-Borate (BBO) NLO crystals in longitudinal configuration to secure a phase-balanced operation for the two polarizations. The device can tolerate deviation from the nominal polarization plane of up to 20° , while the voltage contrast ratio decreases from 3000:1 to about 100:1 at the half wave voltage of about 5.6 kV. This angular aperture is substantial larger than that of standard electro-optic cells, employing, for example, a 98 % deuterated KD_2PO_4 for which the angular aperture is restricted to about 1.6° . Despite apparent improvement in polarization, the high switching voltage limits the modulation frequency to about 200 MHz and makes the dual crystal BBO cell rather unsuitable for fiber optics integrated photonic devices. Electro-optic modulation at lower voltages would require an NLO crystal with a larger electro-optic coefficient and precisely oriented optical axes in respect to the physical coordinates of the device, especially to the propagation direction and the electric field vector. This imposes significant difficulties on fabrication. A total immunity to the polarization states would lead to unrealistic NLO material requirements.

To evaluate the applicability of organic NLO crystals for electro-optic functions, two experimental modulators have been designed: one based on inorganic NLO crystal, Lithium tantalate (LiTaO_3), and the other on organic NLO 3-methyl-4-Nitropiridyne-1 Oxide (MNPO). The electro-optic tensor of both crystals has been correlated with the index ellipsoid to achieve a low modulation voltage (less than 200 V) and a comparable relationship between the voltage level and the resulting polarization state. Lithium tantalate is one of the best NLO materials under recent development for commercial applications. The electro-optic properties of the organic MNPO crystal are yet to be explored. The calculated principal refractive indices under a transverse electric field and simulated electro-optic functions indicate the half wave voltage to be 140 V for the LiTaO_3 device, and 150 V for the MNPO device, respectively. This is substantially lower than the half wave voltage of the BBO cell. The LiTaO_3 device has a maximum modulation frequency of about 1.7 GHz, which is limited by a phase-velocity mismatch between the modulating wave and the light wave, caused by the high value of the dielectric constant ($\epsilon_{33} = 45$) of the LiTaO_3 crystal. In comparison, The MNPO exhibits not only a large electro-optic coefficient, but also a dielectric constant lower by an order of magnitude than that of LiTaO_3 , which allows high-speed modulation of up to 130 GHz.

In the design the modulators are integrated with polarization controllers and input/output optical fibers. The first experimental LiTaO_3 prototype was made in collaboration with Conoptics Inc. and showed larger than predicted half wave voltage, about 320V. The anomalies in operation are being diagnosed to predict the best performance possible with the specific crystal cut and

configuration of the modulating field. As a parallel effort an experimental polymer-based NLO waveguide modulator has been fabricated in collaboration with Akzo Research.

External Collaborations

- Ronald Pizzo, Connoptics Inc.- fabrication of the LiTaO₃ electro-optic modulator
- K. C. Jen, IBM – designing of an NLO- polymer-waveguide electro-optic modulator.
- Wintwield Horsthuis, Akzo Research – fabrication of a polymer electro-optic modulator.

Planned Outcome

It is expected that the effort of this research program will result in working prototype of a model photonic device utilizing an NLO organic crystal with comparable performance to that of inorganic lithium tantalate crystal. The experimental results such as the polarization dependent loss measurements, state of polarization (SOP) and degree-of- polarization (DOP) measurements will be used to assess the polarization-transfer-function, to identify the performance degradation mechanism and to identify ways to improve the functionality. Based on these results we will determine desirable NLO characteristics of polymeric material suitable for use in photonics.

Accomplishments

It has been determined that certain NLO organic crystals, such as 3-methyl-4- nitro-piridyne-1 oxide, exhibit optical properties that can improve operation of photonic devices. Two experimental electro-optic modulators have been designed to compare the polarization characteristics of lithium tantalate, one of the best inorganic crystals, with organic 3-methyl-4-nitro-piridyne-1 oxide. The electro-optic tensor of both crystals has been correlated with the index ellipsoid to achieve a low modulation voltage and a comparable relationship between the voltage level and the resulting polarization state.

An experimental polymer-based NLO waveguide modulator has been fabricated in collaboration with Akzo Research.

Hygrothermal Expansion of Thin Films

C.R. Snyder

Objectives

The objectives are (1) to determine the accuracy and precision of a NIST-designed capacitance cell technique for measuring out-of-plane expansion of thin polymer films; (2) to investigate the dimensional stability of electronics packaging materials with temperature and humidity changes; (3) to develop a new capacitance cell for measurement of conducting and semiconducting samples; and (4) to work with standards-setting bodies to introduce this 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 performed 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

- Josh Jackson, Johns Hopkins Applied Physics Laboratory, Baltimore, MD- provided carbon fiber composite materials for coefficient of thermal expansion (CTE) measurements.

Planned Outcomes

The planned outcome of this project is an improved test method for measuring hygrothermal expansion of thin films. This method will then be used to provide reliable data on the expansion behavior of electronic packaging materials with variations in temperature and humidity.

Accomplishments

A new capacitance cell for measurement of the hygrothermal expansion of conducting and semiconducting thin films has been designed and built. The new cell is currently being tested. CTE measurements made with the previous design of the capacitance cell have been requested by, and supplied to, the Center for Information and Numerical Data Synthesis and Analysis (CINDAS) and SEMATECH.

Outputs

Publications

C.R. Snyder and F.I. Mopsik, *A precision capacitance cell for measurement of thin film out-of-plane expansion. II. Hygrothermal expansion*, Review of Scientific Instruments, **70** (5), 2424 (1999).

C.R. Snyder and F.I. Mopsik, *High Sensitivity Technique for Measurement of Thin Film Out-of-Plane Expansion*, in AIP Conference Proceedings 449 - Characterization and Metrology for ULSI Technology, ed. D.G. Seiler, A.C. Diebold, W.M. Bullis, T.J. Shaffner, R. McDonald, and E.J. Walters (American Institute of Physics: Woodbury, NY, 1998), pp. 835-838.

Electronic Paper

C.R. Snyder, J.F. Douglas and Gary W. Lynn¹

¹University of Tennessee, Knoxville, TN

Objective

The objective of this project is to develop key metrologies for investigating the properties of polymer-dispersed liquid crystals (PDLC's) and electrophoretic media (EM) for use in reflective display technologies.

Technical Description

Laptop computers and other devices using flat panel displays are increasingly prevalent in business as well as private life. With recent advances in display technology such as active matrix addressing, which allows digital spatial switching of pixels, many new commercial applications for non-electron beam displays are becoming feasible both technologically and economically. One application at the forefront is the concept of electronic paper, *i.e.*, bistable reflective display. The advantage to this type of display is the persistence of the image after the power is turned off (on the order of months), and the benefits of reading from reflected light rather than projected light. Two types of materials that are among the candidates for the "pixel" material are polymer-dispersed liquid crystals (PDLC's) and electrophoretic media (EM). For

U.S. industry to compete in this market, it is essential that the fundamental physics governing the long-term stability, optical properties, and switching times of these materials be more thoroughly understood. Dielectric spectroscopy and neutron/x-ray reflectivity have the potential to address these issues.

Measurements will be made on a set of well-characterized materials to evaluate the utility of dielectric spectroscopy and neutron/x-ray reflectivity for characterizing the microstructure of PDLC's and EM. Initial studies aimed at understanding EM will be directed at nanoparticle suspensions to examine the ability of current theories to predict the dielectric properties based on the particle's shape. Dielectric studies will be performed on PDLC's as a function of domain size, chemical moieties, and surfactant concentration. Neutron reflectivity will be performed on thin film sandwiches that will act as a model system for the PDLC's polymer/liquid crystal interface.

External Collaborations

- Timothy J. Bunning, Air Force Research Laboratory, Wright Patterson Air Force Base, OH – provided PDLC samples for time-domain dielectric spectroscopy measurements.
- James E. Martin, Sandia National Laboratory, Albuquerque, NM – provided metal nanoclusters for dielectric spectroscopy measurements.

Planned Outcomes

The planned outcomes of this project are (i) a metrology for characterization of the shape, dispersion, and electrophoretic mobility of nanoparticle dispersions, (ii) an improved understanding of the limitations of the current theories of electrophoretic mobility, and (iii) an improved understanding of the effects of the polymer/liquid crystal interface on switching speeds and bistability.

Accomplishments

- The nematic-isotropic transition was determined for a PDLC containing 24 % E7 (liquid crystal) in crosslinked poly(dipentaerythritol hydroxypentaacrylate) by time-domain dielectric spectroscopy. (The transition temperature was previously undetectable by optical measurements.) Measurements are currently being performed on a PDLC with a 28 % E7 content.
- A sandwich was made of silicon, 8CB (liquid crystal), deuterated poly(methylmethacrylate), and aluminum. From neutron reflectivity measurements, it was determined that the liquid crystal consisted of three distinct layers: (1) a layer anchored to the silicon substrate, (2) a bulk-like layer, and (3) a “mixing” layer.
- The dielectric constant of an isolated Buckminsterfullerene molecule is determined to be 6.2 ± 0.7 from our dielectric spectroscopic measurements using an effective medium, spherical molecule approximation.

Outputs

Presentation

C.R. Snyder, W.L. Wu, and J.F. Douglas, *Polymer Dispersed Liquid Crystal and Electrophoretic Suspensions for Reflective Display Devices*, ATP FY1999 Intramural Project Review, Gaithersburg, MD, August, 1999.

Thermal Properties of Polymer Films and Interfaces

Erik K. Hobbie and Aime S. DeReggi

Objectives

The objectives are to develop a new measurement technique for quantifying the thermal boundary resistance that exists between polymer films and semiconducting substrates, and to apply this technique to situations of practical importance in the microelectronics packaging industry, while at the same time garnering a fundamental understanding of the physical processes governing the transport of heat across such interfaces.

Technical Description

The efficiency of thermal transport perpendicular to the plane of thin polymer films and coatings mounted on conducting and semiconducting substrates is an important factor in the design and packaging of microelectronic circuits and devices. Polymer films on the order of 1 μm thick are currently used, for example, as inter-level dielectrics in micro-electronics packaging. Because the thermal conductivity of metals and semiconductors is relatively high compared to that of a typical polymer, thermal transport across such films will in general be limited by both the thermal diffusivity of the coating material and the thermal boundary resistance of the polymer-metal or polymer-semiconductor interface. From the perspective of synthesizing new polymeric materials and designing new production techniques that optimize the rate at which heat is dissipated in such applications, it is desirable to have an efficient way of measuring one or both of these quantities independently. For polymer films on the order of 10 μm thick, the thermal transit time is on the order of 1 ms, implying that fast measurement techniques are essential for an accurate determination of thermal-transport coefficients. The thermal pulse electro-thermal response technique is ideally suited for this problem, because it provides a space-time resolved thermal profile with a response time that can be anywhere from 100 ns to 1 ms. A list of on-going work using this newly developed algorithm is given as follows.

- The bulk and interfacial thermal transport coefficients of polymer films, composed of such materials as polyimide and polystyrene spin coated onto p-doped silicon wafers, will be measured as a function of temperature in the vicinity of the glass transition. The thickness of the films will be on the order of 10 μm , as this is within the optimal range of the thermal pulse technique and corresponds to the typical dimensions encountered in electronics packaging applications.
- Existing theories (such as the so-called “acoustic mismatch” theory of phonon scattering at solid-solid interfaces) will be used to understand the temperature dependence of the thermal boundary resistance and relate any anomalous behavior observed to the large contrast, or mismatch, in elasticity between the polymer film and the semiconducting substrate.
- Samples obtained from industrial collaborators working at the cutting edge of polymer-semiconductor technology, such as *GaAsTEK*, will be analyzed using the thermal pulse technique to prepare novel materials and devise new applications.

- Round robins within NIST (Polymers, Ceramics, Metallurgy) will be performed on various samples, both prepared in-house and obtained via external collaborations with industry, to assess the accuracy and precision of the thermal pulse technique compared to other more conventional techniques, such as “three omega” or “mirage”.
- From direct knowledge of the spatially-resolved thermal transport characteristics of a polymer film, it will be possible to extract quantitative information regarding the distribution of space charge within that sample. Knowledge of space charge distribution will permit an investigation of such things as the slow temporal evolution of injected charge in films under external bias.

External Collaborators

- Mat Narayanan, ITT*GaAsTEK* Corporation-Provides PI films spin coated on GaAs and Si wafers for studying the temperature dependence of thermal transport.
- Eduardo Gonzalez, Ceramics Division, NIST-Performs “three omega” measurements in NIST round robin.
- Al Feldman, Ceramics Division, NIST- Performs “three omega” measurements in NIST round robin.

Accomplishments

- A theoretical analysis of the thermal pulse technique was developed that allows a measurement of both the bulk thermal diffusivity of the film and the thermal boundary resistance between the film and substrate.
- Using the thermal pulse technique, the thermal diffusivity and thermal boundary resistance of a polyimide spin coated on p-doped Si[111] and a polystyrene spin coated on p-doped Si[111] were obtained at ambient temperature.
- Preliminary measurements were performed on a new polyimide spin coated on both GaAs and p-doped Si[111] wafers as obtained from *GaAsTEK*.
- A round robin was initiated and carried out on measuring the bulk thermal diffusivity of a variety of different materials using a variety of experimental techniques.
- Temperature control was successfully introduced into the thermal pulse instrument for the first time.
- An experimental scheme was proposed and realized for isolating the pure thermal response from the response due to native or injected space charge.

Outputs

Publications

E.K. Hobbie and A S. DeReggi, *Laser-Pulse Technique for Measuring the Thermal Diffusivity of Substrate-Supported Polymer Films*, Review of Scientific Instruments, in press.

E. Gonzalez, E. Hobbie, A. Feldman and A. DeReggi, *NIST Round Robin Study of Thermal Transport in Thin Dielectric Films* (NIST Internal, preprint).

Functionalized Silsesquioxane Cubes as Potential Underfill Encapsulants

Eric K. Lin, Christopher L. Soles and Wen-li Wu

Objectives

The objectives are to evaluate the critical physical properties of novel epoxide-functionalized silsesquioxane cubes to be used as potential underfill materials in flip-chip packaging, to compare these material properties with those of conventional underfill encapsulant formulations, and to establish molecular structure-property relationships for octahedral silsesquioxane based inorganic/organic hybrid materials.

Technical Description

The microelectronics industry has seen increased use of direct chip attachment technology where the chip is attached to the board through an array of solder bumps. Critical to reliable device operation in this technology is the underfill material placed between the chip and the board. The function of the underfill is to reduce the stresses at the solder interfaces that arise from the large thermal expansion mismatch between the chip and the board. Typically, a liquid epoxy underfill is dispensed along one or two sides of the chip and capillary forces wick the underfill into the gap and between the solder bump array ((30 to 50) μm in height). The underfill is then cured into a rigid glass. Generally, underfill materials consist of an epoxy resin highly filled (up to a mass fraction of 75 %) with silica particles, and additives to enhance wettability and adhesion. The silica filler is needed to decrease the coefficient of thermal expansion (CTE) of the underfill to match that of the solder bumps ((20 to 30) $\times 10^{-6}/^{\circ}\text{C}$). There are many material property requirements for an acceptable underfill encapsulant. The cured material must have a low CTE, a high glass transition temperature (T_g), a large modulus, and low moisture uptake. In addition, the flow and surface interaction properties of the uncured fluid must be optimized so that the gap is easily filled and complete wetting is obtained on the different surfaces.

A large number of factors need to be considered in selecting an appropriate underfill system. For example, both the viscous properties of the liquid and the physical properties of the cured resin depend upon filler characteristics such as the particle size distribution, density, shape, and surface characteristics. One of the main limitations of current flip chip processes is the long time needed to fully fill the gap under capillary action. The high concentration of filler plays a significant role in the decreased flow rate and also leads to complicated rheological behavior. In addition, the filler particles can be similar in size to the gap and result in flow defects that eventually lead to device failure. A simpler, one-phase, underfill system would be highly desirable.

We address these concerns by investigating the possible use of single-phase inorganic/organic molecular hybrid materials. Inorganic/organic hybrid materials such as epoxide-functionalized silsesquioxane cubes may provide a single phase fluid alternative to current underfill formulations. Silsesquioxane cubes are synthesized by assembling the Si-O tetrahedron of silica into eight cornered cubes. In some respects, these cubes represent the smallest unit of ceramic silica. The corners of the nanometer-sized cubes are easily functionalized with reactive organic groups such as an oxirane ring (epoxy) as well as many other organic functional groups. They can be polymerized into inorganic/organic hybrid materials utilizing the identical chemistry employed in current underfill formulations. In this work, we measure physical properties critical for underfill applications using model epoxide-functionalized silsesquioxane cube materials and diamine curing agents. Several epoxy cube/diamine combinations are used to observe how physical and structural properties change using different curing agents and degree of epoxy functionality. A variety of experimental techniques are used to characterize both the physical and mechanical properties of these cube-based epoxy resins. The parameters to be evaluated

include structure (x-ray diffraction), thermal expansion (x-ray reflectivity), glass transition temperature (differential scanning calorimetry), viscosity (rheometry), cure shrinkage, density, modulus, moisture absorption, strength, and toughness.

External Collaborations

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

Planned Outcome

This work represents the evaluation of nanostructured inorganic/organic hybrid materials as replacements for traditional filled organic materials as well as for the specific application of underfill encapsulants. Accomplishing this goal will significantly improve the underfill process by creating low viscosity resins that exhibit excellent flow or filling characteristics in addition to meeting critical CTE requirements. Furthermore, this work will also foster an understanding of the molecular structure/property relationships needed to tailor the properties of inorganic/organic hybrid nanostructured materials.

Accomplishments

- The viscosities at 25 °C of the neat epoxy-functionalized cubes are found to be Newtonian with values of 310 cp for the octa-epoxide cube and 960 cp for the tetra-epoxide cube. These viscosities are orders of magnitude lower than those of commercial underfills ($\approx 50,000$ cp), providing for better flow and gap filling properties.
- Very thin and uniform films (300 Å to 800 Å thick with root mean square (rms) surface roughnesses less than 20 Å) of the tetra- and octa-epoxide functionalized silsesquioxane cubes cured with several diamines have been prepared.
- The glass transition temperature of the cured epoxy-functionalized cube material is found to be in excess of 200 °C for each of the diamine curing agents studied.
- The coefficient of thermal expansion (CTE) of the inorganic/organic hybrid material depends heavily on the structure of the curing agent and degree of functionalization. Using very short curing agents and tetra-epoxide cubes, the CTE values very close to those required in commercial underfill applications can be obtained.
- X-ray diffraction reveals that the microstructure of networks of silsesquioxane-based epoxy networks evolves in a non-intuitive manner. Increasing the length of the curing agent results in closer cube spacing in the material. The long length curing agents also create networks with much less structural order than those with shorter length curing agents.

Outputs

Publication

E.K. Lin, W.L. Wu, C.X. Zhang, and R.M. Laine, *Materials Characterization of Thin Films of Epoxide Functionalized Silsesquioxanes*, in Proceedings of the International Microelectronics and Packaging Society: Advanced Packaging Materials: Processes, Properties, and Interfaces, 63, 1999.

Presentation

E.K. Lin W.L. Wu, C.X. Zhang, and R.M. Laine, *Materials Characterization of Epoxide Functionalized Silsesquioxanes as Potential Underfill Encapsulants*, International Microelectronics and Packaging Society: Advanced Packaging Materials, Braselton, GA, 3/99.

Polymer Electrostriction

Aime S. DeReggi, Edward Balizer¹, Fred Bateman² and Dan Neumann³

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² NIST Radiation Physics Division

³ NIST Center for Neutron Research

Objective

The objective is to provide the U.S. transducer industry with definitive information about the large electrostriction recently discovered in certain ferroelectric copolymers after electron irradiation to a high dosage. The mechanism of this large electrostriction is not yet understood but has been hypothesized to be associated with a reversible electric field driven phase transformation made possible by the irradiation.

Technical Description

Neutron scattering is used to investigate the irreversible crystallographic phase changes induced by electron irradiation as well as the reversible changes that might be driven by an electric field. Pulsed pyroelectric measurements are used to characterize the charge distribution produced by the irradiation as well as the polarization distribution induced by an applied electric field. The electrostrictive thickness change, thus the large electrostriction, is measured using a newly devised optical method.

External Collaborations

- Francois Bauer, ISL/France - provided initial research materials.
- Thomas Ramotowski, NUWC/RI - provided additional research material.
- Q. M. Zhang and Vivek Bharti, Penn State University - shared information and made initial electrostriction measurements.

Planned Outcome

The planned outcomes include confirmation of the large electrostriction, determination of the type and the amount of phase transformation responsible for the large electrostriction, verification of suitable irradiation conditions to achieve a large electrostriction, and qualification of the usefulness of the new effect in transducers.

Accomplishments

It was demonstrated that electron irradiation produces, in the normally mixed phase material, an irreversible transformation of the ferroelectric part to a paraelectric phase, with an increase in lattice spacing and, in the paraelectric part, modification to that phase in the form of an increase in the lattice spacing. For a broad range of irradiation conditions, the lattice spacing changes are not large enough to account for the electrostriction. Space charge effects have been found to influence the electrostriction.

Outputs

Publication

E. Balizer, A.S. DeReggi, D.A. Neumann, Fred Bateman, *Polarization and Structural Transitions of irradiated vinylidene fluoride- trifluoroethylene copolymer*, 1999 Annual Report, IEEE Conference on Electrical Insulation and Dielectric Phenomena, to appear in October 1999.

Presentations

E. Balizer and A. S. DeReggi, *Structural Relaxations in Electrostrictive Polymer*, ONR/Penn State Transducer Materials Workshop, April 1999.

S. DeReggi, E. Balizer, D. Neumann, Fred Bateman, *Space Charge Effects on Polymer Electrostriction*, in preparation for MRS meeting, November 29- Dec 3, 1999.

Electrical and Thermal Properties of Thin Polymer Films

Aime S. DeReggi and Erik Hobbie

Objective

The objective is to provide the U.S. microelectronics industry with reliable and *in-situ* methods to characterize the electrical and thermal properties of substrate supported polymer films.

Technical Description

Pulsed laser heating of a voltage biased sample is used to stimulate a pyroelectric response which, together with a theoretically calculated temperature profile, is used to determine the thickness averaged electric field and thermal properties as well as their dependence on position across the thickness. Validation of the method is both internal (simulation) and external (comparison with other methods, interdivision reference sample exchange).

External Collaborations

- Dr. Mel Zussman, Dupont, provided materials information and referred ITT/GaAsTEK to NIST for thermal property measurement.
- Dr. Mat Arayanan of ITT/GaAsTEK provided industrial samples.
- Dr. Peter Bloss, Polymer Institute, Leipzig contributed to the preparation of publications.
- Dr. Thomas Avedisian, Cornell University, who is also investigating thermal measurement methods has participate in information exchange geared to the development of thermal reference samples.
- Dr. Eberhard Hartmann, Institute of Surface Modification, Leipzig University, has provided nanocomposite samples and collaborated in measurements.
- Dr. Gerhard Sessler, Technical University, Darmstadt, collaborated in a methods comparison exercise that resulted in a joint publication.

Planned Outcome

The planned outcomes include validation of the pulsed pyroelectric method and the dissemination of this method for measuring thermal properties with high surface and interface sensitivity.

Accomplishments

- It was shown from general principles, and independently from the normally used numerical analysis procedures, that polyimide films have electrical and/or thermal properties that could be strongly influenced by surface phenomena.
- The pulsed pyroelectric method is now demonstrated to be a powerful surface-sensitive electrical and thermal characterization method.

Outputs

Publications

P. Bloss, A.S. DeReggi, H-J Glasel, E. Hartmann and D. Hirsh, *Polarization distribution in ceramic-polymer nanocomposites*, J. Appl. Phys. Vol. 86, No. 5 pp. 2712-2718 (Sept. 1999).

P. Bloss, A.S. DeReggi, G-M Yang and G-M Sessler, *Thermal and acoustical pulse studies of space charge profiles in electron-irradiated fluoroethylene propylene*, J. Phys. D: Appl. Phys., in press.

Aime S. DeReggi, Erik Hobbie, Peter Bloss and Hartmut Schafer, *Surface-enhanced thermal pulse measurements of thermal and electrical properties of polyimide films*, 1999 Annual Report, IEEE Conference on Electrical Insulation and Dielectric Phenomena, to appear in October 1999.

Aime S. DeReggi, Erik Hobbie, Peter Bloss and Hartmut Schafer, *Surface-enhanced thermal pulse measurements of thermal and electrical properties of polyimide films*, 1999 Annual Report, IEEE Conference on Electrical Insulation and Dielectric Phenomena, to appear in October 1999.

Thin-Film Residual Stress Measurement: Application in Determination of In-plane CTE and In-plane Modulus

Chwan K. Chiang, William F. Guthrie¹, William E. Wallace and Gary W. Lynn²

¹ NIST Statistical Engineering Division

² University of Tennessee, Knoxville, TN

Objective

The objective is to develop a test method based on a residual stress measurement for determining in-plane coefficient of thermal expansion and in-plane elastic modulus of thin polymer films while adhered to a rigid substrate such as silicon wafers.

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. Residual stress can be determined by measuring the bending of the wafer provided the elastic constants of the wafer are known quantities. 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 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. Letters **36**, 162 (1980)). In our work, silicon and GaAs wafers were chosen as the substrates because of their wide usage in electronic industries. A new technique with the potential to greatly simplify the above mentioned procedure is also under development.

External Collaborators

- Dr. David Feiler and Dr. Wei Xia of Rockwell Semiconductor System have provided the spin-on low K dielectric materials.
- Dr. David Babb of Dow Chemical Company has provided the samples and also collaborates on the property measurements.

Accomplishments

- The newly implemented modification on a KLA- Tencor stress measurement system has resulted in a great reduction of thermal induced noise. This improvement enables the analysis of the stress state in detail. Statistical analysis showed that the stress temperature relation of PFCB, a low k candidate polymer from Dow Chemicals, was far more complex than previously conceived.
- A new device is under development for simultaneously measuring the in-plane modulus and the in-plane coefficient of thermal expansion of a thin-film adhered on a wafer.
- The stress-temperature relationship of FOX, a primary low k candidate from Dow Corning, was studied and the change of stress correlated well with an increase in electronic density of the film. This thermally activated stress relaxation behavior is interpreted in terms of the reflow of the glassy hydrogen- silsesquioxane material.

Outputs

Publications

C.K. Chiang, *Measurement of in-plane CTE and Modulus of Polymer Thin-Films*, Bulletin of Am. Phys. Soc., Vol. 44, No.1, 1672 (1999).

C.K. Chiang, W.E. Wallace, G.W. Lynn, D. Feiler and W. Xia, *Stress Relaxation and Densification of Spin-on-Glass Thin Films*, J. Appl. Phys., in press.

Assembly of IC Chips Utilizing Wafer-level Underfill

William E. Wallace

Objective

The objective is to provide design software and materials data to industry for predicting behavior to be encountered during assembly of flip chips that have underfill/solder bump system applied at wafer level.

Technical Description

The NIST Metallurgy and Polymers Divisions are working on the wetting behavior of solder in solder-joint interconnections under the constraints imposed by wafer-level underfill systems. The pre-existing underfill geometry provides constraints on the flow of solder, influencing the self-alignment of the die and the final solder joint geometry. These factors will have profound effects on joint reliability. In addition, if reflow of solder paste into cavities in the underfill polymer is required, surface tension will control the quality of the filled cavity.

The Metallurgy Division is in the process of developing a computer code to calculate expected solder joint geometries given various constraints imposed by the surrounding polymer underfill. Important parameters include surface tension of the solder, interfacial energy of the solder and the polymeric underfill, alignment of the chip with the carrier or the printed circuit board pads, adhesion or traction forces of the underfill during reflow of the solder, solidification shrinkage of the solder, etc. The Metallurgy and Polymers Divisions are jointly conducting an experimental program which includes the development of measurement techniques for various aspects of adhesion and interfacial energy between solder, substrates, and underfill materials. These measurement methods are needed in order to determine the performance of proposed underfill systems and are coupled closely with data needed in the computer modeling calculations.

Planned Outcome

This work is expected to generate design tools for industry in material and geometries selections for a successful design and assembly of wafer level underfill systems. Research results will be disseminated through key publications and our in-place solder design web page within the MSEL Center for Theoretical and Computational Materials Science (CTCMS).

Accomplishments

- Measurements have been made of the contact angles formed at solder / polymer / vapor triple junctions. Contact angles of solder pastes from two different manufacturers, both metal compositions nominally Sn63-Pb37, were measured on each of two different polymers representative of those found in applications, an epoxy and a polyimide. Contact angles of all four combinations fell within the range 155° to 160°, with data scatter varying between 2° and 5° for the multiple measurement used to determine each value.
- Two different Surface Evolver computer codes have been written for the modeling effort. Both are available at the CTCMS web site at <http://www.ctcms.nist.gov/djl/solder/new.html> as part of the library of evolver files modeling different industrial solder joint geometries. The first evolver code, titled “flip chip alignment force” permits modeling of the force-displacement relationship of a pair of circular pads (one above the other) with solder in-between. Contact angles of the solder on the pad and surroundings are independently adjustable, as are the solder volume, density and pad dimensions. Horizontal and vertical forces are calculated as functions of both vertical separation and horizontal misalignment of the pads. The second code, titled “solder paste in a bilayer hole”, models the solder shape for a pad that is surrounded by a (typically nonwetting) medium such as in underfill geometries with sacrificial layers. The codes include input options for the volume fraction of solder in the solder paste.

Impacts

Through the CTCMS web page we have been contact by technical representatives of Delco Electronics on the matter of a collaborative effort in this area.

Outputs

Presentations

Dan Josell, William Wallace, *Assembly of IC Chips Utilizing Wafer-level Underfill*, ATP FY99 Intramural Project Review, Gaithersburg, MD August 1999.

Other

Computer code placed on CTCMS web page.

Spectroscopic Studies of Polymer Surfaces and Interfaces

William E. Wallace and Wen-li Wu

Objective

The objective is to provide U.S. industry with *in-situ* and nondestructive measurement tools to characterize the chemical composition and molecular structure of polymer surfaces and interfaces with emphasis on buried interfaces.

Technical Description

Comprehensive surface and interface analysis requires the use of multiple techniques in concert to determine what chemical moieties are present, their relative abundance, and their molecular orientation. To this end we are pursuing three promising measurement techniques in conjunction with three different research groups at NIST. Vibrationally-resolved sum-frequency generation (SFG), a uniquely interface specific spectroscopy performed in conjunction with Lee Richter (Div. 837), is a non-linear optical technique that is symmetry allowed only in regions of the sample that lack inversion symmetry. A visible and an IR laser photon are combined to form a third whose energy is the sum of the first two. When the IR photon is resonant with a vibrational mode at an interface there is an enhanced probability of sum-frequency mixing leading to a characteristic vibrational spectrum of the interface. Near-edge x-ray absorption fine structure (NEXAFS), a surface-sensitive electron spectroscopy performed in conjunction with Dan Fischer (Div. 852), is the use of a tunable, polarized photon beam from a synchrotron to excite core-level electrons into higher lying unfilled atomic or molecular orbitals. By monitoring the ejection of these secondary electrons, the orientations of bonds can be selectively probed at free surfaces. Secondary-ion mass spectrometry, a surface-sensitive mass spectrometric technique performed in conjunction with Greg Gillen (Div. 837), uses a beam of incident ions to erode the sample surface. Ejected secondary ions are mass analyzed to determine composition. Depth profiling to explore buried interfaces is often performed.

External Collaborations

- Jan Genzer, North Carolina State University - NEXAFS.

Planned Outcome

The effort into the fundamental metrology of polymer surface composition and structure will have repercussions wherever polymers are used as adhesives, protective layers or surface-active agents.

Accomplishments

SFG has been used to measure the orientation of pendant side groups and end groups at polymer surfaces. Systems studied include polystyrene (atactic, isotactic, syndiotactic), poly (α -methyl styrene), poly (methyl methacrylate), poly (vinyl alcohol), and polyimide (PMDA-ODA). Atactic polystyrene of different molecular masses was shown to have a molecular mass dependent orientation of the phenyl ring at the free surface.

NEXAFS has been used to show that surface chains relax faster than bulk chains in uniaxially-deformed polystyrene. Polystyrene samples were deformed at room temperature in a channel die. The electron yield from a polarized incident x-ray beam was used to determine the orientation of the pendant phenyl ring as well as the carbon backbone to depths of 5 nm.. The x-ray fluorescence yield from the same incident beam was used to examine the orientation of the chains to depths of 50 nm. Upon annealing at 60 °C the initial analysis of the data suggests that the surface chains return to random orientation faster than the bulk chains indicating an enhanced surface mobility in amorphous polystyrene.

Neutron Scattering and the Low Energy Excitations in Polycarbonate Copolymers

Christopher L. Soles, R. Dimeo, Jianwei.Liu¹, Albert Yee¹, Alexie Sokolov², and Wen-li Wu

¹University of Michigan, Department of Materials Science, Ann Arbor, MI

²University of Akron, Department of Polymer Science, Akron, OH

Objectives

The objectives of this project are (1) to establish structure-property relationships in a series of polycarbonate copolymers to determine the molecular origins of the Boson peak, a feature common to glassy polymers, (2) to relate the fast (picosecond) dynamics observed in neutron scattering to several of the well characterized slower dynamic processes in glassy polymers and (3) to apply the knowledge obtained from inelastic neutron scattering to several commercially and technically relevant problems in polymer science, such as the deviation of physical properties in ultra-thin films, polymer processing, gas transport, and impact resistance.

Technical Description

The Boson peak is a common feature observable by inelastic neutron scattering and Raman measurements in most glass forming materials. When a beam of neutrons is impinged on a glass, the majority of the scattering is elastic (or slightly broadened in energy - termed quasielastic) and the scattered neutrons leave the sample with an energy equal to the incident energy. However, a small fraction of the neutrons are scattered with a distinct energy shift of ≈ 1 meV to 10 meV, comprising the so-called Boson peak. To date, the molecular origins of the Boson peak are not entirely clear. Prominent theories suggest that the inelastic shift is due to localized (on the scale of 10's of angstroms) harmonic vibrations in densified regions while the quasielastic broadening

comes from the dissipation of these vibrations into the less dense regions. In this scenario, both the Boson peak height and frequency shift depend on the density fluctuations within the glass.

In this work a series of polycarbonate copolymers are used to study the origins of the Boson peak. This series is unique in its molecular architecture that has been systematically varied by inserting cyclohexylene linkages into the main chain at regular intervals. These same copolymers have been studied extensively in terms of their mechanical properties and relaxational behaviors. These preceding studies suggest that incorporating main-chain cyclohexylene linkages into a polyester carbonate significantly enhance the volume fluctuations of the material. In this respect, these materials are ideally suited to critically test the current ideas regarding inelastic neutron scattering and the Boson peak.

As alluded to above, these copolymers are widely studied in terms of their mechanical and physical properties (toughness, dynamic mechanical relaxation behavior, gas transport properties, ultra-thin film properties, etc.). This provides a framework in which to analyze the inelastic and quasielastic neutron scattering data, potentially establishing an industrial relevance to highly theoretical neutron scattering experiments.

External Collaborations

- Jianwei Liu and Albert Yee, University of Michigan - synthesis of copolymers and determination of the mechanical properties.
- Alexei Sokolov, University of Akron - consultation on neutron scattering as well as supporting Raman scattering measurements.

Planned Outcomes

The systematic structural variations induced by incorporating the cyclohexylene into the main chain of the polycarbonate at regular intervals provide a nice material system to establish structure-property relationships regarding the Boson peak. Such relationships should help clarify the molecular origins of the this inelastic scattering feature. The Boson peak is common among a wide variety of glasses, including polymers, ionic salts, covalent solids, etc., and is widely studied. However, it is difficult to attribute subtle differences in the inelastic scattering spectra (peak height and position) to structural parameters when the systems are so varied. For example, there are many differences between silica glass and amorphous polycarbonate and it is nearly impossible to highlight which differences are relevant to the Boson peak. In this respect, a homologous copolymer series where the structural variations are introduced gradually in a controlled manner is anticipated to be powerful tool for understanding this phenomenon.

The state of the art understanding regarding the Boson peak suggests that the inelastic shift of the scattered neutrons is due to localized harmonic vibrations. These vibrations occur in densified regions on the order of nanometers and are dissipated into the surrounding lower density regions. The larger the localized regions are the smaller the frequency shift. Such an interpretation suggests the importance of a new material length scale - the scale of the fluctuations. For example, one might expect significant deviations in the properties of a thin film when the thickness approaches the natural scale of these fluctuations (thermal expansion measurements of ultra-thin films of these copolymers are currently in progress). Furthermore, the mechanical and physical properties of these polycarbonate copolymers are already interpreted in terms of their volume fluctuations. The neutron scattering measurement will provide complimentary information and help sort out differences between frozen in and dynamic density fluctuations.

Volume or density fluctuations have a profound influence on several physical properties that are relevant to many practical issues in polymer science. In this respect, this work should also enable a link between the highly “scientific” topic of neutron scattering and several “basic” application-related problems. For example, it is observed that gas permeation rates increase with the cyclohexylene content for these polycarbonate copolymers. A naive first approximation might attribute this observation to a molecular level “shutter” effect induced by the chair-boat-chair transitions of the cyclohexylene unit. However, it would be a profound distinction if the enhanced transport were due to enhanced static density fluctuations as opposed to dynamics. Similar practical extensions of neutron scattering are being explored with thin film polymer properties, impact resistance, and polymer processing parameters.

Accomplishments

This project is still in its initial stage and the first set of neutron scattering measurements on polycarbonates has just been completed. Pronounced Boson peaks were observed and the detections of Boson peak in polycarbonate using neutron scattering have not been reported in the literature. A detailed data analysis is in progress and supplement measurements using techniques other than neutron scattering are under way.

Fundamentals of Polymers at Surfaces and Interfaces

Wen-li Wu, Eric K. Lin, Darrin J. Pochan and Christopher C. White

Objectives

The objectives are to determine the influence of surfaces and interfaces on polymers by measuring the structure and properties of polymers in ultra-thin films and adjacent to well characterized substrates.

Technical Description

As feature sizes in integrated circuits continue to decrease in size, the changing properties of materials in these confined geometries become important to the development of next generation devices. Polymeric materials play an important role in these devices in applications such as interlevel dielectrics, encapsulants, and lithographic materials. The physical properties of polymer thin films are measured using a variety of techniques including specular and off-specular x-ray and neutron reflectivity, energy-dispersive x-ray reflectivity, total external reflectance x-ray fluorescence, MeV ion scattering, atomic force microscopy, a unique twin quartz resonator, fluorescence probes, and ellipsometry. Technical descriptions for specific projects are detailed below.

- X-ray and neutron reflectometry provide high resolution, *in-situ* measurement of the interfacial structure normal to the sample surface. These techniques are used to determine several important properties of polymer thin films and polymers at surfaces and interfaces. Buried polymer layers are studied with neutron reflectometry. The effects of polymer/substrate interaction on inter-diffusion dynamics are measured by modifying the silicon oxide surface with different self-assembled monolayers. The mobility of polymer chains near an attractive substrate is also determined as a function of the molecular mass of the overlayer.

- Neutron and x-ray reflectivity techniques are used to measure the thermal expansion of ultra-thin (thickness < 100 nm) amorphous polymer films. Material properties of thin films are observed as a function of film thickness and the type of substrate with varying surface energies. These reflectivity techniques are also utilized to observe the segregation of small molecules used as probes in numerous other experimental techniques.
- Neutron and x-ray diffraction techniques, collectively, are used to provide a comprehensive in-plane and out-of-plane characterization of the symmetry and orientation of crystallites in semicrystalline polymers in a thin-film geometry.
- The development of an 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 configuration. 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 instrumental design based on a resonating quartz crystal has been designed and realized. With an ultra-thin polymer layer attached to the crystal, the resonance condition of the quartz crystal is shifted slightly and the width of the frequency peak is broadened.

External Collaborations

- Prof. S. Z. D. Cheng and Prof. F. Harris of the University of Akron prepare high T_g polyimide materials that are soluble in organic solvents.
- Dr. R. Kolb of Exxon Research and Engineering collaborates on synchrotron radiation experiments on semicrystalline polymer thin films.
- R. Trolard of Cambridge Isotopes Laboratories provides detailed molecular analysis of deuterated semicrystalline polymers, and custom synthesis of other deuterated polymers.
- Prof. M. Rafailovich and J. Sokolov of SUNY Stony Brook provide SIMS measurements for polymer thin film studies.
- Prof. P. Nealy of the University of Wisconsin-Madison provides substrates with varying surface energy for polymer thin film studies.

Accomplishments

- Diffusion studies of PMMA chains of three different molecular masses within a layer adjacent to a native silicon oxide surface using neutron reflectometry were completed. The results showed that the polymer inter-diffusion rate was significantly reduced within an interfacial region of thickness equal to about three radii of gyration. It was also determined that reducing the interaction energy between the polymer and the substrate resulted in faster segment desorption kinetics. However, even a slight attractive interaction between the polymer and the surface is sufficient to “pin” the polymer to the surface. Shear deformation parallel to the interface was found to dramatically enhance the surface segment exchange kinetics relative to the static case.
- Fluorinated, low surface energy polyimide was used as both substrate and substrate confinement layers enabling the first observation of thin deuterated polystyrene film material properties with and without a free surface. The low surface energy of the confinement layers excluded specific, enthalpic interactions as a cause of altered thin film properties, thus

allowing the observation of purely entropic confinement effects. Significantly different thermal expansion behavior was observed between uncapped and capped polymer films in samples with thickness between 70nm and 40 nm. Bulk, glassy coefficients of thermal expansion (CTE) were observed well above the bulk glass transition of 100 °C after capping. In films with thickness below 40 nm glassy behavior was observed in both uncapped and capped polymer films up to 40 °C above the bulk glass transition temperature.

- Radiological modified self-assembled monolayers were employed to generate systemically varied surface energy substrates. Subsequent x-ray reflectivity thermal expansion studies on thin (thickness = 60 nm) polystyrene and PMMA films attached to these surfaces showed a consistent shift in the transition from a glassy expansion to a rubbery expansion to higher temperatures with decreasing hydrophobicity. Further studies on the thickness dependence of these observations with polystyrene demonstrated that for hydrophobic surfaces there was little or no shift in the transition from a glassy expansion to a rubbery expansion with decreasing film thickness. The hydrophilic surface samples demonstrated bulk like behavior for all polystyrene films greater than 80nm. Films thinner than 80 nm exhibited an increase in the transition from a glassy expansion to a rubbery expansion to higher temperatures with decreasing film thickness.
- The crystalline morphology of thin films (thickness < 100 nm) of deuterated isotactic polypropylene (iPP) was determined to be monoclinic with a strong orientation of the unit cell c-axis (chain backbone) in the plane of the film. Extended annealing above the melt temperature allowed the films to dewet, apparently from the substrate. Subsequent x-ray reflectivity revealed a remaining surface layer of iPP. This persistent interfacial layer strongly suggests a highly oriented polymer interfacial layer from which the rest of the film auto-dewet.
- The quartz crystal resonator instrument has been developed and used to determine the viscoelastic properties of ultra-thin polystyrene films. At temperatures below T_g of the polymer, the rigid glassy polymer film moves in phase with similar amplitude with the quartz driving surface. As the temperature is raised through the T_g of the polymer, the polymer film becomes more rubbery and begins to move with a motion that is out of phase and with a different amplitude than that of the quartz driving surface. This change in properties is measured by a change in the resonance frequency of the quartz crystal and broadening of the resonance frequency peak.
- A viscosity sensitive fluorescent probe was used to monitor the viscosity of thin polymer films. For supported thin (thickness < 100nm) polystyrene films on quartz, no thickness dependence on the glass transition was observed. Independent x-ray reflectivity measurements also exhibited no shift in the transition from a glassy expansion to a rubbery expansion with decreasing film thickness for polystyrene on quartz. Additional viscosity sensitive fluorescent probe experiments were performed on thin (thickness < 100 nm) free-standing polystyrene films. These films exhibited a decrease in the glass transition temperature with decreasing film thickness.
- Secondary ion mass spectroscopy was used to follow the diffusion of low molecular mass deuterated polystyrene chains in free-standing thin films (thickness <100nm). The temperature dependence of the diffusion constant was used to determine the glass transition

temperature. Using this method, a supported thick (thickness = 200 nm) polystyrene film showed bulk behavior, while a thin (thickness = 40 nm) polystyrene film exhibited a glass transition temperature lower than bulk behavior, and consistent with several other published studies.

Outputs

Publications

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E.K. Lin, R. Kolb, W.L. Wu and S.K. Satija, *Enhanced Polymer Segment Exchange Kinetics at the Melt/Solid Interface due to an Applied Shear Deformation*, *Macromolecules*, 32, 4741 (1999).

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C.C. White and W.L. Wu, *Determination of the Complex Modulus of a Supported Ultra-Thin Polymer Film*, *Applied Physics Letters*, submitted.

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C.C. White, W.L. Wu, Y. Pu, M. Rafailovich and J. Sokolov, *Probe Segregation within an Ultra-thin Polystyrene Film Studied by X-ray, Neutron Reflectivity and SIMS and T_g Determination of Polystyrene on a Quartz Substrate by X-ray Reflectivity*, *Macromolecules*, submitted.

Presentations

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C.C. White and W.L. Wu, *Fluorescence Probe Determination of the Glass Transition Temperature (T_g) for Supported and Free-Standing Ultra-Thin Polymer Films*, American Physical Society, Atlanta, GA, March 1999.

C.C. White and W.L. Wu, *Deviations From Assumed Behavior, The Metrology Of 0.1 Micron Polymer Films, 100nm Gigascale Integration*, Sponsored by the Knowledge Foundation, San Francisco, February 1999.

C.C. White and W.L. Wu, *Determining the Glass Transition Temperature of Ultra-Thin Films*, Materials Research Society Meeting, Boston, MA, December 1998.

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D.J. Pochan, E. Lin, S. K. Satija and W.L. Wu *Effects of a Thin-film Geometry on the Phase Behavior and Morphology of Thin Polymer Films*, Polymers West Gordon Conference, Ventura, CA, January 1999.

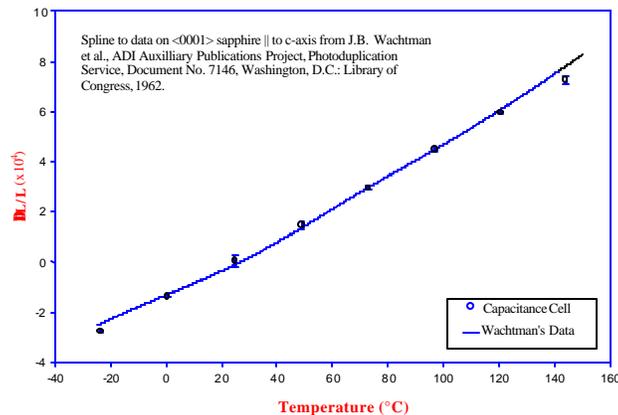
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Standard Test Method

...addressing important needs for standard test methods

High Precision Capacitance Cell Developed for Thin Film Out-of-Plane Expansion

Polymers Division researchers, Fred Mopsik and Chad Snyder, developed a high precision capacitance cell for measuring thermal or humidity induced changes in thickness for films between 5 μm and 1 cm thick. The relative expanded uncertainty in the thickness is 0.1×10^{-6} for isothermal measurements and 1×10^{-6} for thermal cycling under dry conditions (*i.e.* 0 % relative humidity). The accuracy of the cell has been verified using a $\langle 0001 \rangle \text{Al}_2\text{O}_3$ single crystal of 0.5 mm thick as the test standard. Thin film expansion data are needed by microelectronics industries and others to model and to predict the mechanical integrity of multilevel microelectronic chips that are subjected to temperature and humidity changes. No suitable technique was available for thin films in the micrometer thickness range. The process for submitting this cell design and the measurement protocol as a standard test method to the Institute for Interconnecting and Packaging Electronic Circuits (IPC) has been initiated.



Thin film expansion data are needed to model the mechanical integrity of multilevel microelectronic chips that are subjected to temperature and humidity changes.

The cell design is unique in that it is based upon a three-terminal guarded electrode that isolates the sample from the measurement path so that the dielectric constant of the sample is not needed. For this reason, diverse materials such as polymers and ceramics can be measured using the current cell design. As an example, measurements were conducted on a 14 μm thick polymer film. Values determined for the thin polymer film agreed with those obtained by a combination of in-plane expansion measurements and volume dilatometry on larger samples to within the combined uncertainties. A future design modification will enable the expansion measurements of conductive materials such as metals.



Since the method requires the dielectric constant of air to be precisely determined, data reduction software and protocols were developed for humid conditions to estimate thickness values reliably. Theoretical calculations have been performed to estimate the minimum attainable uncertainty in these measurements. The ability of our data reduction software/protocol to provide accurate thickness values within the limits of these uncertainties has been demonstrated. It is expected that this metrology will find a variety of other applications as an extremely sensitive displacement sensor.

POLYMER BLENDS AND PROCESSING PROGRAM

To advance the US polymer blends and processing industry into the next century and maintain leadership in the world market, technology must move well beyond its current state-of-the-art in key areas. Lower operating costs and capital investment, and shorter time from concept to manufacturing are vital to enhancing global competency in the polymers industry. On-line methods to measure quality and control key components are critical for rapid product developmental cycles. Rapid high throughput evaluation techniques, new measurement technology, and real time process control capability are critical for handling processing of complex multicomponent polymer systems.

An important class of multicomponent polymeric materials contain inorganic fillers and nanofillers. A technical revolution of increased industrial interest and research has occurred in nanofillers due to their promise for cost-minimization coupled with the potential for enhanced performance. Recent advances in polymer-clay "nanocomposite" materials have taken the lead in this new research area. Development of new cost-effective techniques for creating a broader variety of macromolecular architectures such as dendrimers also holds promise for unique material properties due to their novel structure and high surface density of functionalized moieties. In the polymer coatings area, molecular self-assembly methods for creating nanostructures is a growing field. New capabilities are also envisioned by interdisciplinary activities to create new fields of technology, such as polymer containing biomaterials. Modeling tools are essential to understand and interpret the dynamical and steady state aspects provided by these new technology areas.

The Polymer Blends and Processing Program has previously established expertise in static and kinetic aspects of phase behavior of polymer blends, effects of shear flow on mixing and separating, and reactive processing to promote compatibility. The focus of the current program areas has shifted to meet the new needs and challenges of the polymers industry outlined above. Current research efforts are focussed in the following areas: (1) Measuring interactions, structure and dynamics of filled and nanofilled polymers, effects of shear on morphology, filler wettability studies, and phase separation of filled systems (2) Control of polymer processing conditions, on-line characterization of morphology, dielectric property, and temperature profiling (3) Characterization of structures of unique macromonomers such as dendrimers, hyperbranched molecules, metal containing dendrimers and dendrimer-polymer network structures (4) Combinatorial high throughput measurements of phenomena in polymer science (such as dewetting of polymer coatings, phase separation in polymer blends) utilizing concepts of library preparation, automated data analysis, validation and feedback (5) Theory and modeling effort in collaboration with CSTL to guide and interpret measurements in the above research areas.

The unique measurement capabilities provided by specialized light and neutron scattering methods continue to be applied for understanding thermodynamics, kinetics and morphology of multicomponent polymer systems. Each program areas interacts with industry to develop measurement methods using tools of fluorescence, light scattering, neutron scattering and reflectivity, x-ray scattering, birefringence, microscopy (AFM, TEM, phase contrast), and rheology. Industrial collaborators include: Dow Corning, Dynisco, 3M, Dendritech, DSM, Dow Chemical, DuPont, Exxon, Kodak, Lucent Technologies, Goodyear, Mobil, Raychem, Sid Richardson, Michelin USA, Southern Clay, Specialty Minerals, Hyperion Catalysis and GE.

Collaborations also exist with a number of national and international universities and national laboratories.

Significant Accomplishments

- Developed, in collaboration with Mobil Chemical, a new optical sensor for real time measurements of polymer orientation and temperature during the biaxial stretching of polypropylene films. The polypropylene contained a fluorescent dye that was used to measure both orientation and temperature.
- Discovered a droplet-ribbon transition as a function of shear rate in sheared polymer blends. The string formation has profound implications for nano and micro scale fabrication via polymer blends, indicating the possibility of in-situ fiber formation to produce ultra-strong materials.
- Confirmed, from the observation of vorticity alignment of sheared polymeric droplets, that droplet elasticity is the key element in the development of vorticity alignment. This discovery provides a direct connection between phenomena observed during extrusion and during plate-plate flow.
- Critical issues such as dynamics of polymers at the carbon black polymer-filler interface and a reliable working definition and measurements of filler dispersion were discussed at the Fillers Working Group meeting held at NIST jointly with industrial partners from Dow Corning, Sid Richardson Carbon Black Co., Michelin Americas, and from Los Alamos National Laboratory.
- Determined, in collaboration with Dow Corning, that the chain deformation behavior of polysilicate filled polymers correlated to the type of fumed silica used and the stress-strain behavior.
- Discovered, in collaboration with Southern Clay Products, that the elastic behavior of the clay-polymer solutions is a result of the synergistic coupling of the polymer deformation and clay orientation in flow. Solution processing of clays is an important but poorly understood area of clay-polymer nanocomposites.
- Established, in collaborative work with the Sid Richardson Company, positive correlation between inelastic spectra and the reinforcing behavior of the carbon blacks in filled polymers.
- Developed techniques to incorporate metal ions (Au⁺, Cu⁺, Cd⁺, Pt⁺), into dendrimers in solution or polymeric networks and methods to convert the incorporated ions into *metallic (AuO, CuO, PtO) or semiconductor (CdS, CdSe) nanoclusters*. These materials have potential applications in optical, biomedical, and electronic applications.
- Established characterization techniques, SANS, SAXS, and TEM, to measure the size, location and polydispersity of metallic and semiconductor nanoclusters incorporated into dendrimers.
- Characterized and quantified dynamical heterogeneity in a model polymer melt, and demonstrated the growing range of spatially correlated monomer motion on approaching the glass transition. Work was internationally acclaimed and resulted in a publication in Nature.
- Predicted, from computer simulations, the observed development of transient target composition wave patterns about filler particles in phase separating blends. Understanding transient morphology development in the presence of fillers is important for developing the next generation of filled blend materials with tailored properties.
- Designed and fabricated novel experimental equipment, based on a temperature gradient heating stage, a velocity-gradient knife-edge coating apparatus and an optical microscope

automated to enable x,y scanning of samples over time, for combinatorial library creation and high-throughput screening.

- Determined a comprehensive temperature thickness dewetting phase map of polystyrene on silicon with temperature-thickness combinatorial libraries and validated by comparison to previous results.

In-Line Optical Characterization of Polymer Extrusion and Blend Morphology

K. Migler, F. Qiao and C.C. Han

Objective

The objective is to develop methods for measuring critical processing parameters based on optical techniques that can be adopted by industry. A deeper understanding of processing phenomena under high shear rate conditions, such as morphology development, fiber formation, and slippage is envisioned by the development of such techniques.

Technical Description

Ultimate blend properties depend critically on the structural morphology. Manufacturers have little understanding of how to generate desired morphologies. This work will utilize visualization techniques that will allow quantification and predictive capabilities of polymer blend morphologies. Velocimetry techniques will allow polymer processing and additives manufacturing companies to assess and understand factors controlling the performance of their materials.

External Collaborations

- Constance Gettinger and Claude Lavallee, 3M Corporation, St. Paul, Minnesota -Extrusion Visualization Measurements.
- Susan Woods, Dyneon Corporation, Oakdale MN, -Velocity profile measurements/ Polymer processing additives.
- Walter Buzanowski, Dow Chemical, Midland, MI -Extrusion Visualization Development.
- David Lohse, Exxon Research and Engineering Company, Annandale, New Jersey - Measurements of polyolefin blends structure during extrusion.

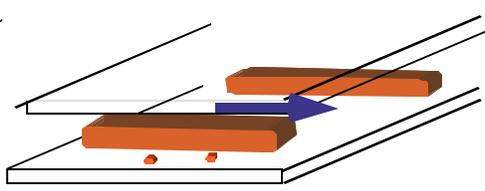
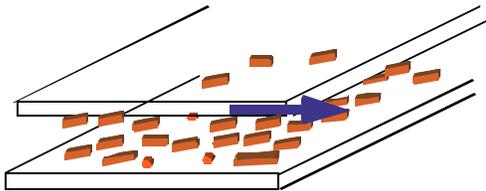
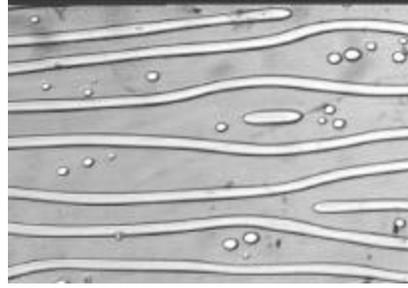
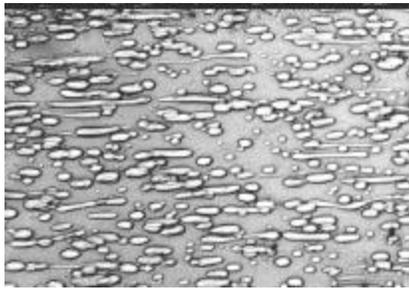
Planned Outcome

New optical based technologies are developed that allow producers to visualize their process in real time. The measurement capability will enable the rational development of next generation of processing materials. A deeper understanding will be attained of the relationship between elasticity, viscosity ratio, shear, and concentration on the morphology of polymer blends.

Accomplishments

- A droplet-ribbon transition in sheared polymer blends was discovered (See Figure). Above a critical shear rate, the minority component is dispersed into droplets that continuously coalesce and breakup in a living equilibrium. Below this critical shear rate, the droplets coalesce into long ribbons whose mass is up to 104 times greater than the droplets.
- Vorticity alignment of sheared polymeric droplets under controlled laboratory conditions was observed. This discovery confirms that droplet elasticity is the key element in the

development of vorticity alignment and provides a direct connection between phenomena observed during extrusion and shear flow between plates.



Above Critical Shear Rate

Below Critical Shear Rate

- Formed collaborations with Dyneon and 3M to utilize the NIST visualization techniques to study Polymer Processing Additives and slippage.
- Collaborating with 3M on their optical flow cell.
- Hosted laboratory tour for a high level delegation from the American Fibers Manufacturer's Association.

Impact

Dow Chemical is building a replica of the NIST Extrusion Visualization facility.

Outputs

Publications

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Presentations

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Phase Behavior in Polymer Blends and Polymer Crystallinity

C. C. Han, H. Grhl¹, A. Esker², A. I. Nakatani, C. L. Jackson, A. Karim, G. Kim³ and Y.A. Akpalu⁴

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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 of strong and steric interactions have on the stabilization of phase separated morphologies; the finite size effects, which influence and control film stability and polymer miscibility, for 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 that semi-permeable, ultra-thin, barrier layers (membranes) have on selective polymer transport process.

Technical Description

Neutron (small angle neutron (SANS)), X-ray, and light (LS) scattering, microscopy (optical (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 in confined geometries and in the bulk. The morphologies

are associated with preferential adsorption, wetting/dewetting, mixing/demixing and crystallization in polymer blends at surfaces. The following approaches are employed:

- AFM capabilities are developed to probe the role surface interactions have on polymer film stability (wetting/dewetting) with homopolymers for subsequent blend studies of these phenomena.
- The effectiveness of a compatibilizer suppressing lateral phase separation in thin films is investigated with neutron reflectivity, x-ray reflectivity and reflection microscopy.
- 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 effect of conformational changes on steric interactions induced through photoisomerization has been examined by SANS.
- Studies are conducted on blends of polystyrene and polycaprolactone which have an upper critical solution temperature, to examine 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.
- Studies of microphase separation and crystallization in semi-crystalline block copolymers of polystyrene(S)-polybutadiene(B)-polycaprolactone(C) and diblocks SC and BC are carried out using optical microscopy (OM), transmission electron microscopy (TEM) and scattering techniques. The bulk films were analyzed by small angle x-ray scattering (SAXS) and wide angle x-ray scattering (WAXS) at room temperature to simultaneously measure both the lamellar spacing of the microphase separated structure by SAXS and quantifies the PCL crystallinity using WAXS (Y. Akpalu).
- Alkyl branch modification of stiff rods (thereby forming “hairy-rods”) in bulk and on a surface are being studied by the aforementioned techniques.
- We prepare and characterize trilayer thin films of deuterated polystyrene (spin-coated)/membrane (prepared by the Langmuir-Blodgett technique)/hydrogenated polystyrene (floated) 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
- M. Libera, Stevens Institute of Technology, Hoboken, New Jersey - Collaboration on TEM of block copolymers.
- G. Wegner, Max-Planck-Institut für Polymerforschung, Mainz, Germany
- Professor Benjamin Hsiao, Department of Chemistry, State University of New York, Stony Brook, New York

Accomplishments

- For the first time the dependence of the crystallization rate on chain length has been measured, and it was found that the chain length distribution can determine whether density fluctuations are observed before crystal growth in linear polyethylene.
- Using simultaneous small and wide-angle x-ray scattering, it was demonstrated that variations in the scattering profiles of linear polyethylene during crystallization can be correlated to the evolution of single chain-folded crystal from lamellae to lamellar aggregates as suggested by recent microscopic observations.
- An in-depth understanding of the relationship between architecture, chain length and compatibilizers on the morphology of polymer blends was accomplished.
- The use of a diblock compatibilizer as a blend component was found to suppress phase separation induced roughening in thin polymer blend films (100 nm). Furthermore, we discovered that temperature has a weak effect on the profile development in compatibilized blend films.
- The LCST bulk phase behavior of a polyisoprene/deuterated polybutadiene blend was determined by SANS measurements.
- A depth profile study of a polyisoprene/deuterated polybutadiene blend showed 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.
- Demonstrated control over the miscibility of polymer blends by manipulating steric interactions through controlled photoisomerization of labeled polymer chains.
- Determined crystallization conditions 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.
- In NR measurements of the interdiffusion of deuterated and protonated polystyrene in the presence and absence of a membrane, it was determined that the presence of a 60 Å thick membrane containing 0.34 mass fraction PS, added to control the porosity of the membrane through formation of a phase separated structure, 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.
- Determined the macroscopic crystalline superstructure (optical range 4μm to 1000 μm) and microphase separated morphology (TEM range 5nm to 100 nm) produced by various annealing treatments of thin films (5 to 10) μm and bulk specimens of polystyrene (PS)-polybutadiene (PB)-polycaprolactone (PC) (PS-PB-PCL) triblock and PS-PCL and PB-PCL diblock copolymers.

- In the thin films, it was shown that crystallization into spherulites can either distort or completely destroy the microphase separated morphology for the PS-PB-PCL triblock copolymer, while spherulites can coexist with the cylindrical microphase separated structure in the case of PB-PCL diblock copolymer. In the bulk films, the microphase separated morphology dominates and large spherulites do not form.
- In the PS₃₅PB₁₅PCL₅₀ triblock copolymer, a lamellar-cylindrical microstructure with PB cylinders at the interphase boundaries is observed by both SAXS and TEM; this structure is similar to the microphase separated structure of ABC type amorphous block copolymers. The simultaneous WAXS confirms the PCL is crystalline and the PCL reflections disappear when the sample is heated to 90 °C.

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Mixing and Structure Formation Under Shear Flow

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Objectives

The objectives are to understand the fundamental mechanisms and to explore the possible applications of mixing and morphology control of polymer blends as a function of shear rate ($\dot{\gamma}$), temperature, composition, and compatibilizer concentration.

Technical Description

The development of in-situ characterization of multiphase materials is supported by fundamental studies focussed on understanding the relationship between the mean-field, the Ising, and the shear generated mean-field-like phase behavior in binary blends; on generating the explanation of phenomena and possible applications of the shear induced promotion and suppression of various phase transition temperatures of blends of homo-polymers and block copolymers; and exploiting the effects of the shear induced distortion of fluctuation wave on the phase separated morphology and the orientation of the ordered state of the block copolymers. The effect of silica nano-particles on the rheological properties of polymers and polymer solutions are also being investigated. By working in collaboration with industry, the current goal is to demonstrate the use of these characterization methods and the knowledge of the structure-rheology relationship of multiphase system to help determine the range of critical processing parameters for specific applications, such as molding, extruding, compounding, and dynamic phase inversion processes.

The success of this study could lead to 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 following approaches are employed:

- Studies are conducted on the shear effect on the phase separation temperature of binary blends, and on the order disorder transition temperature of block copolymers 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.
- Phase inversion processes are being studied by in-situ light scattering/video microscopy, and inversion conditions for different viscosity ratios and volume ratios of the two phases and analyzed.
- The shear orientation of nanocomposite materials (clay) in aqueous polymer solutions, non-aqueous polymer solutions, and polymer melts will be investigated by different techniques, which include rheology, flow-birefringence, rheo-small-angle light scattering, shear-microscopy and small-angle neutron scattering under shear.
- The concept of forming string (or fibril like) morphology at lowered interfacial tension condition are being tested by the LCP/thermoplastic blends with grafting reaction on the interface to introduce block copolymers as compatibilizer.
- Explore the application of using the aligned rod-like LCP polymer in the elongated fibril structure to stabilize the Rayleigh instability in order to maintain the desired morphology for application.

- Using time resolved video optical microscopy to study the anisotropically deformed droplet under shear jump or shear quench and measure the retraction and undulation/breakup predicted by Rayleigh instability.
- Both strain and stress limited dynamic modulus of multiphase polymer blends have been studied, the relationship between the rheological properties and the structure formation (domain deformation, break-up etc.) has been correlated.
- Use on-line light scattering and optical microscopy techniques 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 Polymer Composites 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.

External Collaborators

- A. Halasa, Y. Feng, Goodyear Tire and Rubber Company, Akron, Ohio (Polymer materials supply).
- Don Wiff, Wright Patterson Air Force Research Lab (Interfaces research plans).
- H. Yang, Essilor Co. (Blends collaborative planning).
- 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 (Rheology and light scattering).
- 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

- Shear-induced behavior on solutions of block copolymers in neutral and selective solvents has been examined by SANS extending previous results of effects of shear on block copolymers in solution.
- 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 in the slit channel of our extruder was observed for a 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 results of a study of the stability of fibrillation under different flow conditions by the LS pattern and the optical microscopy images 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.

- Preliminary results of fracture strength of the LCP, as measured by a biaxial tensile testing, show improved mechanical properties along the machine direction.
- Computer programs for time-resolved data analysis of scattering and optical microscopy results has been developed.

Outputs

Publications

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Fluorescence, Dielectrics and Ultrasonics Monitoring for Polymer Processing

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

Objectives

The objectives are to develop experimental methodology using fluorescence spectroscopy, ultrasonics, and dielectrics for monitoring important polymer process parameters such as temperature profiles, molecular orientation, and blend and filler composition. Another objective is to improve understanding of the process by constructing mathematical models based on real-time measurements.

Technical Description

New sensor hardware for process monitoring developed under this program includes optical sensors for fluorescence based measurements of temperature, pressure and dye orientation, and a high temperature ultrasonic transducer that can be used at resin processing temperatures. The fluorescence sensor contains optical fiber links between the light source, processing machine, and detector. The sensor head, which is inserted into the processing machine, contains optical components (lenses, windows etc.) needed for the measurement. To carry out the measurements a fluorescent dye is mixed with the resin at dopant mass fraction of less than 10^{-5} dye in the resin. Several fluorescent dyes have been identified as suitable for polymer processing because they are stable at the high temperatures used for polymer processing in addition to functioning as a temperature/pressure probe or as a probe of molecular orientation. For fluorescence anisotropy measurements, dyes with geometric anisotropy are chosen because they are known to orient with applied extensional stress. For temperature and pressure measurements, dyes whose spectra change in a correlated manner with temperature and pressure are used.

The high temperature ultrasonic transducer can be attached to the exterior surface of a processing machine and has been used as a virtual temperature sensor through the measurement of ultrasonic velocity combined with an equation of state model.

The in-line dielectric sensor, developed by Chemical ElectroPhysics Co., is attached at the exit of a twin screw extruder and is being used to monitor the extrusion and mixing of filled polymers and polymer blends. Models of dielectric mixtures and dielectric dispersion are used to interpret data.

External Collaborators

- Michael McBrearty, Chemical ElectroPhysics Corp., Hockessin, DE, contributes dielectric spectrometer equipment and collaborates with NIST in carrying out experiments to measure dielectric properties of filled polymers.
- Moris Amon, Mobil Chemical Co., Rochester, NY, contributes optical equipment and access to a pilot plant process line for the measurement of fluorescence anisotropy of stretched films during processing.

- Charles Thomas, Department of Mechanical Engineering University of Utah, Salt Lake City, UT, provides a polymer injection molding machine, which will be instrumented with optical and ultrasonic sensors for the purpose of studying physical properties of resins during molding.

Planned Outcomes

Successful achievement of our objectives will provide solutions to outstanding measurement problems facing the U. S. polymer processing industry. These problems involve the general inability to measure accurately real-time physical properties of resins during processing. Such measurement deficiency obscures our understanding of process dynamics and hampers processors' ability to optimize productivity and product quality. This measurement and sensor program will yield improved measurement capability in several fundamental areas: temperature and temperature profiles, pressure profiles, rheology, morphology, molecular orientation and composition. Of particular interest to processors is the capability to measure spatial profiles of temperature, pressure and strain rate. Ultimately, the planned outcome of this work is improved understanding of processes through the construction of mathematical models that are based on real-time measurements.

Accomplishments

- In collaboration with Chemical ElectroPhysics Corp., dielectric measurements of nano-clay filled nylon and other filled resins were obtained during twin screw extrusion using an in-line dielectric sensor. The measurements yielded information about mixing ratios, residence time, composition near the barrel wall, and sensor performance.
- In collaboration with Mobil Chemical, we constructed a new optical sensor for real time measurements of fluorescence anisotropy during the biaxial stretching of polypropylene films. The polypropylene contains a fluorescent dye that is used to measure both orientation and temperature. 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 temperature and pressure dependence of the fluorescence spectrum of benzoxazolyl stilbene doped into polystyrene was examined using statistical techniques in order to separate temperature and pressure effects. The method of data separation involves the construction of functions orthogonal to the pressure effect, which, when integrated against the observed spectrum, yield temperature with no pressure coefficient. Thus, the dye can be calibrated to perform as a temperature sensor that does not need pressure compensation. Pressure measurements can also be obtained.

Impact

- Collaboration with Chemical ElectroPhysics Corp. has involved performance evaluations of an in-line dielectric sensor that is used to monitor the extrusion of filled polymers. As a result of these studies, new sensor design strategies are being adopted and new sensor products are being formulated by Chemical ElectroPhysics Co. The in-line application of this sensor has yielded real-time information about resin flow dynamics and filled resin composition.
- Mobil Chemical Co. is using the NIST anisotropy/temperature sensor 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 and processing

temperature will determine processing strategies that are used to control the properties of the film.

Outputs

Publications

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A.J. Bur, *Fluorescence Anisotropy Measurements of Oriented Polymers*, SPE Ann. Technical Mtg., May, 1999.

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Patent Award

Optical Sensor for Measuring Fluorescence Anisotropy During Polymer Processing to A. J. Bur and S.C. Roth, June 24, 1999.

Theory of Phase Separation and Transport in Polymer Liquid

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Objectives

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

Technical Description

Filler-Induced Composition Waves in Phase-Separating Polymer Blends

The Cahn-Hilliard-Cook theory for phase separation is adapted to describe phase separation of a blend with spherical, cylindrical (fiber) and plane (platelet) shaped filler particles. A surface interaction is incorporated into the filler model to describe the tendency of one of the polymer components to enrich about the filler particle. Separate interaction parameters describe the

magnitude of the chemical potential favoring a particular polymer component and the change of the polymer-polymer interaction near the particle surface.

Modeling the Viscosity of Filled Polymers

A general model of the viscosity of complex-shaped particle dispersions is developed based on an exact virial expansion about the low concentration limit and a mathematical analogy established between the hydrodynamics of concentrated particle dispersions and the problem of calculating the conductivity of particle suspensions.

Modeling Equilibrium Particle Clustering in Solution

A lattice model of associating particle systems is developed for applications to filler dispersions and glass-forming liquids. Basic equilibrium properties (cluster mass and mass distribution, fraction of associated monomer, specific heat, entropy, cluster transition temperature) are calculated based on Flory-Huggins theory.

Modeling Transport in Supercooled Liquids

The dynamic entropy of a supercooled liquid is estimated by calculating the mean first-passage time for particle displacement to a threshold distance about the initial particle position. Caging and persistent particle motion are identified and quantified using this experimentally accessible property.

Modeling Thermal Transport of Polymer Solutions

Universal scaling functions deduced from renormalization group theory are applied to the description of accurate measurements of Soret measurements on semi-dilute and dilute polymer solutions performed at the University of Maryland.

External Collaborators

- K.F. Freed and J. Dudowicz, James Franck Institute, University of Chicago- collaboration on modeling particle clustering.
- J.V. Sengers, R.W. Gammon, Institute of Physical Science and Technology, University of Maryland- performed Soret coefficient measurements on polymer solutions.
- N. Martys, NIST Building and Fire Research- collaborator in modeling fluid phase separation by lattice Boltzmann methods.
- J. Bicerano and D. Brune, Dow Chemical Company, Midland, Michigan- collaborator in modeling the transport properties of filled polymers.

Accomplishments

- Predicted transient target composition wave patterns about filler particles in phase separating blends. Aided design of measurements to observe composition patterns in ultrathin polymer blend films. Observed interference of target patterns, and predicted that filler has little effect on the late-stage phase separation morphology. Theoretical predictions confirmed in measurements.
- Developed systematic theory of particle association at equilibrium in collaboration with J. Dudowicz and K. Freed at the University of Chicago. Quantified many new properties in associating particle systems-phase transition temperature, specific heat, cluster mass as a function of temperature, entropy. Sharp clustering transition is predicted in filled polymer systems as a function of filler composition and temperature.

- Developed a general theory of the suspension rheology of filled polymer liquids. The theory is currently being used by Dow Chemical in their process modeling of polymer materials with clay fillers.
- Developed a new measure of correlated motion in supercooled liquids in collaboration with Paolo Allegrini and Sharon Glotzer of CTCMS.
- Successfully modeled the concentration dependence of the Soret coefficient of polymer solutions.
- Developed a fractional calculus based method for describing relaxation in condensed materials.
- Evaluated critical properties of lattice Boltzmann fluids modeling polymer blends in collaboration with N. Martys.

Outputs

Publications

B.P. Lee, J.F. Douglas and S.C. Glotzer, *Filler-Induced Composition Waves in Phase-Separating Polymer Blends*, Physical Review E, in press.

A. Karim, J.F. Douglas, G. Nisato, D.W. Liu and E.J. Amis, *Transient Target Patterns in Phase Separating Filled Polymer Blends*, Macromolecules **32**, 5917 (1999).

N.S. Martys and J.F. Douglas, *Mean-field Scaling in Lattice Boltzmann Fluid Mixtures*, Proceedings of the 13th ASCE Engineering Mechanics Conference, in press.

J. Bicerano, J.F. Douglas and D.A. Brune, *Model for Dispersion Rheology*. Macromolecular Review, in press.

J.F. Douglas, *Coping with Complex surfaces: An Interface between Mathematics and Condensed Matter Physics*. NSF Workshop Report, in press.

P. Allegrini, J.F. Douglas and S.C. Glotzer, *Dynamic Entropy as a Measure of Caging and Persistent Particle Motion in Supercooled Liquids*, Physical Review E, in press.

J.F. Douglas, *Integral Equation Approach to Condensed Matter Relaxation*, Journal of Physics: Condensed Matter **11**, 329 (1999).

J. Dudowicz, K.F. Freed and J.F. Douglas, *Lattice Model of Living Polymerization: 1. Basic Thermodynamic Properties*, Journal of Chemical Physics, in press.

K. J. Zhang, M.E. Briggs, J.V. Sengers, R.W. Gammon and J.F. Douglas, *Thermal and Mass Diffusion in Semi-dilute Good Solvent Polymer Solutions*, Journal of Chemical Physics **111**, 2270 (1999).

K.A Barnes, J.F. Douglas, A.I. Nakatani, H. Grhl and E.J. Amis, A. Karim, *Suppression of Dewetting in Nanoparticle Filled Polymer Films*, Macromolecules, submitted.

J.F. Douglas, *The Influence of Polymer-Polymer and Polymer-Surface Interactions on the Formation and Swelling of End-Grafted Polymer Layers*, ACS Polymer Preprints, in press.

Presentations

J.F. Douglas, *Integral Equation Approach to Condensed Matter Relaxation*, Second Workshop on Non-Equilibrium Phenomena in Supercooled Fluids, Glasses, and Amorphous Materials, Pisa, Italy, October 1998.

J. Bicerano, J.F. Douglas and D. Brune, *Rheology of Filled Polymers*, Gordon Research Conference on Composites, Ventura, California, January, 1999.

J.F. Douglas, *Development of Collective Motion in Cooled Liquids*, Department of Chemistry, University of Chicago, January, 1999.

J.F. Douglas, Dynamic Entropy as a Measure of Caging and Persistent Particle Motion in Supercooled Liquids, American Physical Society March Meeting, Atlanta, 1999.

Heterogeneous Dynamics of Polymers and Filled Polymers: Theory and Simulation

S.C. Glotzer, T.B. Schroeder, P. Allegrini and J.F. Douglas

Objectives

The objectives are to develop a comprehensive understanding of spatially heterogeneous dynamics in glass-forming polymer melts through theory and simulation, and apply this knowledge to (1) explain changes in the relaxation dynamics of bulk and confined polymers and (2) elucidate how filler particles alter the glass transition of polymer materials.

Technical Description

Fundamental understanding of the dynamics of polymer melts and filled polymers near their glass transition temperature is poor, limiting the accurate prediction of important material behavior and properties. Molecular dynamics computer simulations allow the investigation of the detailed local dynamics of model polymer melts and related systems, yielding information on correlated monomer motion and the dependence of these correlations on temperature, pressure and density. Molecular dynamics simulations of a model unentangled polymer melt approaching the glass transition will be conducted, and dynamical heterogeneity and correlations in the monomer motion will be investigated. Molecular dynamics simulations of a model simple glassforming liquid will be conducted, and spatially heterogeneous dynamics will be compared with that observed in a polymer melt to elucidate the role of chain connectivity. The use of higher order density correlation functions in characterizing and quantifying dynamical heterogeneity will be explored.

External Collaborations

- J. Baschnagel and C. Bennemann, Johannes Gutenberg University, Mainz, Germany - atomistic simulation of glass formation in polymeric liquids.
- P. Poole, University of Western Ontario, London, Ontario, Canada, - theoretical modeling of supercooled liquids-four point functions and polyamorphism.
- S. Franz, International Center for Theoretical Physics, Trieste, Italy - glass-formation in structural and spin glasses - mean-field spin glass models.

- G. Parisi and C. Donati, University of Rome, La Sapienza., Rome, Italy - fundamental theoretical modeling and simulation of the properties of glass-forming liquids.
- V. Novikov, Institute of Automation and Electrometry, Novosibirsk, Russia - theoretical characterization of the properties of glass-forming liquids and modeling the origin of the Boson peak and four point density correlation functions in cooled liquids.
- S. Sastry, Jawarhlal Institute of Science, Bangalore, India - theoretical characterization of the properties of glass-forming liquids-energy landscape and free volume characterization.

Planned Outcome

The expected outcome of this work is a better, fundamental understanding of the relevant factors that influence the effect of filler particles and confinement on the dynamics of polymers near the glass transition.

Accomplishments

- Demonstrated the growing range of spatially correlated monomer motion on approaching the glass transition through characterization and quantification of the dynamical heterogeneity in a model polymer melt. This growing length scale may be responsible for shifts in the glass transition temperature in the presence of fillers.
- The growing spatial correlations of localized particles with decreasing temperature was demonstrated by investigating the dynamical heterogeneity in a model supercooled liquid using a 4-point, time-dependent density correlation function.
- The decoupling of diffusion and relaxation in a glassforming liquid was shown to result from the increasingly heterogeneous dynamics present in the liquid on decreasing temperature.
- The generalized susceptibility of a 4-point density correlation function was calculated analytically for a model glass within the effective potential theory, and for a model glass-forming system within the mode coupling approximation, thereby providing the first theoretical calculations of a diverging correlation length in a glassforming system without quenched disorder. The latter result compared very well with results from molecular dynamics simulations.
- A dynamic entropy approach was used to demonstrate and quantify localization and persistent particle motion in molecular dynamics simulations of a supercooled model liquid.

Outputs

Publications

S.C. Glotzer and C. Donati, *Quantifying Spatially Heterogeneous Dynamics in Glassforming Liquids*, J. Phys.: Cond. Mat. **11**, A285-A295 (1999).

C. Bennemann, C. Donati, J. Baschnagel, and S.C. Glotzer, *Growing Range of Correlated Motion in a Polymer Melt On Cooling Towards the Glass Transition*, Nature, **399**, 246 (1999).

C. Donati, S.C. Glotzer and P.H. Poole, *Growing Spatial Correlations of Particle Displacements in a Simulated Liquid on Cooling Toward the Glass Transition*, Physical Review Letters **82**, 5064 (1999).

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C. Donati, S.C. Glotzer, P.H. Poole, W. Kob, and S.J. Plimpton, *Spatial Correlations of Mobility and Immobility in a Glass-forming Liquid*, Physical Review E, **60**, 3170 (1999).

P. Allegrini, J.F. Douglas and S.C. Glotzer, *Dynamic Entropy as a Measure of Caging and Persistent Particle Motion in a Supercooled Liquid*, Physical Review E, in press.

S. Sastry, P.G. Debenedetti, F.H. Stillinger, T.B. Schroeder, J. C. Dyre, and S.C. Glotzer, *Potential Energy Landscape Signatures of Slow Dynamics in Glass Forming Liquids*, Physica A, in press.

S. Franz, C. Donati, G. Parisi, and S.C. Glotzer, *Theory of Non-linear Susceptibility and Correlation Length in Glasses and Supercooled Liquids*, Physical Review Letters, submitted.

S.C. Glotzer, V. Novikov and T.B. Schroeder, *Time-dependent Four-Point Density Correlation Functions in Supercooled Liquids*, J. Chemical Physics, submitted.

Presentations

S.C. Glotzer, *Spatially Heterogeneous Dynamics in Glass-forming Liquids and Polymers*, American Crystallographic Association Annual Meeting, Buffalo, NY, May 1999.

S.C. Glotzer, *Dynamical Heterogeneity and Cooperative Motion in Glassforming Liquids and Polymers*, American Physical Society Meeting, Atlanta, GA, March 1999.

C. Bennemann, C. Donati, J. Baschnagel and S.C. Glotzer, *Growing Range of Correlated Motion in a Polymer Melt On Cooling Towards the Glass Transition*, American Physical Society Meeting, Atlanta, GA, March 1999.

S.C. Glotzer, *Cooperative Relaxation Mechanisms in Glass-forming Liquids*, Materials Research Society Fall Meeting, Boston, December 1998.

S.C. Glotzer, *Spatially Heterogeneous Dynamics in Glass-Forming Liquids from Simulation*, Euroconference on Supercooled Liquids and Glasses, Pisa, Italy, September 1998.

C. Donati, P.H. Poole and S.C. Glotzer, *Quantifying Correlated Motion in Supercooled Liquids and Polymers*, poster at Euroconference on Supercooled Liquids and Glasses, Pisa, Italy, September 1998.

T.B. Schroeder, S. Sastry, J. Dyre and S.C. Glotzer, *Inherent Dynamics of a Supercooled Model Liquid*, poster at Euroconference on Supercooled Liquids and Glasses, Pisa, Italy, September 1998.

P. Allegrini, J.F. Douglas and S.C. Glotzer, *Dynamic Entropy as a Measure of Caging and Persistent Particle Motion in a Supercooled Liquid*, poster at Euroconference on Supercooled Liquids and Glasses, Pisa, Italy, September 1998.

S.C. Glotzer, *Using Computer Simulations to Learn about Liquids and Polymers*, George Mason University, September 1998.

S. Franz, C. Donati, G. Parisi, and S.C. Glotzer, *Theory of Non-linear Susceptibility and Correlation Length in Glasses and Liquids*, Andalo Workshop on Glasses and Supercooled Liquids, Andalo, Italy, March 1998.

Measurements of Polymer-Filler Interactions in Filled Polymers

A. Karim, K. A. Barnes, J. F. Douglas, D.-W. Liu, C. L. Jackson and A. I. Nakatani

Objectives

The objectives are to: (1) estimate relative polymer-filler interactions and filler dispersion in polymer blends by measuring induced shifts of phase boundaries and altered kinetics of phase separation and (2) determine how fillers modify surface properties to enhance polymer film wettability on inorganic surfaces and compare with model filler surfaces.

Technical Description

Phase separation of polymer blends in the presence of fillers will be examined by light scattering, direct optical microscopy (OM) and transmission electron microscope. The measurements should lead to the cloud point determination of phase boundary and morphology changes of phase separated structures in presence of fillers. Small angle neutron scattering (SANS) is to be used to characterize the dispersion and distribution of fillers. The stabilization and wettability of polymer films through fillers will be studied for different filler types, surface treatments, film thickness, and temperature using atomic force microscopy (AFM), OM and reflectivity. Wettability of polymer films on replicated filler surfaces such as mica sheets, evaporated carbon films treated by ion-plasma or silanol chemistry will be investigated.

Planned Outcome

Developing an understanding of factors affecting polymer adhesion to fillers and stability of filled coatings is important for predictions on long-term durability of such coatings.

Accomplishments

- Prepared surface treated fillers and conducted cloudpoint and optical microscopy measurements on phase separation in filled polymer systems as a function of surface treatment and mechanical history. The difficult to investigate “early stage” of phase separation structures was captured in the process.
- The phase boundaries of blends of polystyrene/polybutadiene were observed to shift vertically as well as laterally by the presence of the different and differently treated fumed silica fillers. Shifts of the phase boundary affect the kinetics of morphology development of the phase separated structures in addition to filler induced morphological changes.
- A comparison of a pure blend of polystyrene/polybutadiene to a blend containing a model nanofiller, C₆₀ (buckminster fullerene) at mass fractions 0.05 and 0.005 was made under similar evolution times for the phase separation process. For low C₆₀ mass fractions (<0.01), the phase boundary is stabilized by the presence of the nanofiller. For higher concentrations of C₆₀, the phase separation process is essentially pinned by the presence of the nanofiller. This result points to the importance of effects of large surface area to volume ratio of nanofillers on blend thermodynamics and morphology.

- The TEM showed that the polybutadiene phase preferentially wets the aggregates of C₆₀ in the film and the phase evolution is slowed due to the shift in the phase boundary caused by this preferential wetting. The staining process used to prepare TEM specimens effectively halts the phase evolution and stabilizes the morphology.
- Observed a novel suppression dewetting of polymer thin films by the presence of C₆₀ nanofillers on inorganic oxide substrates. This is unusual because fillers typically act as nucleating sites enhancing the dewetting of polymer thin films. The suppression is attributed to the creation of nano-roughness at the substrate boundary.

Outputs

Publications

A. Karim, J.F. Douglas, A.I. Nakatani and E.J. Amis, *Modification of the Phase Stability of Polymer Blends by Surface Treated Fillers*, Polymer Communications, submitted.

K.A. Barnes, J.F. Douglas, A.I. Nakatani, H. Grhll and E. J. Amis, *Suppression of Dewetting in Nanoparticle Filled Polymer Films*, Macromolecules, submitted.

L. Sung, A. Karim, J.F. Douglas and C.C. Han, *Modification of Thin Film Phase Separation by a Surfactant*, Macromolecules, submitted.

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K.A. Barnes, J.F. Douglas, A.I. Nakatani, H. Grhll, E. J. Amis, and A. Karim, *Suppression of Dewetting in Nanoparticle Filled Polymer Films*, Macromolecules, submitted.

G. Nisato, B. Ermi, J.F. Douglas, and A. Karim, *Excitation of Surface Deformation Modes of a Phase-Separating Polymer Blend on a Patterned Substrate*, Macromolecules, **32**, 2356 (1999).

A. Karim, D.W Liu, J.F Douglas, A.I. Nakatani, and E.J. Amis, *Modification of the Phase Stability of Polymer Blends by Surface Treated Fillers*, Polymer, submitted.

D. Raghavan, X. Gu, T. Nguyen, M. VanLandingham, and A. Karim, *Mapping Polymer Heterogeneity using Atomic Force Microscopy-Phase Imaging and Nanoscale Indentation*, Macromolecules, submitted.

A. Karim, J.F. Douglas, A.I. Nakatani, K.A.Barnes and D.B. Majumdar, *Statics and Dynamics of Filled Polymers and Nanocomposites*, SAMPE 99, Detroit, Conference Proceedings.

E.P. Giannelis, H.Chen, J. Demeter, E. Manias, N. Hadjichristidis, and A.Karim, *Mobility of Polymers in Nanometer Slits: Kinetics of Polymer Melt intercalation in Layered Silicates*. ACS Preprint, New Orleans, 1999.

A. Karim, *Interactions of Polymers with Fillers and Nanocomposites*, NIST, June 18-19, 1998: A Workshop Report, NISTIR 6312.

Presentations

A. Karim, *Polymer-Filler Interactions in Phase Separated Systems; Phase Separation on Patterned/Heterogeneous Surfaces* – presented at American Chemical Society, National Meeting, Boston, MA, Aug. 1998, Workshop on Polymer Interphases and Interfaces organized by BFRL and Polymers Division, NIST, Dec. 1998, Dept. of Materials Science, University of California, Santa Barbara, Dec. 1998, Polymers West Gordon Conference, Ventura, CA, Jan. 1999, Dept. of Materials Science, SUNY Stony Brook, NY, Feb. 1999, Condensed Matter Symposia, Physics Division, Kansas State University, Manhattan, KA, Mar. 1999, CTCMS Workshop on Multiscale Modeling of Materials- Challenges and Opportunities, NIST, May 1999, Gordon Conference, Organic Thin films, Newport, RI, July 99, Polymer Physics: Theory vs. Experiments, Telluride, CO, Aug. 1999, AFM Workshop on Soft Materials, Biotechnology Division, NIST, Aug. 1999.

K.A. Barnes, J.F. Douglas, D.-W. Liu, A.I. Nakatani, E.J. Amis and A. Karim, *Filler-Induced Suppression of Dewetting in Thin Polymer Films*, American Physical Society Meeting, Atlanta, Georgia, March 1998.

A. Karim, K.A. Barnes, J. F. Douglas, D.W. Liu, A.I. Nakatani, and E.J. Amis, *Influence of Fillers on Phase Separated Blend Morphology*, American Physical Society Meeting, Atlanta, Georgia, March 1998.

A. I. Nakatani, K. A. Barnes and A. Karim, *Kinetics and Morphology of Phase Separation in Filled Polymer Blends*, Poster, American Physical Society Meeting, Atlanta, Georgia, March 1998.

K.A. Barnes, J.F. Douglas, D.-W. Liu, A.I. Nakatani, E.J. Amis and A. Karim, *Filler-Induced Suppression of Dewetting in Thin Polymer Films*, Poster, Polymer Physics Gordon Research Conference, Newport, RI, Aug. 1999.

Probing Local Dynamics, Structure and Ordering in Filled Polymers and Nanocomposites

A. I. Nakatani, K. A. Barnes, G. Schmidt, C.C. Han and A. Karim

Objective

The objective is to develop measurement techniques to characterize localized polymer static and dynamic properties in filled systems. The measurement techniques should yield unique information on the structure, dynamics and ordering in filled polymers and nanocomposites not available by conventional methods.

Technical Description

Inelastic neutron scattering, SANS, NMR, and rheo-optics are used to characterize the dynamics, structure and ordering of intercalated polymer-clays and filled polymer networks. Filter-analyzer neutron spectroscopy and neutron time-of-flight spectroscopy are used to characterize a large

range of spatial and dynamic scales, while their ordering properties will be measured by rheo-optical methods.

External Collaborators

- M. Gerspacher and H. Yang, Sid Richardson Carbon Company, Fort Worth, Texas - Collaboration and supply of well characterized carbon black materials and compounding expertise to produce carbon black filled samples.
- W. Chen, G. V. Gordon, and R. G. Schmidt, Dow Corning Corporation, Midland, Michigan - Collaboration and supply of materials for experiments on chain dimensions of filled polymers during stretching.
- C. Evans, Southern Clay Products, Inc., Gonzalez, Texas - Supply of materials for experiments on clay-polymer solutions by rheo-optical methods and SANS.

Planned Outcome

A molecular level characterization of static and dynamic properties of filled polymers and nanocomposites will be attained which is vital for major advances in the area.

Accomplishments

- Measured spectra of pure polyisoprene, carbon black filled polyisoprene, and extracted carbon black filled polyisoprenes (bound rubber) by filter analyzer neutron spectroscopy (FANS) and neutron time-of-flight (TOF) spectroscopy for different types of carbon black. Changes in FANS and TOF spectra correlate with the reinforcing behavior of the carbon blacks.
- Measured the birefringence and in-situ SANS patterns on clay solutions, polymer solutions, and clay-polymer solutions under flow. The elastic behavior of the solutions is a result of the synergistic coupling of the polymer deformation and clay orientation in flow.
- Measured the small angle neutron scattering from labeled, crosslinked poly(dimethyl siloxane) filled with fumed silica prepared by Dow Corning as a function of deformation, type of fumed silica, and labeled chain concentration. The chain deformation behavior is related to the type of fumed silica and is correlated to the stress-strain behavior of the filled networks.

Outputs

Publications

A.I. Nakatani, R. Ivkov, P. Papanek, H. Yang, and M. Gerspacher, *Inelastic Neutron Scattering from Filled Elastomers*, Rubber Chemistry and Technology, submitted.

A.I. Nakatani, W. Chen, R.G. Schmidt, G.V. Gordon and C.C. Han, *Chain Dimensions in Polysilicate-Filled Poly(Dimethylsiloxane)*, Macromolecules, in press.

Presentations

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A.I. Nakatani, *Chain Dimensions in Polysilicate-Filled Poly(Dimethylsiloxane)*, Dow Corning Corporation, Midland, Michigan, February, 1999.

A.I. Nakatani, *Chain Dimensions in Polysilicate-Filled Poly(Dimethylsiloxane)*, Sid Richardson Carbon Company, Fort Worth, Texas, October, 1998.

Combinatorial Measurements of Polymeric Coatings

J. C. Meredith, A. Karim and E. J. Amis

Objective

The objective is to develop high throughput measurements for rapid characterization of polymer coatings properties. Specifically, the effect of composition, temperature, thickness, and surface energy on the wettability, phase behavior, and microstructure of polymer thin film coatings will be studied on samples having gradients in material characteristics.

Technical Description

Polymeric coatings are critical to the electronics, automotive, biomedical, packaging, and optical industries. Two fundamental properties of polymer thin films used as coatings are wettability and phase behavior (*i.e.*, in blended films). Each of these properties depends on a number of variables, including temperature, composition, film thickness, and substrate-film interactions, in a complex way. Combinatorial techniques, originally developed for pharmaceutical research, allow one to investigate phenomena in multiparameter space in orders of magnitude less time than with conventional 1-sample for 1-measurement approaches. Combinatorial investigations involve three steps: library (sample) creation, high-throughput screening, and informatics. In polymer thin-film sample libraries, each about the size of a microscope slide, temperature and thickness or temperature and composition are systematically varied. By coupling with a high-throughput detection and measurement apparatus (*i.e.*, optical microscopy), the wetting and phase behavior are followed in multiparameter space (*i.e.*, time-temperature-thickness). Informatics involves the use of intelligent and automated algorithms for reducing data, analyzing phase transitions, and characterizing microstructures in multiparameter space.

Planned Outcomes

Development of high-throughput measurement technology for rapid characterization of phase transitions and microstructure will accelerate scientific discovery needed to develop next-generation coating materials. In addition, combinatorial methods allow industry to rapidly develop new materials to match the market's changing needs, enhancing competitiveness. Combinatorial methods are usually used only for the discovery of new materials. Recent work in the Polymers Division indicates that combinatorial methods can also be used for scientific measurements, that is, to generate new knowledge. Specifically, we envision the possibility of discovering novel phase transitions, microstructures, and kinetic regimes that might have been missed using conventional methods.

Accomplishments

- Novel experimental equipment needed for library creation and high-throughput screening was fabricated. Three versions of a temperature gradient heating stage were designed and fabricated. A velocity-gradient knife-edge coating apparatus was developed in-house for the purpose of spreading films with controllable thickness and concentration gradients. Using robotic translation stages, an optical microscope was automated to enable x,y scanning of samples over time to screen combinatorial libraries.
- The dewetting of polystyrene on silicon was studied with temperature-thickness combinatorial libraries. The combinatorial method was validated by comparison to previous results. We generated a comprehensive map of the effects of temperature and thickness on dewetting, based on data collected in a few hours. The results revealed novel observations of film stability and kinetic transitions as well as a time-temperature-thickness superposition for metastable dewetting kinetics.
- Using a temperature-composition gradient library, we observed the LCST phase diagram for polystyrene-poly(vinylmethyl ether) in a single experiment. The phase boundary from the combinatorial library screening compares favorably with cloud points measured with conventional light scattering.
- Combinatorial methods were initiated to assay protein adsorption and cell behavior on blends of the biodegradable polymers poly(lactide) and poly(caprolactone). For example, constant composition blends exposed to a one-dimensional temperature gradient (crossing the system LCST of 86 °C) have a range of crystalline and phase-separated microstructures. The morphology of adsorbed protein A was sensitive to the gradient in microstructure induced by LCST phase separation. Hence, libraries containing systematic gradients in properties can be used to assay protein-polymer and cell-polymer interactions. Collaboration with the NIST Biotechnology Division is underway to assay osteoblast-like cells on temperature-composition combinatorial libraries.

Output

Publication

J. C. Meredith, A. Karim, and E. J. Amis, *Combinatorial Materials Science: Polymer Thin Film Dewetting*, for submission to Nature.

Presentation

J. C. Meredith, A. Karim, and E. J. Amis, *Combinatorial Mapping of Polymer Thin Film Dewetting*, Reactive Polymers, Ion Exchange, and Adsorbents Gordon Conference, July 20, 1999.

Dendrimers with Polymers, Metals, and Small Molecules

Barry Bauer, Franziska Groehn, Brent Viers, Giovanni Nisato, Da-Wei Liu, Catheryn Jackson, Ginam Kim¹ and Eric Amis.

¹Stevens Institute of Technology, NJ.

Objectives

A data base will be produced that provides basic information on dendrimeric materials that can be applied technological applications that are currently being developed. Model materials will

be produced and measurement techniques will be developed to give US industry tools for synthetic development.

Technical Description

SANS is sensitive to the organization of organic material and SAXS is sensitive to metals and semiconductors. Together they can map out the distribution of the internal structure of complex dendrimer molecules and complexes of dendrimers with other species. TEM provides an independent way of confirming the scattering measurements. The evolution of structure from low generation to high generation dendrimers is conveniently measured by SAXS. This information may allow one to judge the proper generation required for a given application. SANS can measure the location of parts of dendrimers through deuterium labeling.

Standard synthetic procedures are used to produce materials with controlled structures for the development of measurement techniques. Dendrimers are obtained through collaboration with Dendritech and DSM companies and are modified through addition of metal ions that are reduced to zero valent metal clusters or reacted to form semiconductor nanoclusters. SANS, SAXS, and TEM are then used to characterize the products formed and to build an understanding of synthesis-structure rules.

Dendrimers are dispersed in polymeric matrices through interpenetrating polymer network techniques in which dendrimers are dissolved in monomers that are then polymerized forming the polymeric matrix. End-functionalized linear polymers are reacted with dendrimer end groups forming networks with an unprecedentedly high functionality and excellent synthetic control. SANS, SAXS, and TEM are then used to characterize the products formed and to build an understanding of synthesis-structure rules.

External Collaborations

- Michigan Molecular Institute and Dendritech, 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 has spent 6 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.
- Ralf Kleppenger, Catholic University of Leuven - collaboration has been established to do SANS of supplied materials.
- Ivan Gitsov, Cornell University, Ithaca, New York - collaboration was established for measuring SANS at NIST 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.
- Bert Meijer and Aissa Ramzi - Eindhoven - collaboration has been established to do SANS of supplied materials.
- Robert Briber and Sangwook Choi, University of Maryland - collaboration has been established to do SANS of supplied materials.
- Warren Ford - Oklahoma SU - collaboration has been established to do SANS of supplied materials.
- Juan Fernandez De la Mora - samples have been supplied to measure electrospray mobility.

- Paul S. Russo - LSU - samples have been supplied to measure diffusion.

Planned outcome

There is a strong effort in US industry to exploit the unique structure of dendrimers in a variety of applications. Knowledge of the inherent properties of dendrimers will allow for planned syntheses of new materials and may inspire new research programs based on insights that are gained from our data.

Measurement techniques will be established for Industry to apply to new materials that are developed. Size, shape, polydispersity, and interactions of dendrimers will have a major impact on their properties and applications, and such information will be made available.

Nanoclusters of metals and semiconductors have a variety of potential applications and are being studied worldwide. Dendrimers represent a radically new class of these materials, and knowledge gained on synthesis-structure relationships will accelerate the development of these materials.

Accomplishments

- Dendrimers/metal ion samples have been synthesized and characterized as to the size, shape, and location of the metal ions in the dendrimers.
- Metal nanoclusters inside of dissolved dendrimers have been synthesized and characterized from the ionic material.
- Semiconductor nanoclusters have been synthesized inside of dendrimers in solution.
- Collaborations with other NIST Divisions have been established for work on dendrimer nanoclusters with the Biotechnology and Analytical Chemistry Divisions of CSTL, the Optical Technology and Surface and Microanalysis Divisions of Physics, and the Building Materials and Metallurgy Divisions of MSEL. Collaboration with Naval Research Lab. (NRL) has also been established.
- Dendrimer IPN's have been synthesized and characterized and nanoclusters have been inserted and analyzed yielding information on the size and dispersion of the dendrimers and the metals in the polymeric matrix.
- Dendrimers have been used as crosslink points in networks for the first time.

Impacts

Hydrophobically modified dendrimers produced by DSM for applications of polyolefin dyeing have been measured at NIST and shown to be multi-phase. Suggestions, based on this observation, have been made for use of their product with polymers other than polyolefins.

Outputs

Publications

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A. Topp, B.J. Bauer, D.A. Tomalia, and E.J. Amis, *Effect of Solvent Quality on the Molecular Dimensions of PAMAM Dendrimers*. *Macromolecules*, (1999), 32, 7232.

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A. Ramzi, B.J. Bauer, R. Scherrenberg, P. Froehling, J. Joosten and E.J. Amis, *Fatty Acid Modified Dendrimers in Bulk and Solution: Single Chain Neutron Scattering from Dendrimer Core and Fatty Acid Shell*. Macromolecules (1999), 32, 4983.

S. Choi, R.M. Briber, B.J. Bauer, A. Topp, M. Gauthier, and L. Tichagawa, *Small Angle Neutron Scattering Of Solutions Of Arborescent Graft Polymers*, Macromolecules, in press.

A. Topp, B. J Bauer, T. J. Prosa, R. Scherrenberg, and E.J. Amis, *Size Change of Dendrimers in Concentrated Solution*, Macromolecules, in press.

B.J. Bauer, T.J. Prosa, D.W. Liu, C.L. Jackson, D.A. Tomalia and E.J. Amis, *Molecularly Dispersed Dendrimers in a Polymeric Matrix*, ACS Polymer Preprint (1999), 40(1), 406.

E.J. Amis, B.J. Bauer, F.I. Groehn, T.J. Prosa, D.W. Liu, K.A. Barnes, C.L. Jackson, B. D. Viers, A. Karim and J.D. Douglas, *Preparation and Characterization of Polymer/Dendrimer Blends Progress Report for 1999*, NISTIR 6353.

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Barry Bauer, *Dendrimers as Microgels*, Vistakon, Johnson & Johnson Vision Products, Inc., Jacksonville FL 32216, December 7, 1998.

Barry Bauer, *Small Angle Scattering Studies of Dendrimer Blends and Interpenetrating Polymer Networks*, SERMACS 1998, Research Triangle Park NC, November 5, 1998.

Barry Bauer, *Dendrimers, Polymers of Unique Dimension*, Polymers West Gordon Conference, Ventura CA, January 13, 1999.

Barry Bauer, *Dendrimers*, Lehigh University, Bethlehem PA, April 27, 1999.

Barry Bauer, *Molecularly Dispersed Dendrimers in a Polymeric Matrix*, Spring 1999 ACS Meeting, Anaheim CA, March 21, 1999.

Giovanni Nisato, *Characterization of Charged PAMAM Dendrimer Interactions in Solution by Small Angle Neutron Scattering*, Fall 1998 ACS Meeting, Boston MA, August 25, 1998.

Eric J. Amis, *Dendrimers, Polymers of Unique Dimension*, SERMACS 1998, Research Triangle Park NC, November 5, 1998.

Franziska Groehn, *Dendrimer-Gold Nanostructures*, Polymers West Gordon Conference, Ventura CA, January 12, 1999.

Franziska Groehn, *Dendrimer-Metal Hybrid Colloids Studied by SAXS, SANS and TEM*, SAS 99, Brookhaven National, Laboratories, Brookhaven NY, May 1999.

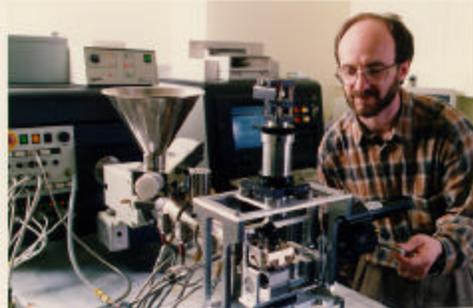
rent D. Viers, *Highly Functional Dendrimer/PEG Stars*, Elastomers Networks and Gels Gordon Conference, July 20, 1999. Industrial Collaborations

Measurement Science

...addressing important needs for physical measurements

Polymers Division Research is Highlighted in *Physics Today* and at the March Meeting of the American Physical Society

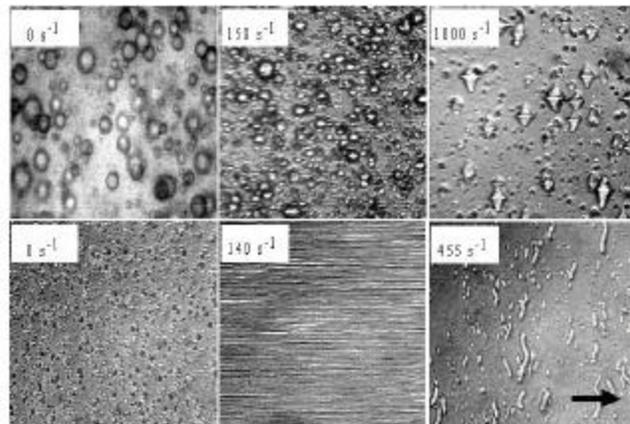
A recent paper by Kalman Migler and Erik Hobbie was featured in the Physics Update section of *Physics Today* and on the Web Site for the Annual Meeting of the American Physical Society. The paper that was presented at the Annual Meeting reports the development of a new



instrument that permits visualization of polymer blends during extrusion. Many plastics sold today are combinations of two or more incompatible polymers. Mixing these components to obtain the proper morphology is key to producing materials with desired properties. The instrument consists of a stroboscopic microscope and laser-based light scattering system that performs real time non-invasive microstructural measurements in multi-phase polymeric materials during polymer processing.

A surprising discovery made with the new instrument was how polymer droplet morphology changed with shear rate.

A surprising discovery made with this device was that above a threshold shear rate, polymer droplets in an incompatible polymer matrix could change their morphology from alignment along the flow direction to alignment perpendicular to it. The ability to access the high stress and pressure regimes typical of polymer processing was critical in uncovering this phenomenon. Since the announcement of this work, the vorticity alignment phenomenon has been found in several other polymer blend systems and raises hopes of designing materials with improved mechanical properties. Such studies can help industry understand what morphology is formed during processing, why it is formed, and how it can be controlled -- information that can have a direct impact on the next generation of improved processes and materials.

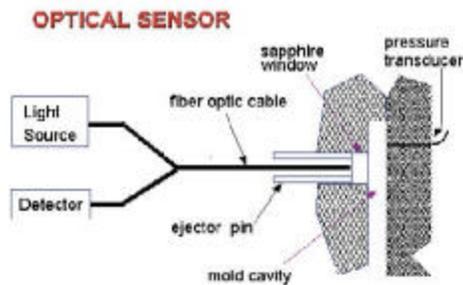


Measurement Science

...addressing important needs for physical measurements

Polymers Division Scientist Receives the Future Technology Award

Anthony Bur of the Polymers Division received *The Future Technology Award* at the Society of Plastics Engineers (SPE) annual technical meeting. The award, sponsored by Maro Publishing Co., is given for insightful research that provides the basis for future technology development in polymer science and engineering. Only 4 papers out of over 750 presented at the May 1999 SPE annual technical meeting in New York City were recognized with this award. The paper presented by Bur, "*In-Situ Measurement of Product Shrinkage During Injection Molding Using an Optical Sensor*", describes the development of and measurements using an optical sensor that is inserted into the mold cavity of a polymer injection molding machine.

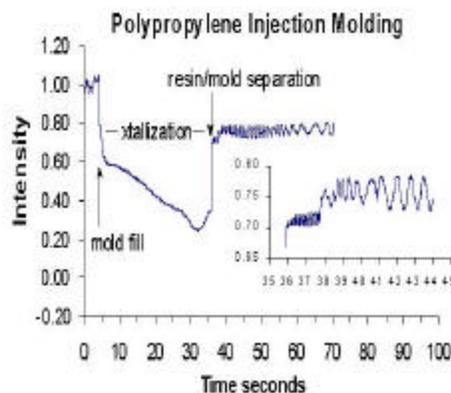


The sensor is a simple and inexpensive device consisting of a diode laser light source, optical fibers for light transmission, a sapphire window interfaced with the mold cavity, and a silicon diode photodetector. As light is transmitted into the mold, it reflects from any interface at which there is a change in the index of refraction, such as the interface between resin and sapphire window and the

The simplicity of sensor design that uses inexpensive components enhances probability that R&D laboratories and processors will use the sensor to monitor molding

resin boundary with the mold surface. As the solidifying resin cools, it contracts and pulls away from the window or the wall of the mold thereby yielding additional interfaces from which the light reflects. From the interference patterns of the reflected light the thermal contraction, product shrinkage and rate of shrinkage can be measured.

The sensor can be used to detect asymmetric shrinkage when the two sides of a product shrink at different rates. Such asymmetric shrinkage can be an indicator of warpage in the molded product. The simplicity of design that uses inexpensive components enhances the probability that R&D laboratories and processors will use the sensor to monitor molding operations.



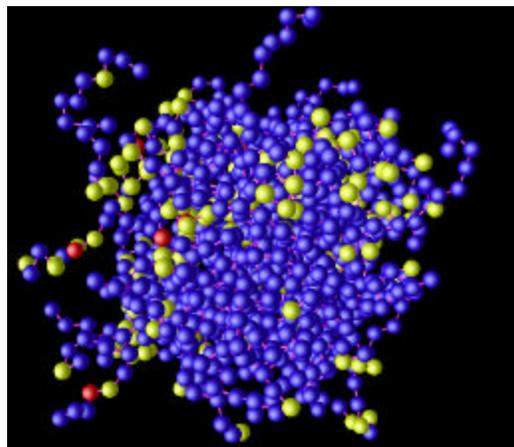
Computational Materials Science

... investigating important problems in materials theory and modeling with novel computational approaches

Growing Length-scale in Glass-forming Liquids Using Simulation

As reported in the May 20 issue of *Nature* and the June 21 issue of *Physical Review Letters*, Polymers Division scientist Sharon Glotzer and co-workers have identified a growing length scale associated with the approach to the glass transition in liquids on cooling.

When liquids are cooled to form glasses (amorphous solids), they become increasingly viscous and eventually “freeze” without crystallizing. It has long been suggested that the “slowing down” of liquids before they vitrify is related to an increasing length scale in the liquid, but neutron scattering measurements of density fluctuations have been unable to detect any evidence of a growing correlation length such as that usually associated with the approach to a conventional critical point (like the familiar gas-liquid critical point in a fluid.). But using molecular dynamics computer simulations and focusing on the atomic motions in both simple and polymeric glass-forming liquids, Glotzer and her colleagues showed the tendency for increased correlation between the displacements of atoms. The length scale of this correlated motion (which measures the distance over which atoms move -- or don't move -- together) grows with decreasing temperature and may diverge at low temperature. Related to this length scale is a dynamical variable that behaves like the static order parameter that characterizes conventional critical phenomena. By identifying this new *dynamical* measure of order in glass-forming liquids, the researchers established a possible link between the glass transition and the critical phenomena familiar from equilibrium statistical physics.



**Collaborations: Johannes Gutenberg University
University of Rome**



Sharon Glotzer is one of this year's recipients of the Presidential Early Career Award for Scientists and Engineers (PECASE). These prestigious awards recognize some of the finest scientists and engineers who, while early in their research careers, show exceptional potential for leadership at the frontiers of science and engineering. The Presidential Award is the highest honor bestowed by the U.S. government to its scientists and engineers beginning their independent careers. The award to Glotzer was given for her work in theory and computer simulations of the structure and dynamics of "soft" materials, including polymers, liquid crystals, supercooled liquids and glasses, and for her leadership in the emerging field of computational materials science.

Industrial Collaboration

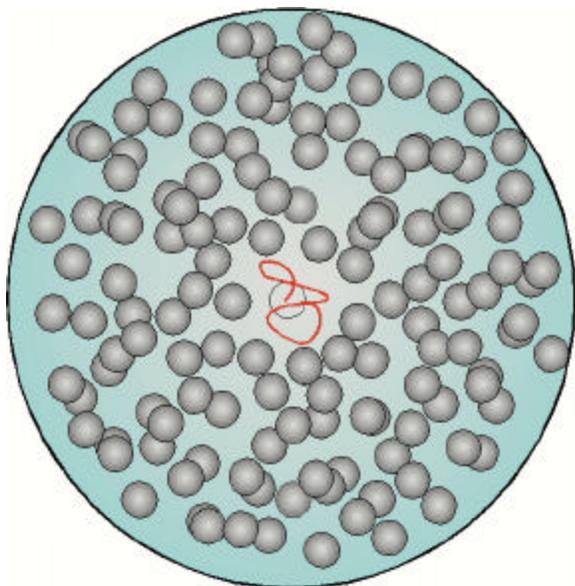
... addressing important needs for physical measurements

Collaboration with Dow Corning Corporation

Alan Nakatani and Charles Han, in collaboration with Dow Corning Corporation, have made critical measurements on filled polymers using small angle neutron scattering (SANS) instrumentation at the NIST Center for Neutron Research. The measurements probed the influence of fillers on the silicone polymer chain dimensions as a function of filler concentration and polymer molecular mass. Silicone polymers blended with particulate fillers are used commercially in rubber products and sealants. The interactions between the fillers and the polymers are key factors that influence product performance. Molecular simulations have predicted that polymer chain dimension in the presence of fillers is a function of the filler particle size and concentration. However, tests of these predictions have not been available.

Measurements showed that chain dimensions vary with particulate size as predicted by molecular simulations.

The SANS measurements, on materials supplied by Dow Corning, showed that polymer chains which are approximately the same size as the filler particle in the unfilled material experience a decrease in chain dimensions at all filler concentrations.



In contrast, for larger chains, at low filler concentrations, an increase in chain dimensions relative to the unfilled chain dimensions is observed. Both results are in agreement with existing predictions from molecular simulations. However, at even higher filler contents, which are beyond the scope of the molecular simulations, the chain dimensions reach a maximum value before decreasing to values that are still larger than the unfilled chain dimensions. A simple excluded volume model was proposed to account for the experimental results.

Extension of experimental data beyond the existing calculations supplements current predictions.

The extension of the experimental data beyond the existing calculations provides researchers with the necessary data to supplement current predictions. Furthermore, the measurements suggest that changes in chain dimensions in filled polymers should be considered when predicting their mechanical performance.

POLYMER COMPOSITES PROGRAM

The composites group was formed to address the technical barriers impeding the penetration of polymer composites into the commercial marketplace. The outstanding properties of composites mean they can be used to make products that are superior and competitive in international markets. Industries as diverse as transportation, construction, marine, off-shore oil, medical devices, and sporting goods can benefit significantly from the use of these materials. For this to happen, however, two significant barriers must be addressed: the lack of rapid, reliable, cost-effective fabrication methods; and the poor understanding and predictive capability for long term performance. These barriers were identified in a series of industry workshops, exchange visits, and consultations. In response to these challenges, the composites program initiated two tasks: one on processing science and the other on durability.

The processing work began in 1988 with a focus on processing by the method of Liquid Composite Molding (LCM). We now have three research thrusts, LCM, sensors and control, and microstructure. The LCM work consists of both experimental and modeling projects in flow through porous media to measure critical processing parameters and develop design tools for industry. The sensors and control work consists of projects to develop optical fiber sensors to provide real-time processing information such as cure state, flow-front position and gelation time, and to make use of that information in closed-loop control structures. The microstructure work consists of projects to develop standard test methods for assessing interfacial adhesion, to develop optical coherence tomography for synthetic materials, and to develop test methods to assess the performance of hybrid reinforced composites.

In the last two years, the work in LCM has been reduced as the group expands activity in hybrid composites. This transformation in the program is driven by recent workshops and conferences that demonstrate a strong focus on hybrids by the off-shore oil industry, a strong interest in hybrids by the infrastructure community, and the need in the automotive industry for innovative developments in composites.

Significant Accomplishments

- Provided NIST generated specimens and data to the Offshore Oil Industry Consortium for characterization of the failure surface for hybrid reinforced composite tubulars. All offshore oil designs for composite tubulars have converged on hybrid reinforcements as the necessary means of achieving the required mix of performance metrics. The Consortium's activities in design were severely hampered by the inability to obtain samples with controlled microstructure until NIST worked closely with manufacturers to develop sample specimens of sufficient quality for failure surface development.
- Determined that the rate dependent behavior observed in the fiber fragmentation tests of model composites is closely linked to the existence of stress concentrations at the ends of the fiber fragments. Demonstration of the way chemical structure of the interface affects mechanical failure in composites provided a framework for developing models of composite failure in terms of the microstructure.
- Demonstrated the potential of our 3-D, multiphase fluid dynamics model, based on a lattice/Boltzmann formulation, by predicting the permeability of a complex woven glass

structure used for composites reinforcement. The composites industry has long sought predictive models for process development and design, and this new capability is the first that can realistically address the general problem of the many types of fiber architectures used in the composites industry.

- Designed, built and tested an optical coherence tomography (OCT) system for nondestructive evaluation of materials including composites, coatings, and biomaterials. Developed level set image processing algorithms for image de-noising and feature recognition to support the imaging system. OCT addresses the need for rapid, low cost, nondestructive microstructure characterization critical to materials development efforts in the automotive, coatings, and biomedical industries.
- Sponsored the award of a Phase II SBIR contract for commercial development of fiber optic sensor system for composites monitoring based on prior developments in our laboratories. Quality control is a critical factor hindering the introduction of structural composites in large commercial applications requiring high-speed manufacturing. A sensor system able to rapidly measure critical processing behavior in an unobtrusive manner does not currently exist in the composites industry, and market research indicated that the fiber optic system under development has potential to meet industry requirements.

Hybrid Reinforced Polymer Composites

D. L. Hunston, K. M. Flynn, W. G. McDonough, J. P. Dunkers, G. A. Holmes, R. S. Parnas, C. L. Clark¹, S. S. Wang² and J. Williams²

¹NIST, Research Library and Information Program

²University of Houston, Houston, TX

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 micro-structures of these materials influence the behavior and complicate the interpretation of test results. This provides industry with the tools needed to design and optimize these innovative materials for their applications.

Technical Description

There is a great deal of interest in composites that 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 among various properties and between cost and performance. Industries currently exploring the use of hybrids include off-shore oil production, civil 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 important properties of hybrid tubes cannot be understood with current theories; properties measured with tubes do not always 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 developed or adapted to these types of systems.

The approach in this program is to select a model hybrid material and fabricate specimens with systematic variations in microstructures. Features of interest include void content and distribution, resin and fiber properties, interface strength, and fiber mix characteristics. The two different fibers can be combined in various ratios and mixed as separate layers (interply), as tows within each layer (intraply), or within the tows themselves (intratow). The second step in the program is to develop and adapt measurement tools for characterizing the microstructure in these materials. The mechanical properties are then determined in collaboration with Drs. Wang and Williams at the University of Houston. The University of Houston group is conducting tests on large specimens while NIST characterizes small-scale samples. Based on these results, structure-property relations will be developed to explain what the tests measure and why. The results will also resolve issues such as why properties measured with different test methods do not agree. Based on this knowledge, industry will be able to formulate materials and designs that take full advantage of the unique properties of hybrid materials.

Because the variety of possible hybrid microstructures is almost unlimited, the work focuses initially on two areas. The first is the intraply materials of interest to the off-shore oil production industry. One particular question being addressed is the discrepancies identified in the University of Houston studies between results for tube and plate. A second area of research is interply hybrids, such as those being considered for civil infrastructure applications like bridges. In such materials, failure generally occurs between layers of different fibers so modification of this region is the logical approach to improving properties. The studies at NIST will vary the microstructure in this region to establish the structure property relationships and a basic understanding of interply failure so designs can be optimized.

External Collaborations

- Doug Johnson, Lincoln Composites, provides assistance in materials selection and fabrication.
- Composites Engineering and Applications Center, Oil Industry Consortium, Houston, provides support for the testing done at the University of Houston.

Planned Outcomes

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

Accomplishments

- An in-house, specimen-preparation technique has been developed to fabricate simple bar samples that have known volume fractions of carbon fibers, glass fibers, and resin. Tests with these samples provide verification for micro-structural measurements to characterize composition.
- Cure studies have shown that undetected moisture absorption by the curing agent, prior to its use in fabricating samples, is not a major problem. When large quantities of moisture are absorbed, the curing agent becomes cloudy and thick so the change is easily seen. When small amounts are absorbed, there is little effect on the properties of the cured material.

- Tests on intraply hybrids tubes and plates have shown that most properties are well behaved. The exception is transverse shear where the tube and plate tests gave different results.
- Contrary to expectations, hybrid composites of glass and carbon reinforcements have been found to have a higher strength and stiffness than either the all glass or all carbon samples. Future studies will focus on transverse shear.
- Measurements have shown that one factor contributing to the differences in properties between tubes and plates was that plates had a significantly higher void content than the tubes. This alone, however, would not explain why some properties behave as expected, based on fiber content, while others do not.
- The hybrid tubes tested in this study had void contents higher than the all carbon or all glass tubes used for comparison. Nevertheless, the hybrid tubes had properties that were equal to or greater than what would be expected based on fiber content. Consequently, a better understanding of processing might enable fabrication of tubes with even better performance.

Impact

The data generated in this program has been used to significantly improve the design model that Lincoln Composites and others plan to use in the design of composite risers for deep-water oil platforms.

Outputs

Publications

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Z. Miyagi, S. Zaghi, D.L. Hunston, and H. Brinson, *The Sandwich Bending Specimen for Characterizing Adhesive Properties*, 119-121 in Proc. Adhesion Society Meeting (Adhesion Society, Blacksburg, 1999).

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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*, *Plastics in Building Construction XXIII* (5), 7-12 (1999).

D.L. Hunston, *NIST's In-house Research on Durability of Polymer Composites*, in Proc. Federal Workshop on the Interagency Transfer of Polymer Composite Technology, Part II (NIST, Washington, DC, 1999).

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Presentations

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Z. Miyagi, S. Zaghi, **D.L. Hunston**, and H. Brinson, *The Sandwich Bending Specimen for Characterizing Adhesive Properties*, Proc. Adhesion Society Meeting, Panama City Beach, FL, Feb. 21-24, 1999.

D.L. Hunston, *NIST's In-house Research on Durability of Polymer Composites*, Federal Workshop on the Interagency Transfer of Polymer Composite Materials Technology, Part II, Washington DC, December 10, 1998.

D.L. Hunston, *Thermoset Adhesives*, Adhesion Society Short Course, Panama City Beach, FL, Feb. 19, 1999.

Microstructure Studies: Non-destructive Characterization by Optical Coherence Tomography

J. P. Dunkers, F. R. Phelan, C. G. Zimba, K. M. Flynn, D. P. Sanders, M. J. Everett¹, R. Prasankumar² and J. G. Fujimoto²

¹ Lawrence Livermore National Laboratory, Livermore, CA.

² MIT, Cambridge, MA

Objective

The objective of this work is to image composite microstructure, damage, and defects using optical coherence tomography (OCT). Knowledge of reinforcement position and orientation are applied to the prediction of reinforcement permeability to optimize mold filling.

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 is a non-invasive, non-contact optical imaging technique that allows the visualization of heterogeneities 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 μm to 30 μm). To perform OCT imaging, broad-spectrum laser light (20 nm to 70 nm bandwidth) centered at 1.3 μm 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 superluminescent diodes are used. Transverse resolution in OCT is determined by the focal spot size of the probing beam, which is usually 10 μm to 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 and damage.

Accomplishments

- A collaboration was established with Dr. Matthew Everett, Group Leader of the Medical Technology program at Lawrence Livermore National Laboratory to build a fiber-optic OCT system for NIST. The system was constructed using a 70 nm bandwidth near infrared source which will provide 7 μm spatial resolution in the composite. The NIST OCT system demonstrates greatly improved image contrast and depth of penetration over previous results with similar composites.
- Very good agreement was obtained between permeability predicted from OCT-determined structure and experimental measurements. It was discovered that the roughness of the tow boundaries in the black and white processed images had a large effect on the predicted permeability. Automated processing algorithms that produced artificial tow boundary roughness suppressed the predicted permeability when compared to its actual value. The tow boundary roughness had as much of an influence on the predicted permeability as the fractional tow area.
- OCT images processed using level-set methods provided the best agreement with the experimental permeability and optical microscopy images. Level-set methods rely on the image gradient and curvature for de-noising and feature recognition algorithms and therefore do not blur boundaries like many traditional de-noising routines.

External Collaborations

- M. J. Everett, Lawrence Livermore National Laboratory - consultation and construction of NIST OCT system.
- P. Davis, Optiphase, Inc. - consultation on fiber-optic polarization sensitive OCT.
- R. Prasankumar and J. Fujimoto, MIT - hardware and expertise in OCT.

Impacts

As a result of progress NIST has made in demonstrating the potential of OCT for imaging polymer composites, Optiphase, Inc. of Van Nuys, CA is currently designing a fiber-optic polarization sensitive OCT instrument that is optimized for the composites industry.

Outputs

Publications

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J.P. Dunkers, *Optical Coherence Tomography of Polymer Composites*, 13th Technical Conference of the American Society of Composites, Baltimore, MD. September 23, 1998.

R S. Parnas, *Flow Prediction in Real Structures Using Optical Coherence Tomography and Lattice Boltzmann Mathematics*, 5th International Conference On Flow Processing In Composite Materials, Plymouth, U.K., July 1999.

Microstructure Studies: Measurement of Interface Strength after High Speed Processing of Fast Reacting Resins

W. G. McDonough, G. A. Holmes, J. P. Dunkers, K. M. Flynn and R. S. Parnas

Objectives

One objective is to expand the usefulness of the single fiber fragmentation test (SFFT) to fast reacting resin systems. By expanding the range of processing conditions when making the fragmentation specimens, the effects of processing on interfacial shear properties can then be measured. Another objective is to develop the single fiber fragmentation test into an automated and routine process with an analytical package that can be used to assess the interfacial properties of composites.

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 oven. This method cannot work with rapidly curing resins of interest to the automotive industry because those resins will gel and sometimes foam before the molds are filled. Consequently, an injection molding procedure has been developed which closely mimics the processing speed, temperature, and pressure observed in processes such as resin transfer molding and resin injection molding. The dog bone samples made using this procedure are then tested by the SFFT to determine how interfacial adhesion is modified under rapid processing conditions.

One of the limitations of the single fiber fragmentation test has been the variability of the test results. This variability has been cited as one of the reasons why the test is not being used more extensively. One way to reduce the variability is to automate the test. NIST has an automated test apparatus and this apparatus is being used to generate the test data for this project. It is anticipated that the reduced variability and uncertainty in the test data generated by the automated machine will help increase the interest in using this test to assess interfacial properties of polymeric composites.

External Collaboration

- Thomas Dearlove, Automotive Composites Consortium – provides information on processing requirements.
- Eric Pohl, Osi - Collaborating in the study of the strength and toughness of industry coatings.

Planned Outcome

Provide the automotive and civil infrastructure industries with methods for estimating the tradeoffs between processing speed and composite properties. By demonstrating that using an automated machine can significantly reduce the variability and uncertainty in the test data, companies will be interested in using the single fiber fragmentation test to help them develop and assess new and existing polymeric composite systems.

Accomplishments

- A specially designed injection system was built that successfully allowed the molding of fast-curing resin systems to produce 10 single-fiber dog-bone specimens from a single injection. This accomplishment allows researchers to examine processing effects on interfacial properties as well as to study interfacial properties of fast-reacting resin systems.
- An automated single fiber fragmentation testing machine that allows more reproducible testing as well as more control of the testing parameters was implemented.
- It was demonstrated that the single fiber fragmentation test could be used to assess changes in the interfacial properties of vinyl ester resins caused by changing the time-to-gelation from 45 minutes to 2 minutes.
- Measurements showed that longer post cures of vinyl-esters lacking promoters yielded interfacial properties comparable to those of resins with promoters subjected to normal cure schedules.
- Extensive interfacial damage was observed in the vinyl ester specimens, this contrasts with the clean interfaces observed in epoxy specimens, and this difference in interfacial failure may have implications on the durability of vinyl ester composites.

Outputs

Publications

W. McDonough, G. Holmes and R. Peterson, *Interface Adhesion of E-glass Fibers in Model Polyisocyanurate Networks*, Proc. American Society of Composites Baltimore, MD, 1688-1699, 1998.

Presentations

W. McDonough, *Testing Technologies to Evaluate the Micro-Structure of Composite Materials*, National Research Laboratory of Metrology, Tsukuba, Japan, 1999.

Processing: Fiber Optic Sensors for Process Monitoring

J.P. Dunkers, R.S. Parnas, C. Zimba, K.M. Flynn, S. Keuh¹, R. Bannerjee² and K. Murphy³

¹The University of Delaware

²WebCorp, Inc.

³F&S Optics, Inc.

Objectives

The objectives are to develop measurement methods based on optical fibers for monitoring the resin flow that occur in composites manufacturing, and to begin commercialization efforts for such technology.

Technical Description

The cost of polymer matrix composites must be reduced for composites to be competitive against traditional materials in consumer markets. One strategy is to decrease the cost of manufacturing the composite through process optimization and reduction of scrap. The introduction of fiber optic sensors into the liquid molding process provides a non-invasive means of obtaining real time information for control decisions. A unique fiber optic flow sensor is developed and implemented in this work. The flow sensor gives a yes/no response to the presence of resin and is based on long period grating (LPG) technology. Multiple LPGs sensitive to different wavelengths can be written onto one fiber at different locations along the fiber, providing site specific information about the resin flow with minimal sensor intrusion. The LPG is designed to couple a specific wavelength of light from the single mode core to the cladding material resulting in an attenuation of transmitted light from the core when the sensor is dry. When the resin reaches the sensor, light propagates only in the core and is no longer coupled into the cladding, providing the yes/no response.

External Collaborations

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

Planned Outcome

Demonstrate the 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

Long period grating (LPG) fiber optic sensors were successfully demonstrated as flow sensors for resin transfer molding. The trade-off between sensor length and number of sensors on the fiber was investigated. The longer sensors (2 cm vs. 1 cm) showed a sharper attenuation that enabled more sites to be resolved. However, the longer sensors also limit the number that can physically be written onto the fiber. In addition, the sensors were placed in a mold between various types of reinforcement to test their performance under actual processing conditions of compaction, flow, and heat. Random, unidirectional, and woven e-glass reinforcements and woven carbon fiber reinforcements were used. It was found that the bending of the fiber at the

sensor site caused by the compaction of the reinforcement caused the response to vanish. The severity of the problem was dependent upon the type of reinforcement and fiber volume fraction. The sensor performed well in all cases when a small diameter tube was secured over the sensor site while still allowing penetration of the resin.

A Phase I small business innovative research award to F & S Optics to develop novel fiber optic devices for composite process monitoring was completed. F & S constructed a pre-aligned and connectorized optical launch system for Fourier transform near-infrared cure monitoring with high index fibers. This system is housed inside the FTIR spectrometer and replaces the cumbersome optic and detection system previously used outside of the spectrometer. Unlike the old system, the new launch system does not require much set-up time. It also provides higher energy throughput. F & S also designed and built a prototype LPG sensor system for liquid composite molding. For this system, the maximum number of sensors that can be written onto one fiber is in the range of 5-10.

F & S will continue their program with a Phase II award. The LPG sensor system will be optimized for the following: spacing, length, and operating band of LPGs, size of evanescent wave, and coupling parameters, frequency response and noise factors. After the flow monitoring is completed, the refractive index based intensity response of the LPGs will be studied for cure monitoring. Finally, F & S is working with a composite manufacturer to test the LPGs sensor system in a sandwich panel composite.

Outputs

Publications

S.R.M. Kueh, S.G. Advani and R.S. Parnas, *Sensor Placement Study for Online Flow Monitoring in Liquid Composite Molding*, Polymer Composites, submitted.

R.S. Parnas, S.R.M. Kueh and S.G. Advani, *A Minimalist Sensor System for Mold Filling*, Proceedings of the 12th International Conference on Composite Materials, Jul. 1999.

S.R.M. Kueh, S.G. Advani and R.S. Parnas, *Virtual Sensor Simulation Study of Flow During Resin Transfer Molding Process*, Proceedings of the 13th Annual ASC Technical Conference on Composite Materials, Sept. 1998, p 744-760.

Presentations:

R.S. Parnas, *A Minimalist Sensor System for Mold Filling*, 12th International Conference on Composite Materials, Paris, France, July 5, 1999.

J.P. Dunkers, *On-line Fiber Optics Flow and Cure Sensing of Resin Transfer Molding, On-Line Sensing and Control for Liquid Molding of Composite Structures*, Annapolis, MD. April 14, 1999.

S.R.M. Kueh, *Virtual Sensor Simulation Study of Flow During Resin Transfer Molding Process*, 13th Technical Conference on Composite Materials, Baltimore, MD. September 21-23, 1998.

Liquid Composite Molding: Interface Sensitive Optical Fiber Sensor

J.P. Dunkers, R.S. Parnas, J. Lenhart¹, and J. VanZanten²

¹The Johns Hopkins University, Baltimore, MD

²North Carolina State University

Objective

The objective is to develop a method of measuring the chemical and physical properties of the polymer matrix in the first 100 nm around glass fibers in a composite.

Technical Description

Fluorescence can be used to measure a variety of polymeric properties. In order to study the properties of epoxy resin near glass, a fluorescent dye molecule, is covalently grafted to the glass surface. This molecule, abbreviated DMSCA, contains the dimethyl amino nitrostilbene fluorophore tethered to a triethoxy silane coupling agent. Typical silane coupling agent chemistry can be used to graft DMSCA to glass surfaces. DMSCA was diluted to trace levels on the surface with a co-silane coupling agent in order to simulate a model interface for glass fiber reinforced composites. Fluorescence from the grafted DMSCA was measured during cure of an epoxy resin over-layer. Both an intensity increase and a shift in fluorescence can be observed from the grafted DMSCA during epoxy cure. The layers were characterized by fluorescence, contact angle, atomic force microscopy, scanning electron microscopy, and UV-vis and infrared spectroscopy in order to understand the role of the coupling agent layer structure on interphase formation and fiber / resin adhesion.

External Collaborators

- William Birch, Corning, France - silane deposition procedures.
- Joe Lenhart, The Johns Hopkins University - silane layer characterization.
- John VanZanten, North Carolina State University-silane layer characterization.
- Steve Pollack, Howard University – synthesis of fluorescent probes.

Planned Outcome

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

Accomplishments

- The effects of silane layer thickness and type of co-silane upon emission shift of DMSCA was established.
- Through changes in the fluorescence from the grafted DMSCA it was concluded that the chemical and physical properties of epoxy resin cured over mixed silane layers differed from those of bulk resin.
- It was discovered that a shift in the fluorescence spectrum from grafted DMSCA could be used to detect resin penetration into the coupling agent layer before gelation.
- DMSCA was successfully grafted to a glass fiber-optic sensor thereby making the technique practical as a process control tool for composites manufacturing.

- An algorithm was developed to analyze the fluorescence response when the dye coated fiber optic is immersed in epoxy resin.

Output

Publications

J.L. Lenhart, J.H. Van Zanten, J.P. Dunkers, C.G. Zimba; C.A. James, S.K. Pollack and R.S. Parnas, *Using An Immobilized Fluorescent Dye to Investigate the Glass/Resin Interface*. Journal of Colloid and Interface Science, submitted.

J.L. Lenhart, J.H. van Zanten, J.P. Dunkers, C.G. Zimba, C.A. James, S.K. Pollack and R.S. Parnas. *A Fiber Optic Sensor for Composite Cure Monitoring*. Proc. SPIE Vol. 3589: Process Control and Sensors for Manufacturing, 126(1999).

Presentations

J. Lenhart, *A Fiber Optic Sensor for Composite Cure Monitoring*, "SPIE's International Symposium on NDE Techniques for Aging Infrastructure and Manufacturing, Newport Beach Marriott Hotel, Newport Beach, CA, March 4, 1999.

J. Lenhart, *A Sensor for Monitoring Cure Near the Fiber/Resin Interface*, Johns Hopkins University, Chemical Engineering Graduate Student / Industry Symposium, Baltimore, MD, December 1998.

J. Lenhart, *A Practical Fluorescence Sensor For Monitoring Composite Cure*, AICHE, Miami, Fl, November 1998.

J. Lenhart, *A Fiber Optic Sensor for Composite Cure Monitoring*, 13th Technical Conference on Composite Materials, Baltimore, MD, September 21-23, 1998.

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

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Objective

The objective of 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 single fiber fragmentation test (SFFT), but the work may expand to other measurement methods if the program is successful. Participants include 15 laboratories in 8 countries.

The internal research program at NIST seeks to quantify the impact of non-ideal matrix behavior on the fiber-matrix interfacial shear strength. This is accomplished by monitoring the change in load with increasing strain during SFF testing and by monitoring the evolution of the fiber fragmentation process with increasing strain and changes in loading rate. Results from these experiments will be used to develop new models that account for changes in matrix behavior during the testing procedure (Holmes *et al.* 1999). This research will also guide the establishment of a consensus testing procedure for the VAMAS round robin testing program.

The NIST program also seeks to impact two impediments to the efficient design and use of composites in structural applications. These are the prediction of composite strength, especially in hybrid composites, and the management of energy dissipating mechanisms during use and failure. It is well known (*e.g.*, Chamis 1974) that the interface plays a key role in both of these areas. Specifically, the energy absorbing capability of the fiber-matrix interface and the matrix material in the vicinity of a fiber break are important considerations in designing composites with a specified strength. Since interface strength is enhanced by the use of adhesion promoting silane coupling agents, the optimal silane formulation must balance fiber-matrix adhesion with the fracture toughness of the fiber-matrix interphase region. It is generally known that weak and very strong interfaces result in inferior composites by promoting fiber pullout and matrix cracking, respectively. However, the specific factors that control interface strength and toughness have not been completely delineated and quantified. This aspect of the research program will focus on the influence of silane agent coupling morphology on interface strength and energy dissipation mechanism occurring during fiber fracture. Success in this area will provide a framework for designing composites with controlled strength and failure profiles.

External Collaborations

- Eric Pohl, OSi, is collaborating in the study of the strength and toughness of industry coatings.
- Larry Drzal, Michigan State University, is collaborating on test method development.
- Graham Sims, VAMAS, and 14 other participating laboratories are engaged in round-robin testing in an effort to establish standardized tests for interfacial shear strength.
- John Nairn, University of Utah, is investigating the dynamics of debond region formation.
- Leigh Phoenix, Cornell University, is correlating NIST data with theoretical models.

Planned Outcome

Establish international protocol for single fiber fragmentation test.

Accomplishments

- A consensus test procedure was established for the international round robin and statistical test design was used to randomly divide samples among the 14 participants.

- Complete analysis of the fragmentation data from single fiber composites made from bare E-glass fibers and diglycidyl ether of bisphenol-A / meta-phenylenediamine (DGEBA/m-PDA) epoxy resin revealed that differences in the fragment distributions arise when specimens are tested using different test protocols.
- Differences in fragmentation distributions at the early stage in the testing procedure suggest the presence of stress concentrations at the end of the generated fiber fragments that promote molecular level interface failure.
- The NIST Nonlinear Viscoelastic model predicted high stress concentrations at the fiber ends at low strain values in one of the fiber fragmentation test protocols. These predictions are consistent with stress concentrations at the fiber-matrix interface promoting interface failure at the molecular level.

Outputs

Publications

G.A. Holmes, R.C. Peterson, D.L. Hunston, and W.G. McDonough, *E-glass/DGEBA/m-PDA Single Fiber Composites: The Effect of the Matrix Modulus on Interfacial Shear Strength Measurements*, Polymer Composites, in press.

G.A. Holmes, R.C. Peterson, D.L. Hunston, and W.G. McDonough, *E-glass/DGEBA/m-PDA Single Fiber Composites: Interface Debonding During Fiber Fracture*, Polymer Composites, in press.

D.L. Hunston, G.A. Holmes, R.C. Peterson, and W.G. McDonough, *Strain Rate Effects in the Single Fiber Fragmentation Test for Fiber-Matrix Adhesion*, pp. 432-433 in *Polymeric Materials: Science and Engineering Preprints*, Vol 81 (ACS, Division of PMSE, Washington, DC, 1999).

G.A. Holmes, R.C. Peterson, D.L. Hunston and W.G. McDonough, "*E-Glass/DGEBA/m-PDA Single Fiber Composites: The Effect of Strain Rate on Interface Shear Strength Measurement*," Polymer Composites, in press.

D.L. Hunston, G.A. Holmes and R.C. Peterson, *Viscoelastic Properties of a Resin Commonly used in the Single Fiber Fragmentation Test*, *Journal of Reinforced Plastics and Composites*, in press.

G.A. Holmes, R.C. Peterson, D.L. Hunston, W.G. McDonough and C.L. Schutte, *The Effect of Non-Linear Viscoelasticity on Interfacial Shear Strength Measurements*, ASTM STP 1357

G.A. Holmes, R.C. Peterson, D.L. Hunston and W.G. McDonough, *How Nonlinear Viscoelastic Matrix Behavior Influences Interfacial Shear Strength Measurements*, *Proceedings of 4th Int. Conf. on Constitutive Laws for Engineering Materials: Experiment, Theory, Computation and Applications*, Rensselaer Polytechnic Institute, Troy, NY (July 27-30, 1999).

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.

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Presentations

D.L. Hunston, G.A. Holmes, R.C. Peterson and W.G. McDonough, *Strain Rate Effects in the Single Fiber Fragmentation Test for Fiber-Matrix Adhesion*, Symposium on Adhesion: chemistry, Process, and Mechanics, Polymeric Materials: Science and Engineering Division of ACS, ACS National Meeting, New Orleans, August 22-26, 1999.

G.A. Holmes, R.C. Peterson, D.L. Hunston and W.G. McDonough, *How Nonlinear Viscoelastic Matrix Behavior Influences Interfacial Shear Strength Measurements*, International Conference on constitutive Laws, Rensselaer Polytechnic institute, Troy, NY, July 27-30, 1999.

Liquid Composite Molding: Lattice Boltzmann Techniques for Process Modeling

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² Nottingham University, Nottingham, UK

Objectives

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

Technical Description

We have developed a lattice Boltzmann (LB) method for simulating fluid flow in the reinforcement materials used in composite processing operations. LB methods involve the solution of the discrete Boltzmann equation for the particle distribution function on a lattice. Each particle distribution function represents a packet of particles moving with a fixed velocity along the lattice. Macroscopic flow quantities such as velocity and density are recovered by taking moments of the distribution function as follows

$$\mathbf{r}(\underline{x}, t) = m \sum_{\mathbf{a}=1}^N n_{\mathbf{a}}(\underline{x}, t)$$

$$u(\underline{x}, t) = \frac{m}{\mathbf{r}(\underline{x}, t)} \sum_{\mathbf{a}=1}^N v_{\mathbf{a}} n_{\mathbf{a}}(\underline{x}, t)$$

where m is the particle mass, $n_{\mathbf{a}}$ is the particle distribution function, and $v_{\mathbf{a}}$ is a discrete representation of the velocity space on a lattice. The Navier-Stokes equations are recovered from

the LB formulation thus defined. To model flow in reinforcement materials that have both open and porous regions, the velocity in porous regions is defined as

$$\underline{U} = \underline{u}(x,t) + \frac{\underline{\tau}F(x,t)}{\underline{\mathbf{r}}(x,t)}$$

where $\underline{\tau}$ is a relaxation time, and the function \underline{F} is given by

$$\underline{F}(x,t) = -\underline{\mu}\underline{\underline{K}}^{-1}\underline{\mathbf{r}}(x,t)\underline{u}(x,t)$$

where μ is the viscosity, \underline{u} is the Navier-Stokes velocity, and $\underline{\underline{K}}$ is the micro-permeability tensor of the reinforcement material in the porous region.

Planned Outcome

To model multi-phase flow in reinforcement materials, and provide the developed simulation tools to manufacturers for optimizing the production of composite materials.

Accomplishments

One area of simulation this past year was flow verification, in which we compare the LB simulation to experimental results. Some results comparing the LB simulation with experimental results for flow through arrays of porous circles are shown in Table 1.

Array Type	Array Spacing (cm)	Measured Tow Permeability (cm ²) X 10 ⁷	Measured Array Permeability (cm ²) X 10 ⁵	Array Permeability (cm ²) LB Simulation
Square	0.08	2.68 ± 0.54	7.97 ± 1.59	7.4e-5
Hexagonal	0.08	2.95 ± 0.59	2.61 ± 0.52	2.97e-5

Table 1: Comparison of measured permeabilities, including 20% standard deviations in the experimental measurements, with the LB model for flow through arrays of permeable circles.

The results with finite spacing between tows are in excellent agreement with the experiments. However, the results for the cases in which the inclusions touch (not shown), show considerable error. This is probably due to mesh spacing effects and we are investigating how to eliminate this.

The LB simulation has also been used to predict the permeability of a Knytex D155 material whose structure was determined by OCT imaging. Comparisons of a small sample of permeability calculations with an experimental measurement are shown in Table 2.

Sample Name	Imaging Method	Image Set	Axial K x 10 ⁻⁴ (mm ²)	Brinkman Fraction
Experimental	-	-	5.3 ± 1.1	0.770
Data Set 2	Manual	75-95	3.81	0.788 ± 0.021
Data Set 3	Automated No Smoothing	75-95	2.83	0.768 ± 0.021
Data Set 4	Automated Smoothing	75-95	3.18	0.750 ± 0.027

Table 2: Comparison of permeability computed from OCT images and experimental data for Knytex D155 unidirectional, including 20 % standard deviations in experimental permeability measurements and image analysis values for the Brinkman fractions.

Image sets within this table were processed using both a rapid “Automated” procedure and a “Manual” method. In the “Manual” method, the tow outlines were drawn by sight and filled in to obtain the binary image. In general, all the computationally predicted values are lower than the experimental value, with the closest being Data Set 2, which was processed manually. We found that the artificial roughness in the images between the border the tows and the resin has a large influence on the magnitude of the flow. The roughness results from noise in the original OCT images that the automated image processing routine is not able to eliminate. Data Set 4 shows that smoothing of the boundaries, which reduces the artificial roughness, can be used to get closer agreement with the experimental values. Thus, the key to using LB to accurately predict permeability from OCT imaging lies in developing image processing techniques which eliminate spurious noise, and accurately determine the boundaries of the reinforcement structure.

Another significant result is that the OCT / LB approach was able to capture the effect of crossing threads on the permeability in the “unidirectional” Knytex material. In previous work we found that a 2-D calculation of the permeability for the Knytex material (which does not account for the crossing threads) yielded a prediction roughly 6 times higher than the experimental value. The fact that the values computed here are on the same order of magnitude as the experimental value indicates that 3-D effect of the crossing threads is being correctly captured.

Further permeability computation work was begun in the past year in the form of collaborations with Katholieke Universiteit Leuven and the University of Nottingham who have programs in modeling the geometric structure of reinforcement materials. The outputs from their geometry modeling programs are input directly into the LB simulation to predict the permeability of the reinforcement materials. Finally, we have laid the groundwork for applying LB methods to non-Newtonian flows. LB methods have been shown to be quite powerful for modeling multi-phase flows, but have been limited to Newtonian fluids. We have developed an expression for the equilibrium distribution function which is applicable to fluids of any type of rheology. This result will enable the modeling of nonlinear rheological behavior of curing thermosets and of polymer melts in the processing of composite materials.

Impact

The LB simulation software has been transferred to Corning, Inc., and Katholieke Universiteit Leuven.

Outputs

Publications

F.R.Phelan Jr., R.C. Peterson, and M.A. Spaid, *Void Formation, Displacement and Transport in Heterogeneous Fiber Media. Part 1: Experimentation*, Polymer Composites, in press.

R.C. Peterson, and F.R. Phelan, Jr., *An Investigation of Void Formation Dynamics in Fiber Preform Materials*, ASC 13th Technical Conference, p. 271, (1998).

J.P. Dunkers, F.R. Phelan, C.G. Zimba, R. Prasankumar, J.G. Fujimoto, and R.S. Parnas, *Flow Prediction in Real Structures using Optical Coherence Tomography and Lattice Boltzmann Mathematics*, Proc. 5th Int. Conf. on Flow Processes in Composites, Plymouth, UK, (July 1999).

F.R. Phelan Jr., J.P. Dunkers, C.G. Zimba, K.M. Flynn, R.S. Parnas, R.C. Peterson, X. Li, and J.G. Fujimoto, *Numerical Prediction of Permeability Using A Lattice Boltzmann Method and Optical Coherence Tomography*, ICAC Sixth International Conference on Automated Composites: Proceedings, (1999).

Presentations

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K.M. Pillai, and C.L. Tucker III, and Phelan Jr., F.R., *Simulation of Injection/Compression Liquid Composite Molding*, 1998 ASC Conference, Baltimore, MD, (September 21-22, 1998).

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Processing: Permeability Measurements and Database

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¹Standard Reference Data Program, NIST

Objective

The objective is to provide permeability measurement methods and data for the design tools used by the composites industry. This year we will expand the database to include data from other sources in preparation for the release of Version 2.0. New data on carefully deformed materials is being measured to aid designers in using the baseline data in complex geometries.

Technical Description

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

External Collaborations

- 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 FY2000 on the world wide web with an expanded data set.

Accomplishments

Version 2.0 of the database has been developed by documenting data submitted by external collaborators, and the size of the database has been doubled. Version 2 has also been implemented in HTML as a web page and is currently being tested internally at NIST before release to the public.

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

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.

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

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Measurement Science

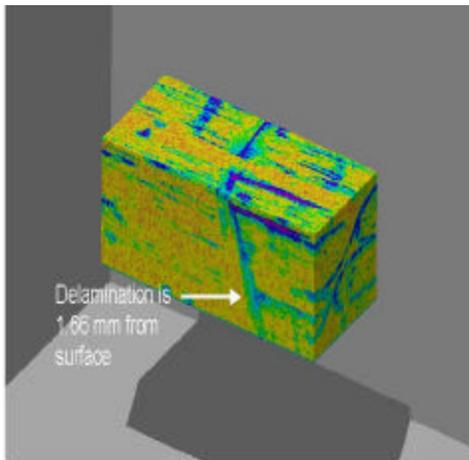
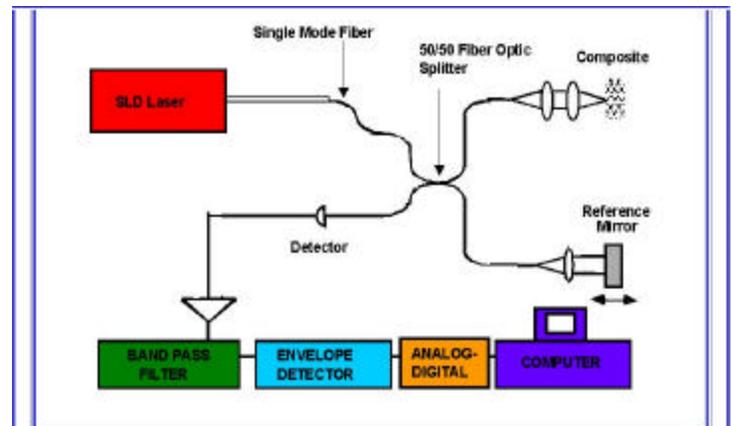
... addressing important needs for physical measurements

A New Method to Image Polymer Composites

The application of a new imaging technique to non-destructively quantify microstructure and damage in polymer composites has been demonstrated in collaboration with researchers at the Massachusetts Institute of Technology (MIT) and Lawrence Livermore National Laboratory. The method, called Optical Coherence Tomography (OCT), is based on interferometric analysis of light scattered by the object. Although originally developed at MIT for imaging biological tissues, the collaboration extended the method to produce images of the internal 3-D glass fiber architecture in nearly opaque glass reinforced epoxy and vinylester composites. Polymers Division scientists, Joy Dunkers and Frederick Phelan, used this information in a fluid mechanics model to yield the first prediction of the reinforcement permeability based on actual fiber architecture. The permeability characterizes the fluid infiltration behavior that is critical for optimum processing. The technique was also applied to image the fiber distribution and orientation in short fiber samples of interest in the automotive industry. Another application was qualification of surface and subsurface damage for a polymer composite after it was subjected to impact loading. Better methods to image internal defects is a critical industry need since damage to composite laminates is frequently not visible at the surface.

Method addresses critical industry need to image internal defects in composites.

The advantage of this new technique is that it can non-destructively acquire 2-D, cross sectional images (6 mm x 3 mm) through the intact sample in under a minute at spatial resolutions of about 10 micrometers.



These 2-D images can then be assembled into a 3-D reconstruction of the material and its internal microstructure. The penetration depth of the light depends on the materials involved, but images extending up to 1 cm into the sample have been obtained. Because the technique is based on light scattering, samples with significant amounts of carbon fiber are a problem, but a variety of composites made with glass or Kevlar fibers have been imaged. One of the most important advantages of OCT is the potential to obtain data at a fraction of the cost for alternative methods. Work is now underway with the automotive, plastics, and offshore oil industries to explore application of OCT to problems in their areas.

POLYMER CHARACTERIZATION

The Polymer Characterization Program provides measurement methods, data and standard reference (SRMs) 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 behaviors. As a result, the focus of the program is on techniques that measure molecular mass and its distribution, solid state structure, mechanical 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 and electron microscopy as well as spectroscopic methods such as solid state nuclear magnetic resonance (NMR) and infrared spectroscopy.

The mechanical behavior of polymers depends on the chemical structure, the environmental history (such as temperature and humidity), and the loading or deformation history. Because of these many influences, experimental characterization of the mechanical response of polymers for every conceivable situation is impractical. Instead, methods are developed that reduce the number of tests required to describe the nonlinear thermo-viscoelastic properties of polymers. In this approach, the frameworks of continuum solid and fluid mechanics are applied to interrelate mechanical responses measured in simplified geometries and representative environmental and deformation histories. The results of such measurements are used to evaluate parameters used in models, which are based on the underlying physics of macromolecules and/or phenomenology. The success of a given model is assessed by comparing subsequent predictions against measurements made in more complicated deformation states. Measurements in various geometries are obtained with a number of different instruments, including the NIST Torsional Dilatometer, conventional rotational rheometers, 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. Non-Newtonian rheological standards are also developed to exhibit the typical polymeric behaviors of shear thinning and normal stresses; these standards are also used for calibration of rheological instruments and for research into improved measurement methods.

Significant Accomplishments

- Determined the intrinsic viscosity of polyethylene SRM 2885 and SRM 2886 and the mass average molecular mass, M_w , by high temperature light scattering for polyethylene SRM 2886 and SRM 2887. These data are needed to certify these polyethylenes as molecular mass standards for calibration of gel permeation chromatographs.
- Determined the laboratory-to-laboratory reproducibility in measuring the molecular mass distribution using matrix assisted laser desorption/ionization, MALDI, time-of-flight, TOF, mass spectrometry, MS, by organizing and completing an interlaboratory comparison of well-characterized polystyrene that involved 18 institutions.
- Established that secondary peaks in the MALDI mass spectrum of polystyrene, PS, are primarily due to the formation and decay of adducts of PS with matrix molecules and metal cations.
- Discovered that a composite of polypropylene-graft-maleic anhydride (PPgMA) -clay (mass fraction clay = 4 %) exhibits a mixed nano-morphology of exfoliated clay layers, dispersed stacks of 2-3 clay layers, and intercalated large tactoids.
- Resolved difficulties with resonance in a new model transducer design used in a commercial rheometer; the manufacturer will implement this change in instruments supplied with the new transducer.
- Resolved the origins of x-ray scattering intensity near wave vector = 0 in semicrystalline polymers. The peaks that are commonly observed in the raw scattering cross sections in this range are assigned to inhomogeneities in the structure other than lamellar crystallites.
- Determined, by NMR, that the density of alkane coverage attached to silica-gel surfaces is not uniform on a 20 nm distance scale. This information is used in evaluation of columns used in high performance liquid chromatographic separation.

Standard Reference Materials

Charles M. Guttman, William R. Blair, Bruno Fanconi, John R. Maurey and Carl R. Schultheisz

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 is used to calibrate size exclusion 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 (130 °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 of low polydispersity, M_w/M_n , of less than 1.2 (M_w is the mass average molecular mass and M_n is the number average molecular mass), are the most useful materials for calibrating SEC. The NIST polyethylene standard reference materials, SRMs, are the only available narrow fractions of polyethylene. These SRMs will soon be out of stock.

The lack of commercial standards arises out of the difficulties in 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 (6,000, 88,000 and 190,000) g/mole, to be designated SRM 2885, 2886 and 2887, respectively, in sufficient quantity to produce three additional narrow fraction polyethylene SRM's.

Planned Outcomes

The three new polyethylene standards, SRM 2885, 2886 and 2887, together with existing standards, SRM 1482 and 1483, will improve calibration of size exclusion chromatographs by providing the polymer industry with molecular mass calibrants for polyethylene covering the range 6,000 g/mol to 190,000 g/mol.

Accomplishments

New Polyethylene Molecular Mass Standards

All three new polyethylene SRM's have been purified by recrystallization and bottled. The bottled materials have been evaluated for homogeneity. No bottle-to-bottle variation was found. The intrinsic viscosity of SRM 2885 and SRM 2886 has been determined. The M_w by high temperature light scattering has been completed for SRM 2886 and SRM 2887. The light scattering on SRM 2885 is in progress as is the intrinsic viscosity measurements of SRM 2887.

Mass Spectrometry of Polymers

Charles M. Guttman, William R. Blair, Robert I. Goldschmidt, William E. Wallace, Stephanie J. Wetzel 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. Specific activities for FY 99 are to (1) develop sample preparation techniques that show consistent repeatable signals in the MALDI-TOF-MS, (2) develop data analysis procedures for quantitative comparisons of MALDI-TOF-MS and SEC results and (3) conduct interlaboratory comparison on a well-characterized polymer sample.

Accomplishments

- An interlaboratory comparison, involving 18 institutions (10 industry, 5 academic, 3 government), was conducted using well-characterized polystyrene (by NMR for M_n , by light scattering for M_w and by FTIR for the presence of the t-butyl end group) to determine the laboratory-to-laboratory reproducibility in determining the molecular mass distribution using MALDI-TOF-MS. MALDI mass spectrometry returned an M_n of (6600 ± 100) u and an M_w of (6700 ± 90) u. These numbers were below those of the classical methods, but still within the overlapping uncertainty ranges.
- The application of high-resolution MALDI-TOF-MS to determine the complex three-dimensional polymer structure was demonstrated.
- Secondary peaks observed in the MALDI mass spectrum of the polystyrene that was used in the interlaboratory comparison were shown to arise from two sources: either adducts of the matrix with the polymer or fragmentation of the polymer along the main chain. None of the secondary peaks were attributable to additional end groups.
- Post-source decay (PSD) analyses of the interlaboratory PS sample and also of a PS of M_n of about 3900 indicate that the secondary series are primarily due to the formation and decay of adducts of PS with matrix molecules and metal cations. Some fragmentation of the PS polymers alone also occurs with the loss of between one to four repeat units. These results are in contrast to our fragmentation studies earlier on PEO where fragments of all chain lengths less the molecular mass of the polymer were found.
- Autocorrelation function analysis was shown to be a powerful method of resolving polymer architecture and copolymer composition from mass spectra of some samples.
- MALDI-TOF-MS of polymethacryloxypropyltrimethoxysilane revealed that this polymer, when synthesized in the bulk, exhibited mainly a ladder-like structure in which 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.

External Collaborations

- S. Samal of Ravenshaw College, Cuttack, India - seeks to develop matrix materials that are compatible with synthetic polymers.
- Professor J. Girard at American University - methodology is developed to compare SEC and MALDI-TOF-MS.
- Paul Kowalski of Bruker Instruments - fragmentation processes that occur in MALDI-TOF-MS are investigated.

Outputs

Publications

W.E. Wallace, C.M. Guttman and J.M. Antonucci, *Polymeric Silsesquioxanes: degree-of intramolecular-condensation measured by mass spectrometry*, Polymer, in press.

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W.R. Blair, B.M. Fanconi, R.I. Goldschmidt, C.M. Guttman, W.E. Wallace, S.J. Wetzel and D.L. VanderHart, *Comparison of Classical and MALDI-TOF-MS Analysis of a Polystyrene Interlaboratory Sample*, The 46th ASMS Conference on Mass Spectrometry and Allied Topics, Dallas, TX, June, 1999.

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Characterization of Polymer Morphology by Microscopy Techniques

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Objectives

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

Technical Description

The characterization of polymer morphology is important to better understand the relationship between structure and properties in many materials. Techniques used TEM, scanning electron microscopy (SEM), optical and atomic force microscopy. The combination of microscopy techniques with other methods such as scattering, diffraction or spectroscopic methods gives a more complete description of the structure of complex blends, composites or other multiphase materials. Many types of materials have been studied, including polymer blends, block copolymers, liquid crystalline polymers, dendrimers and organic-inorganic hybrid materials, including polymer/clay nanocomposites.

External Collaborations

- Professor Reimund Stadler, University of Bayreuth, Bayreuth, Germany - provide semi-crystalline block copolymers
- Professor Matthew Libera, Stevens Institute of Technology, Hoboken, NJ - collaboration on TEM of block copolymers
- Dr. Henri Chanzy of CERMAV and CNRS in Grenoble, France - TEM of dendrimers and nanocomposites
- Dr. Donald Tomalia, Michigan Molecular Institute, Midland, MI - provide dendrimer samples
- Professor Emmanuel Gianellis, Cornell University, Cornell, NY - Collaboration on preparation and characterization of polymer-clay nanocomposites

Planned Outcomes

- Provide the scientific and industrial community examples of rigorous characterization of the morphology of new polymeric materials, such as semi-crystalline block copolymers, dendrimers and polymer-clay nanocomposites, using a combination of microscopy and scattering techniques.

- In polymer-clay nanocomposites, demonstrate the strengths and weaknesses of TEM compared to x-ray diffraction methods, in accurately categorizing the morphology of immiscible, intercalated, exfoliated, or mixed materials on a series of control samples.

Accomplishments

- Polarized light microscopy (PLM) and TEM results on thin films (5 to 10 μm) and bulk specimens of polystyrene (PS)-polybutadiene (PB)-polycaprolactone (PCL) (PS-PB-PCL) triblock and PS-PCL and PB-PCL diblock copolymers elucidated the macroscopic crystalline superstructure (optical range 4 to 1000 μm) and microphase separated morphology (TEM range 5 nm to 100 nm) produced by various annealing conditions. In the thin films, it was shown that crystallization into spherulites can either distort or completely destroy the microphase separated morphology for the PS-PB-PCL triblock copolymer, while spherulites can coexist with the cylindrical microphase separated structure in the case of PB-PCL diblock copolymer. In the bulk films, the microphase separated morphology dominates and large spherulites do not form. The bulk films were analyzed by small angle x-ray scattering (SAXS) and wide angle x-ray scattering (WAXS) at room temperature to simultaneously measure both the lamellar spacing of the microphase separated structure by SAXS and quantifies the PCL crystallinity using WAXS. In the PS₃₅PB₁₅PCL₅₀ triblock copolymer, a lamellar-cylindrical microstructure with PB cylinders at the interphase boundaries is observed by both SAXS and TEM; this structure is similar to the microphase separated structure of ABC type amorphous block copolymers. The simultaneous WAXS confirms the PCL is crystalline and the PCL reflections disappear when the sample is heated to 90 °C.
- TEM of thin sections prepared by cryomicrotomy of the 1 % to 2 % poly(amidoamine), PAMAM, dendrimers (generation 8 through generation 10) in interpenetrating polymer networks (IPNs) of hydroxyethylmethacrylate showed that the dendrimers were well dispersed and visible as individual molecules. Sodium phosphotungstate was used as a stain for the dendrimers, which resulted in clearer images than that obtained with osmium tetroxide.
- The diameters of dendrimer particles, dispersed in IPNs, measured by TEM were in good agreement with the SAXS results. Characterization by SAXS can measure R_g , from which the corresponding particle diameter can be calculated, assuming a uniform dense sphere.
- The networks described above with generation 8 PAMAM dendrimers can be swollen in water and infused with metal salts, which are then reduced to form colloids (copper, gold, etc.) within the dendrimers. Preliminary TEM has imaged the metal colloids and located them within the dendrimers in the network.
- Morphology characterization of polymer-clay nanocomposites (PLCs) using TEM and x-ray diffraction (XRD) has shown that polypropylene-graft-maleic anhydride (PPgMA) clay nanocomposite (mass fraction clay = 4 %) forms a mixed nano-morphology of exfoliated clay layers, dispersed stacks of 2-3 clay layers, and intercalated large tactoids. PLCs are a new type of filled polymer material wherein the silicate layers of the clay are separated at the nanometer scale, providing both improved mechanical properties, increased thermal stability and reduced flammability. By XRD, only the intercalated structure could be detected, demonstrating the importance of combining the TEM and XRD techniques. For the polystyrene-clay nanocomposite (3 % clay), either an intercalated or a mixed nano-

morphology is obtained, depending on the surface treatment of the clay. The phenolic cyanate ester-clay "nanocomposites" are primarily neither intercalated or exfoliated, thus are more like conventional filled polymer systems, where the clay particles are immiscible and simply dispersed in the polymer matrix. Correlation of the morphology with the thermal stability, flammability properties and mechanical behavior of these nanocomposites is vital to designing effective new materials.

- The TEM showed that the polybutadiene phase of polystyrene/polybutadiene (60/40) blend containing a model filler, C60 (buckminster fullerene), preferentially wets the aggregates of C60 in the film and the phase evolution is slowed due to the shift in the phase boundary from that of the pure blend caused by this preferential wetting. The TEM samples are prepared by staining that effectively halts the phase evolution and stabilizes the morphology. Earlier stage phase structures can be captured by this method compared to what was previously accomplished using optical microscopy.

Outputs

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Characterization of Polymers by Spectroscopic Techniques

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Objective

The main objective is to develop and use nuclear magnetic resonance (NMR) techniques to characterize, in solid polymers, those molecular and morphological features that influence solid-state properties.

Technical Description

Various NMR phenomena and experimental approaches to solid-state characterization are employed; the most useful being: (1) **Proton spin diffusion**, which is characteristic of an extended network of dipolar-coupled protons, e.g. a typical of organic solid. Spin diffusion is evidenced by the flow of proton polarization following the imposition of a polarization gradient. This flow is in a direction that restores spin equilibrium. Thus, properly designed proton spin diffusion experiments yield information about spatial relationships and domain size (typically for the 3 nm to 50 nm range) in organic polymers. (2) **Multiple pulse proton techniques**, which offer a way to quench spin diffusion and simultaneously, especially in the presence of magic angle sample spinning (MAS), achieve some chemical shift resolution for protons in solids. Protons can be detected with excellent sensitivity; hence, these multiple-pulse techniques

combine sensitivity with a mild measure of chemical differentiation. (3) ^{13}C spectra, obtained using MAS, which offer the best chemical resolution for organic solids, albeit lower sensitivity is an issue. Also, one can often distinguish signals arising from the same chemical species in different states of order, e.g. crystal or non-crystal, or in different conformations. 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 physical or conformational different sites.

Characterization of the structure of isotactic poly(propylene). This work is collaborative between Dr. Rufina Alamo of Florida Agricultural and Mechanical University-Florida State University and NIST. We are interested in the morphological distribution of stereo, regio, and comonomer ‘defects’ in iPP chains, since a bias against the incorporation of a particular defect by the growing crystallites will influence polymer properties. Solid state NMR methods are used to determine the average concentration of defects in the crystalline regions of iPP. The correct assignment of NMR resonances that belong to each of the defect types in their respective crystalline environments is a critical part of the determination of defect levels. Knowledge of how many carbons from each defect contribute to each defect resonance is necessary before one can relate relative intensities to defect concentrations. We have, with the help of Marc Nyden of the NIST Building and Fire Research Laboratory, taken the approach of performing *ab initio* chemical shift calculations on defect-containing, methyl-terminated oligomeric molecules, involving 7 or 8 repeat units. The conformation adopted by these oligomeric molecules is defined by a molecular dynamics calculation in which: a) 26 iPP stems (each 21 monomers long) are assembled into positions defined by the α -crystalline iPP lattice; b) a defect is introduced into the center of a central stem in this lattice; and c) with the outer perimeter of stems held fixed, the defective chain along with its nearest neighbor plus all next nearest neighbors are allowed to move under simulated thermal annealing conditions followed by energy minimization. Based on reasonable agreement between experimental chemical shifts and these computed values, and based on measured relative integrals for the defect resonances in the NMR spectra of the crystalline regions, we have deduced the defect levels. Only for the regio-2,1-erythro defect, a particular stereo-isomer of the head-to-head defect, does the ambiguity of resonance assignment remain...even though, of all the defects we considered, there is no doubt that this defect is most discriminated against by the growing crystallites. When experimental and computational results agree, we may, in this way, also obtain information about the conformation of the iPP chain near the defect.

Characterizing the organization of chemically-tethered alkane chains (mean length of 30 carbons) attached to silica-gel surfaces. This work is a collaboration with Matthias Pursch, a post doctoral research associate working with Lane Sander in the Analytical Chemistry Division. These organic coatings are principally in the form of monolayers. Such surface-modified silica gels are used in inverse-phase high pressure liquid chromatography (HPLC). These gels provide shape-selective separations for certain families of molecules, e.g. polyaromatic hydrocarbons or b-carotene isomers. There is a strong correlation between molecular shape-selectivity in HPLC applications and the density of coverage for the organic coating. Using ^{13}C NMR, we can infer, on the basis of chemical shift information, whether alkane carbons are locked into a mainly-trans conformation (suggesting an organized, dense layer) or whether the chains undergo dynamic averaging over both gauche and trans conformational states (typical of disorder and lower density). The resonance shape of the methyl carbon at the end of the alkane chain is sensitive to whether the carbon is at an air/organic interface or embedded in an organic matrix. (This allows

one a second criterion...besides the conformational criterion... to satisfy when modeling this surface layer.)

Composites of nylon 6 and clay. In a collaborative study with Jeffrey Gilman of the NIST Building and Fire Research Laboratory, we have looked at several samples that are composites of nylon 6 and various clays, both naturally occurring, paramagnetic montmorillonites and synthetic laponite clays. These materials contain mass fractions of about 5% clay in exfoliated form. The clay is initially treated with a combination of inorganic and organic chemicals in order to condition the surfaces of the clay layers so that the nylon 6 develops some chemical affinity for the surfaces. Then samples were prepared both by polymerization of the nylon in the presence of the clay or by mixing the clay with already-polymerized nylon 6. Using ^{13}C NMR, the most obvious impact on the nylon 6 spectrum, due to the presence of the clay, was the change of crystal habit. Without the clay, melt crystallization of the nylon 6 leads to crystal formation exclusively of the α -allomorph. In the presence of the clay, the major crystal population is the γ -allomorph. Since we can, via ^{13}C NMR, measure the ratio of α - to γ -allomorphs, we pursued the idea that this ratio could be a measure of the uniformity of mixing of the clay and the nylon 6. For a given batch of montmorillonite with a given level of paramagnetic impurity and a given concentration in the nylon 6, T_1^{H} may correlate with the uniformity of the clay dispersion throughout the nylon 6 matrix.

External Collaborations

- R.G. Alamo, Associate Professor in Chemical Engineering, Florida Agricultural and Mechanical University, Tallahassee, FL - materials, liquid-state NMR characterization, molecular mass, DSC data, crystallization-kinetics data and crystal-allomorph data for the isotactic poly(propylene), iPP.
- L. Mandelkern, Professor of Chemistry at Florida State University, Tallahassee, FL – assisted in the iPP work.
- J.A. Randall of Exxon Research, Baytown, TX - characterization of olefinic polymers by solution-state NMR, interpretation of solution-state NMR spectra, and consultations for understanding the relationships between defect structures and polymer properties.
- E. Pérez of the Institute for Polymer Science in Madrid, Spain - characterizing vinyl polymers with long aliphatic branches.
- R.H. Atalla, professor at the Forest Products Laboratory, United States Department of Agriculture, Madison, WI - structural characterization of cellulose, its processing and its biogenesis.
- Norritsu Terashima, professor emeritus in Nagoya, Japan - chemical characterization of lignin, provided a few, well chosen and well-characterized samples of ^{13}C -enriched lignins.

Planned Outcomes

- Develop a greater understanding of the mechanism whereby different 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.

- For derivatized, organic-coated silica gels that are used for inverse-phase, high-pressure, liquid chromatography (HPLC), develop some insight into the relationships between molecular order or mobility in the n-alkane tails of the molecules of the coating and molecular-shape selectivity for component molecules in the analyzed HPLC mixture.
- Develop a better understanding of blend morphology. A particular interest is the characterization of mixing when one uses the strategy of creating compatibility by decorating one blend component with a few groups that strongly interact with the other component. For these blends we are interested both in the uniformity of concentration on a scale less than 10 nm and in the micro-phase separation which occurs in the presence of chemical agents which compete with the strongly-interacting groups (e.g. the influence of water when the strong interactions involve hydrogen bonding).
- Develop a better understanding of crystallization and its relation to tacticity in “hairy” or longer-branched (n=16 or 18), 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. This will have a wide-ranging impact on everyone who is trying to improve spectral resolution in organic solids.
- Develop a greater understanding of the synthesis process in native lignins in higher plants. A better understanding of lignin structure may aid in designing new delignification processes for paper making or may lead to some utilization of lignin as a chemical feedstock. At present, lignin is basically a high-volume throw-away product in the paper-making industry; its normal role is an energy source via combustion.

Accomplishments

- In iPP, we find the most common stereo and regio (2,1) defects are incorporated into the crystalline regions at concentrations about 48 % and 28 %, respectively, of the overall concentration. The ethylene-comonomer defect has a corresponding concentration level near 40%. The butylene comonomer is found to have a crystal concentration of approximately 52% of the overall concentration. Other 1-alkene defects have lower concentrations.
- We conclude that for the 2 comonomer defects, the 3_1 helix, the conformation of the defect-free iPP chain in all of its crystal forms, is well preserved for the backbone carbons. In contrast, for the stereo (and the probably the regio defect as well) the usual sequence of backbone dihedral angles, e.g. (...g⁺tg⁺tg⁺t...) for the 3_1 helix, is strongly modified by replacing a “tg⁺tg⁺” sequence with an approximate “ttg⁻” sequence or a “g⁺tg⁺t” sequence with an approximate “g⁻ttt” sequence.
- NMR experiments determined, on a 20 nm distance scale, that the density of alkane coverage attached to silica-gel surfaces is not uniform (this most likely means that the long interior channels in the silica gel particles vary in their density of coverage because reactant/product concentrations are probably a function of distance from the particle surfaces during the formation of the layers). Even in the regions of highest coverage density, where carbons are confined to a mainly-trans conformation, there is fast, large-amplitude molecular mobility, mainly consisting of rotation about the chain axis (this reinforces the notion that during HPLC separations, partial penetration of these layers by analyte molecules is possible).

- NMR results confirmed that the α - to γ - ratio in nylon 6 / clay composites was a function of thermal history. We also found that the paramagnetic clays caused a 30 % to 40 % reduction in the proton longitudinal relaxation time, T_1^H .
- A new 300 MHz (7.05 T) spectrometer was received and installed.

Outputs

Publications

D.L. VanderHart, R. G. Alamo, M. R. Nyden, M.H. Kim and L. Mandelkern, *Observation of Resonances Associated with Stereo and Regio Defects in the Crystalline Regions of Isotactic Polypropylene*, *Macromolecules*, submitted.

M. Pursch, D.L. VanderHart, L. C. Sander, X. Gu, T. Nguyen, S.A. Wise and D.A. Gajewski, *C₃₀ Self-Assembled Monolayers on Silica, Titania and Zirconia: HPLC Performance, Atomic Force Microscopy, Ellipsometry and NMR Studies of Molecular Dynamics and Uniformity of Coverage*, *J. Am. Chem. Soc.*, submitted.

D.L. VanderHart, M.R. Nyden, R.G. Alamo and L. Mandelkern, *Incorporation of Stereo, Regio and Comonomer Defects into the Crystalline Regions of Isotactic Polypropylene: Results from NMR, Molecular Dynamics and Chemical Shift Calculations*, Abstracts of the American Chemical Society, National ACS meeting in San Francisco, CA, March, 2000.

Presentations

D.L. VanderHart, *Partitioning of Defect Structures within the Semicrystalline Morphology of Polymers Using Solid State NMR*, Florida Agricultural-Mechanical University, Tallahassee, FL, Feb. 26, 1999.

D.L. VanderHart, R. Alamo, M. Nyden and L. Mandelkern, *Ethylene Defects in Isotactic Polypropylene: Partitioning, Conformation and Chemical Shift Calculations*, Experimental NMR Conference, Orlando FL, Mar. 2, 1999.

D.L. VanderHart, R.G. Alamo, M.R. Nyden and L. Mandelkern, *A Study of Ethyl Residues in Isotactic Polypropylene-co-Ethylene Copolymers: Morphological Partitioning by NMR and Conformational Verification via Chemical Shift Calculations*, 1999 Centennial Meeting of the American Physical Society, Atlanta, GA, Mar. 25, 1999.

D.L. VanderHart, *Spinning Like 60...and for What? Perspectives on Linewidths for ¹³C CPMAS Spectra*, Symposium Honoring the 60th birthday of Dennis Torchia, National Institutes of Health, Bethesda, MD, June 25, 1999.

Development of Standard Reference Materials: Non-Newtonian Fluids for Rheological Measurements

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Objective

The objective is to develop and thoroughly characterize two polymeric fluids (a polymer solution and a polymer melt) that exhibit non-Newtonian behaviors. These fluids are intended to serve as benchmarks 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, demonstrating shear-rate dependent viscosities and normal stresses. Such fluids see wide application in everyday life (injection molding, paints and coatings, food products, etc.), and the ability to accurately measure 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 Materials (SRM 2490 and SRM 2491) will provide a way for comparing the performance of different instruments, as well as providing tools for research into better methods of measuring the rheological properties of polymeric fluids. The new fluids will be certified for the shear-rate dependence of viscosity and first normal stress difference at temperatures of 0 °C, 25 °C and 50 °C. The linear viscoelastic responses will also be certified along with the temperature dependence of the shift factors.

The new polymer solution, SRM 2490, supersedes the previous SRM1490 Nonlinear Fluid Standard, which was composed of a high-molecular-weight polyisobutylene dissolved in normal hexadecane (also called cetane, a name that reflects its presence in whale oil). 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 normal hexadecane, which has a melting point of 18 °C (64 °F). The new solution will consist of polyisobutylene (molecular mass of approximately 10^6 g/mol) dissolved in 2,6,10,14-tetramethylpentadecane (also called pristane, a name that reflects its presence in shark livers). Pristane is a branched alkane of a slightly higher molecular mass than normal hexadecane; the branching prevents crystallization or vitrification down to at least -60 °C, and the higher molecular mass reduces the rate of evaporation of pristane as compared to normal hexadecane.

A polydimethylsiloxane melt is under investigation for SRM 2491. This material was chosen primarily for its excellent safety characteristics and good handling qualities. The properties of this fluid are expected to show less temperature dependence than those of the polymer solution, SRM 2490.

This project will also include a round robin test of the candidate for SRM 2491 involving instrument manufacturers and users in industry and at universities. The round robin provides information regarding the lab-to-lab variability in the measurements; the variability in the measurement of the first normal stress difference is of particular interest. The Statistical Engineering Division at NIST will be involved in evaluating the results of the round robin.

External Collaborations

Cannon Instruments has been contracted to mix and package the polymer solution SRM 2490.

Participants in the round-robin will include instrument manufacturers, industrial users of polymeric materials, and researchers at universities:

Instrument Manufacturers

ATS RheoSystems
Bohlin Instruments
Brookfield Engineering Laboratories
Capillary Rheometer
Goettfert
Haake

Paar Physica
Rheometric Scientific
TA Instruments
TherMold Partners
Vilastic Scientific

Industrial Users

DuPont
Fluid Dynamics

National Starch and Chemical
Procter and Gamble

Universities

David Boger
Ralph Colby
Francis Gadala-Maria
William Graessley
Chris Macosko
Jaye Magda
Gareth McKinley
Skip Rochefort

University of Melbourne
Pennsylvania State University
University of South Carolina
Princeton University
University of Minnesota
University of Utah
Harvard University
Oregon State University

Accomplishments

Cannon Instruments has been contracted to mix and package the polymer solution SRM 2490, which should be available for sale in 2000 through the Standard Reference Materials Program. Some difficulties with resonance in a new model transducer design used in our rheometer were solved; this change will be implemented in other instruments using the new transducer. Industry interest in the new fluid and participation in the round robin has been high.

Outputs

Publications

C.R. Schultheisz and G.B. McKenna, *A Nonlinear Fluid Standard Reference Material: Progress Report*, Proceedings of SPE ANTEC, Volume I, Processing, pp. 1125-1129, New York, New York, May 3-6, 1999, Society of Plastics Engineers.

C.R. Schultheisz and G.B. McKenna, *Thermal Expansion and Its Effect on the Normal Force for a Modified Force Rebalance Transducer*, Proceedings of SPE ANTEC, Volume I, Processing, pp. 1142-1145, New York, New York, May 3-6, 1999, Society of Plastics Engineers.

Presentations

C.R. Schultheisz, *A Nonlinear Fluid Standard Reference Material: Progress Report*, 70th Annual Meeting of the Society of Rheology, Monterey, California, October 4-8, 1998.

C.R. Schultheisz, *Thermal Expansion of the Force Rebalance Transducer in a Rheometric Scientific ARES Rotary Rheometer*, 70th Annual Meeting of the Society of Rheology, Monterey, California, October 4-8, 1998.

C.R. Schultheisz, Non-Newtonian Fluid Standard Reference Materials – SRM 2490 and SRM 2491: Progress Report, 71st Annual Meeting of the Society of Rheology, Madison, Wisconsin, October 18-21, 1999.

Structural Recovery, Physical Aging and Nonlinear Viscoelasticity of Polymer Glasses

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Objectives

The objectives are to use the NIST Torsional Dilatometer to investigate the time scales for volume recovery and physical aging (the evolution of the mechanical response to a deformation) following upward and downward temperature jumps and to investigate viscoelastic modeling of the torque, axial normal force and volume change in response to the torsional deformation.

Technical Description

For an amorphous polymer below its glass transition temperature, rapid temperature changes place the material in a non-equilibrium thermodynamic state, and the glass then evolves (slowly) into thermodynamic 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 has suggested that there may be different time scales for equilibration of the different properties. If that is true, it suggests that the 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 different measurements are typically made on separate samples, leading to questions of homogeneity and equality of thermal histories between samples. The NIST Torsional Dilatometer is an instrument that allows simultaneous measurement of volume recovery and mechanical response to a torsional deformation on the same sample, making direct comparisons possible.

In the torsional stress relaxation experiments used to probe the material, the torsional deformation also induces small volume changes and forces along the axis of the cylinder, which are also recorded by the torsional dilatometer. The axial normal force and volume change in response to the twisting are nonlinear effects. Interestingly, previous work has shown that the relaxation of the volumetric change in response to the torsion is very different from the relaxational behavior of either the torque or the normal force. Whereas the torque and normal force decay monotonically, the volume change associated with the torsion shows a significant non-monotonic decay at lower temperatures. The simultaneous measurements of torque, normal force and volume change have been fit to a nonlinear viscoelastic model which incorporates four time and temperature-dependent modulus functions. The model is based on the series solution for torsion of an elastic, compressible material developed by Murnaghan [Murnaghan, F.D. (1951) *Finite Deformation of an Elastic Solid*. Wiley, New York.].

Accomplishments

Replication of previous measurements on a model epoxy system indicate 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. 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 could be caused by additional curing or by a decrease in the moisture content of the material.

The nonlinear viscoelastic model of the torque, normal force and volume change is reasonably successful, considering the constraints imposed. One constraint is that all four modulus functions are forced to adhere to the same time-temperature shift behavior (thermorheological simplicity). A second constraint is that only a single stretched exponential relaxation function is used for each modulus function.

Outputs

Publications

C.R. Schultheisz and G.B. McKenna, *Investigation of Nonlinear Material Behavior Using Simultaneous Measurements of Volume Recovery and Physical Aging*, Proceedings of Society of Experimental Mechanics Annual Conference on Theoretical, Experimental and Computational Mechanics, pp. 96-99, June 7-9, 1999.

C.R. Schultheisz and G.B. McKenna, *Simultaneous Measurement of Torque, Axial Force and Volume Change in the Torsional Dilatometer and the Implications for Constitutive Modeling*, Proceedings of the Fourth International Conference on Constitutive Laws for Engineering Materials: Experiment, Theory, Computation and Applications, pp. 441-444, July 27-30, 1999.

Presentations

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

C.R. Schultheisz, *Simultaneous Measurement of Torque, Axial Force and Volume change in the Torsional Dilatometer – Experiments and Analysis*, 71st Annual Meeting of the Society of Rheology, Madison, Wisconsin, October 18-21, 1999.

Structural Characterization of Polymers by Small Angle X-Ray Scattering

J. D. Barnes

Objectives

The objectives are (1) to provide the U. S. polymer industry with standardized and reliable tools for characterizing polymer microstructure using scattering methods and (2) to provide resources to other projects within the NIST Polymers Division and to collaborators from academia or industry.

Technical Description

Scattering methods have long been used to characterize the entire spectrum of polymeric materials ranging from semicrystalline fibers, films, and sheets to colloidal particles. These methods suffer from the fact that their results are displayed in reciprocal space while end users of these materials like to visualize the structures in real space. It has sometimes been said that people who ask for a scattering pattern would prefer to see an electron micrograph.

Mathematical methods that can be used to provide real space descriptions of scattering specimens have been developed for isotropic scatterers composed of dispersed particles. The project described here seeks to extend these ideas to dense materials whose microstructure possesses an orientation texture. This requires the acquisition of high quality scattering data under carefully controlled conditions and the application of modern methods of mathematical analysis.

Complicating this work is the absence of standardized formats for data interchange and a poor understanding of the precision and accuracy of scattering instrumentation and analytical methods. This project has provided leadership to international standardization bodies in an effort to improve the performance of SAS measurement systems.

External Collaborations

- Dr. Ty Prosa, Kutztown University, produced software tools for converting data formats.
- Dr. Peter Kofinas, University of Maryland, provided block copolymer samples and facilities for channel die extrusion of semicrystalline polymers.
- Dr. Rainer Kolb, Exxon Corp, provided beam time and assistance with synchrotron x-ray measurements as well as samples for inter-laboratory test program.
- Dr. Anthony Roberts, University of Queensland, Australia, provided computer simulations of semicrystalline polymer microstructures for comparison with scattering data.
- Drs. Dmitri Svergun and Marc Malfois, European Molecular Biology Lab, Hamburg, Germany, provided standard data formats for use in reporting inter-laboratory test results.
- Dr. Sanjeeva Murthy, Allied Signal Corp, supplied PCTFE and Nylon 66 resins.
- Dr. Vladimir Volkov, Institute of Crystallography, Russian Academy of Sciences, participated in preparation of proposal for CRDF funding.

Planned Outcomes

- The inter-laboratory test program initiated this year is expected to produce a more objective assessment of the suitability of SAXS measurements for parameterizing microstructure in polymeric materials.
- Further development of the Temperature Induced Contrast Variation method for characterizing lamellar microstructures is expected to lead to realistic simulations of the real-space character of these structures, which are ubiquitous in semicrystalline polymers.

Accomplishments

- Standardization Activities - Dr. Ty Prosa, working under contract, produced software tools for converting data formats that are commonly encountered at NIST to the core format used by the data reduction tool suite for the SAXS facility.

- In collaboration with the Institute of Crystallography of the Russian Academy of Sciences, a proposal entitled "Computational Tools for Nanoscale Metrology in Biological and Materials Science Using Small-Angle Scattering", was submitted to the Civilian Research and Development Foundation for the Independent States of the Former Soviet Union. This activity, if funded, would build on Russian skills in mathematical physics and computer programming to provide a powerful set of data interpretation tools for SAS measurements.
- The first phase of an inter-laboratory test program to characterize the performance of measurement systems for SAXS was launched with 15 laboratories participating. This effort also serves as a test bed for a draft standard data format for one-dimensional SAS data.
- Microstructure of Semicrystalline Polymers - Additional experiments on scattering from semicrystalline polymers as a function of temperature have firmly established that the contrast variation that arises as a consequence of the difference in thermal expansion between the amorphous and crystalline components of the microstructure is an effective means for removing interfering effects due to other inhomogeneities in the samples. In all systems studied to date the scattering that is attributable to the lamellar crystallites does not exhibit a maximum at $q=0$. The peaks that are commonly observed in the raw scattering cross sections in this range must, therefore, be assigned to other kinds of inhomogeneities in the structures.

Outputs

Publications

J.D. Barnes, *Orientation Texture from Polymeric Materials Using Scattering Methods*, SPE ANTEC Conference proceedings (1999).

J. . Barnes, R. Kolb, K.A. Barnes, A.I. Nakatani and B. Hammouda, *Microstructure Analysis Using Temperature Induced Contrast Variation in Small-Angle Scattering*, Proceedings ACS PMSE Division, **81**, 359 (1999).

S.G. Musselman, T.M. Santosusso, J.D. Barnes and L.H. Sperling, *Domain Structure and Interphase Dimensions in Poly(urethaneurea) Elastomers Using DSC and SAXS*, J. Polym Sci, Pt B, Polymer Physics, **37**, 2586 (1999).

P.L. Drzal, J.D. Barnes, and P. Kofinas, *Path Dependent Microstructure Orientation During Plane Strain Compression of Semicrystalline Block Copolymers*, *Macromolecules*, in press.

J.D. Barnes, R. Kolb, K.A. Barnes, A.I. Nakatani and B. Hammouda, *Microstructure Analysis Using Temperature Induced Contrast Variation in Small-Angle Scattering*, J. Appl. Cryst., in press.

Presentations

J.D. Barnes, *Temperature Induced Contrast Variation in Small-Angle Scattering from Polymers*, APS Centennial Meeting, Atlanta, GA, March 1999.

J.D. Barnes, *Orientation Texture from Polymeric Materials Using Scattering Methods*, SPE ANTEC Conference, New York, NY, May 1999.

J.D. Barnes, *Statistical Assessment of SAS Data Quality*, canSAS II workshop, Brookhaven, NY, May 1999.

J.D. Barnes, R. Kolb, K.A. Barnes, A.I. Nakatani and B. Hammouda, *Microstructure Analysis Using Temperature Induced Contrast Variation in Small-Angle Scattering*, SAS 99, Brookhaven, NY, May 1999.

J.D. Barnes, R. Kolb, K.A. Barnes, A.I. Nakatani and B. Hammouda, *Microstructure Analysis Using Temperature Induced Contrast Variation in Small-Angle Scattering*, ACS National Meeting, New Orleans, LA, August 1999.

Hygrothermal Aging Studies of a Commercial Structural Adhesive

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Objective

The objective is to determine the failure mechanisms of structural adhesives under hygrothermal aging conditions by studying the hygrothermal aging of an epoxy-based, particulate-filled, commercial adhesive and its mechanical performance as an adhesive in joints with different bond thicknesses under wet and dry environments.

Technical Description

Water absorption and exposure to other environments degrade the mechanical strength and physical properties of adhesives. The degradation may be strongly affected by the presence and nature of fillers within the adhesives, because the environmental agent can preferentially attack the interface between resin and fillers. Therefore, knowledge of the behavior of adhesives under adverse conditions is necessary to predict long-term performance. Also, in the study, a cycle of water absorption/desorption/re-absorption in the adhesive is considered to mimic environmental exposure in typical applications. Consequently the absorption of water by adhesives is generally not able to reach saturation level, nor is desorption completed to the fully dry condition. 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 films of adhesive, 300 μm thick, have been produced by curing the epoxy between Teflon slabs in a pressure vessel at 130 °C and 1.38 MPa (200 psi) for 13 h. Differential scanning calorimetry experiments demonstrated that the curing time, which is 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 and 45 °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 by using an analytical balance (OHAUS Analytical Plus, measuring to 0.01 mg), and finally the mass uptake is determined. The standard uncertainty of the mass uptake measurement is about ± 0.03 % to 0.05 % of the reported value. The re-absorption procedure is conducted on specimens that

were completely dried after reaching saturation in the initial sorption procedure. Afterwards, the specimens with zero water content were put back into distilled water baths at the same temperature used in absorption procedure for re-absorption. During the re-absorption procedure, specimens are taken periodically from the bath for water uptake measurements, and then returned to the bath for subsequent mass uptake measurements.

To elucidate chemical changes in adhesive structure due to the water uptake, Fourier transform infrared (FTIR) analysis is used with attenuated total reflection (ATR) technique. The FTIR spectra are recorded from (4000 to 650) cm^{-1} using a Nicolet 550 spectrometer. The ATR accessory used a KRS-5 substrate at 45°.

Planned Outcomes

- To better understand the effect of fillers in the adhesive on the diffusion characteristics and associated behavior, such as T_g depression and swelling.
- Provide scientific background useful to material manufacturers in developing adhesives with better fracture resistance.

Accomplishments

- Identified that the water uptake has a non-Fickian diffusion behavior with a dual sorption mode.
- Successfully applied a time-dependent surface concentration to model the non-Fickian behavior for absorption and re-absorption.
- Confirmed that the water fraction contained in the free volume is the decisive factor for the T_g depression, and the swelling does not alter the apparent free volume of this adhesive.
- Concluded that the depression of T_g proceeds to a definite value, which is independent of the hygrothermal aging history and the final equilibrium water content of the adhesive but dependent on the water fraction contained in the apparent free volume.
- Disproved the free volume concept for predicting the T_g depression, in which the apparent free volume of a solution is the additive sum of the free volumes of its components.

Outputs

Publications

M. Chiang and M. Fernandez-Garcia, *The Effect of Hygrothermal Aging on Swelling and T_g Depression for a Particle-Filled, Epoxy-Based Adhesive*, Proceedings of the 22nd Annual Adhesion Society Meeting, Feb. 1999.

Presentations

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

M. Chiang and M. Fernandez-Garcia, *The Effect of Hygrothermal Aging on Swelling and T_g Depression for a Particle-Filled, Epoxy-Based Adhesive*, The 22nd Annual Adhesion Society Meeting, Pensacola, FL, Feb. 1999.

Measurement Science

...addressing important needs for physical measurements

New Wear Machine Developed

NIST CRADA research with four orthopedic companies recently culminated in the successful development of an accelerated-wear-test machine. Based on this achievement, the companies (Biomet Inc., Johnson & Johnson Professional, Zimmer Inc., and Osteonics Inc.) are now planning to extend their CRADAs with NIST for another two years. To generate improved products, companies need to be able to rapidly acquire information on the phenomena and basic processes involved in the long term wear of new materials, particularly ceramics and ultrahigh molecular weight polyethylenes, under a variety of loading and cyclic conditions. The design objective was to develop a machine that could accelerate wear without compromising the basic wear mechanisms that

With the new machine, accelerated screening of materials can now be completed in as little as a week.



take place in the human body. John Tesk of the Polymers Division and Stephen Hsu of the Ceramics Division, working with Ming Shen, an engineer from the University of Maryland, have developed a new test machine that meets these needs. The machine can evaluate a diverse combination of materials including those involved in either artificial hip or knee joints. The simulated wear rates correctly ranked materials for which test information was available from other sources. In addition, wear debris particles and changes in surface texture, caused by the accelerated wear were also similar to those seen from the wear of actual implants in the body. With the new machine, accelerated screening of materials can now be completed in as little as a week.



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. This program focuses on (1) development of improved dental restorative materials with greater durability, wear resistance and clinical acceptability; (2) development of improved bone fixation materials and (3) evaluation of biomaterials.

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

Although only a minor component of these composites, the interfacial phase that develops from the interaction of a 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 and Craniofacial

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 and Craniofacial 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 the 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

- Validated the newly developed near-infrared (NIR) method for the analysis of conversion in dental polymers for both thin film and bulk polymer sampling techniques using traditional mid-IR spectroscopy. In each case, the NIR approach provided equivalent values of conversion, but with significantly enhanced sensitivity.
- Developed practical synthetic routes to fluorinated dimethacrylate monomers that provide extremely hydrophobic polymers with good mechanical strength properties.
- Demonstrated that pretreatment of enamel and dentin with an aqueous acetone solution of N-phenyliminodiacetic acid yielded improved bonding of a resin-modified glass ionomer cement and a compomer to these substrates.
- Demonstrated that the micro-shear bond test was well suited to assess the effects of regional tooth structure and sectioning orientation on the composite-to-enamel or composite-to-dentin bond strengths. In the case of enamel with a non-priming adhesive system, bond strengths were significantly influenced by the anisotropic nature of this substrate. They were high at the surfaces perpendicular to the enamel prisms and significantly lower at surfaces parallel to the enamel prisms.

Dental Resins Based on Fluorinated Monomers and Oligomers

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Objective

This project is designed to develop practical new fluorinated resins that will provide dental composite restoratives with significantly reduced water sorption and improved durability compared with current dental materials.

Technical Description

A variety of fluorinated dimethacrylate monomers and several corresponding hydrocarbon model monomers were prepared and characterized. Photopolymerization studies were conducted on fluorocarbon and hydrocarbon analog monomers. Water uptake of a broad series of fluorocarbon and hydrocarbon dimethacrylate polymers was measured and compared correlated with the computer predicted values of log P (octanol/water partition coefficient) and HLB (hydrophilic-lipophilic balance). Near-infrared (NIR) was used as one method to quantify water in polymers and the interactions between the water and the polymer network. The NIR can differentiate between free water and that which is hydrogen bonded either with other water or to carbonyl groups in the polymer. The project is reaching a conclusion with only a few long-term studies still underway here and some other on-going studies to be conducted by guest researchers that have returned to their home institutions.

The NIR technique was also developed as a highly versatile and convenient tool for the measurement of conversion in the cross-linked methacrylate polymers. The technique was validated in comparison to traditional mid-IR methods. The use of real-time NIR was explored as a method to directly follow polymerization kinetics and provide the termination and propagation kinetic parameters as a function of conversion. The NIR was also used to study the participation of the individual comonomers during the copolymerization of methacrylate and vinyl ester monomer systems.

The systematic structural variation of functionalized methacrylate monomers was undertaken in an effort to identify new monomers with enhanced reactivity in free radical photopolymerizations. A variety of functional groups were included in the study as were variations in the spacer segment separating the methacrylate and the functional groups. Molecular modeling, real-time FT-IR (Fourier transform infrared), photo-DSC (differential scanning calorimeter) and EPR (electron paramagnetic resonance) were tools used to determine the polymerization reactivities and to aid in the identification of the mechanism by which enhanced reactivity is achieved.

External Collaborations

- 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

A significant improvement in the long-term durability of dental polymers resulting from the use of fluorinated resins is expected to extend the service lifetime of composite restoratives to be more comparable with that of amalgams. The use of fluorinated resins should also decrease the potential for staining discoloration, which is another reason that composite restorations require replacement.

- Because of improvements in the convenience and sensitivity, the NIR measurement methods for the analysis of methacrylate conversion are expected to expand to other research and industrial laboratories. The techniques reported are expected to have benefits beyond the field of dental materials.
- Improvements in monomer reactivity and conversion are sought for dental resins since efforts to reduce the amount of any unpolymerized material are expected to enhance biocompatibility of the dental polymers. In other applications, the ability to reduce initiator concentrations or to cure at higher throughput are desirable traits.

Accomplishments

- *Fluorinated resins and composites:* In comparisons between fluorinated and hydrocarbon methacrylates with similar structures, monomers with fluorinated rigid core groups and additional fluorine-substitution on side chains of limited length provided the optimum balance of mechanical strength properties and hydrophobicity in the polymers. These optimized fluorinated monomers can be combined with conventional dimethacrylates to yield resins with excellent mechanical strength and extremely low water sorption. Compared with hydrocarbon analogs, the fluorinated monomers provided modestly enhanced polymerization rates and equivalent to higher degrees of conversion. An excellent correlation was found between the measured water uptake and the predicted hydrophobicity of hydrocarbon polymers; however, water uptake in the fluorinated polymers varies considerably with the individual monomer structure and is poorly predicted by structure-based calculations. From the NIR studies of hydrocarbon and fluorocarbon polymers, absorbed water was generally in the associated form. With certain hydrophobic fluorinated polymers, the small amount of water that is absorbed exists predominantly as free water rather than associated water. This likely has a positive influence on the improved retention of mechanical properties observed for the fluorinated polymers.
- *Copolymerizations of methacrylate and vinyl ester monomers:* Using NIR analysis, the conversion of the individual monomers in a resin based on urethane dimethacrylate and neoacid vinyl ester were continuously measured during the course of the photo-copolymerization. The methacrylate network formation was very rapid and complete while the vinyl ester participation was primarily in the later stages of the polymerization. The toughness of the hybrid resin system was superior to that of a model all methacrylate resin system based on urethane dimethacrylate and hexyl methacrylate. The toughness of the hybrid resin also exceeded that of the conventional dental resins tested by a factor of two while matching optimized mechanical strength properties.
- *Near-infrared analyses of dental resins:* The near-infrared (NIR) analytical technique was validated against traditional mid-IR techniques used for the measurement of methacrylate conversion. The limits of sample dimensions over which linear response is obtained were determined in a generalized manner that can be applied to other methacrylate resin systems. The use of an internal reference was evaluated and found to be unreliable in the NIR. However, sample thickness, before and after polymerization, was used as a normalization factor that produced excellent agreement between the conversion values obtained by NIR and mid-IR. The studies also demonstrated that the NIR technique was consistently more sensitive than the mid-IR procedures.

- *Polymerization kinetics of functionalized methacrylate monomers*: A series of methacrylate monomers was prepared with a variety of functional groups in the side chain. These included linear carbonate, cyclic carbonate, ester, and urethane groups. The cyclic carbonate functionalized methacrylates produced the most reactive monomers while the urethane-based monomers were also highly reactive and rapidly reached complete conversion. These monomethacrylate monomers were significantly more reactive than HEMA and even more reactive than dimethacrylates, such as triethylene glycol dimethacrylate, which is widely used in dental polymer applications.

Impact

The NIR technique developed for the analysis of methacrylate conversion has become the method of choice in the Dental and Medical Materials Group at NIST. It has also been adopted at the University of Colorado in Chris Bowman's group and it is being evaluated in at least two other laboratories.

Outputs

Publications

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Dental Composites with Improved Interfaces

Joseph M. Antonucci, Walter G. McDonough, Joy P. Dunkers, Martin Y. M. Chiang, Carl R. Schultheisz, and Jianmei He

Objectives

The objectives are to develop polymeric dental composites with enhanced interfacial strength and durability and to design and develop an improved micro-shear test for the study of dental adhesion.

Technical Description

Synthesis of Silylated Resins: Previously, it was demonstrated that simple exchange (transesterification) 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 NMR spectroscopies indicates that a significant number of hydroxyl groups of BIS-GMA, 2,2-bis[p-(2'-hydroxy-3'-methacryloxypropoxy)phenyl]propane, have been converted to silyl ether groups. The extent of the transesterification appears to be amenable to control by proper selection of reactant composition and reaction conditions. This synthesis has been extended to the preparation of silyl derivatives of other hydroxylated monomers such as a monofunctional analog of BIS-GMA. Carboxylated monomers such as PMDM (the diadduct from the condensation reaction of 2-hydroxyethyl methacrylate with pyromellitic acid dianhydride) also can be silylated by this method. 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. A patent based on this technology has been filed.

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 $(\text{RSiO}_{1.5})_x$, 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-methacryloxypropyl-trimethoxysilane were used to synthesize reactive oligomers having basically $(\text{RSiO}_{1.5})_x$ 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 masses (polydispersity = 3.51) and $M_w \cong 7000$ g/mol. 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 suggests that this $(\text{RSiO}_{1.5})_x$ has significant elements of ladder structure with some linear branched and polyhedral structure as well. The methacrylic functionalized oligo-silsesquioxanes are readily polymerized by free radical methods to yield clear, hard cross-linked polymers and are undergoing evaluation as comonomers in dental resin systems and composites.

In an effort to understand the influence of the size and nature of the organic substituent, R, on the molecular structure and properties of $(\text{RSiO}_{1.5})_x$, several types of organosilsesquioxanes have been synthesized and characterized by FT-IR and NMR spectroscopies. MALDI TOF mass spectrometric analysis of some of these new $(\text{RSiO}_{1.5})_x$ indicates that when R is n-decyl rather than n-propyl intramolecular condensation, i.e., cyclization, is favored over intermolecular condensation. Of especial interest has been the synthesis of oligomeric organofluoro-silsesquioxanes from commercially available fluoroorganosilane agents. By co-oligomerization of fluoroorganosilanes with methacrylic silane agents, it appears feasible to synthesize methacrylic organofluorosilsesquioxanes. Because of their high fluorine contents, these types of silsesquioxanes would be expected to have low dielectric constants and water absorption values.

Effect of Silane Coupling Agent and Filler Type on Composite Durability: The aim of this study was to evaluate the effects of the silane coupling agent and filler type on durability of flexural strength of dental composites after water immersion, including an accelerated aqueous aging test. Four experimental photo-polymerizable composites were prepared from a resin system consisting of equal masses of BIS-GMA and TEGDMA. A barium boroaluminosilicate glass powder (mean particle size: 0.94 μm) and a crushed quartz (mean particle size: 0.28 μm) were selected as fillers, and silanized with either 3-methacryloxypropyltrimethoxysilane (MPTMS) or 10-methacryloxydecyl-trimethoxysilane (MDTMS). MDTMS is more hydrophobic than MPTMS because of its greater hydrocarbon content. The composite pastes were formulated with mass fraction of 75 % of the silanized fillers. Twenty (2 x 2 x 25) mm rectangular bar-shaped specimens of each composite were prepared for the three point flexural test. Ten specimens were stored in distilled water at 37 °C for 24 h and ten specimens were additionally stored in distilled water at 90 °C for another 17 d. The mean \pm s. d. of the flexural strength (MPa) are summarized as follows (n = 10):

	Quartz, MPTMS	Quartz, MDTMS	Glass, MPTMS	Glass,MDTMS
37 °C, 1 day	123 \pm 14	126 \pm 11	88 \pm 12	98 \pm 15
90 °C, 17 days	95 \pm 6	109 \pm 8	57 \pm 4	79 \pm 11

The flexural strengths were analyzed using 3-way ANOVA ($P < 0.05$). The main factors (filler type, coupling agent and storage condition) were significant; with respect to the interactions, the interaction between coupling agent and storage condition was significant; however, the interaction between filler type and storage condition was not significant. These results suggest that more hydrophobic coupling agents might improve the durability of dental composites on prolonged exposure to aqueous environments, and parallel the results of a previous microbond study of E-glass fibers that compared MDTMS and MPTMS surface treatments with a similar resin system.

Improvements of a Micro-Shear Test for the Study of Dental Adhesion: The microbond test (MBT), a single fiber shear test, has been adapted to measure the adhesion of dental resins to tooth structure. Whereas the widely used macro shear bond tests typically use a bonding diameter of (2 to 8) mm, the micro shear bonding diameters have been as small as 0.70 mm. The smaller diameters give researchers the ability to test several bonded specimens on one dentin or enamel surface, thus allowing mapping of the mineralized surface. The original instrument design was modified to minimize unwanted alignment changes during testing which was a source of uncertainty in the results. Recently, it was found that the propagation of error in shear strength values from measuring specimen diameters via a video camera and monitor was a combined standard uncertainty of approximately 2.5 MPa. This uncertainty was similar in

magnitude to the total test uncertainty. When the diameters were re-measured using a microscope and camera with greater precision, the propagated error from the diameter measurement was reduced to 0.3 MPA. By increasing the precision in the diameter measurement and minimizing alignment changes, the uncertainty in the test data should now reflect, more closely, the specimen tested, and not the uncertainty in the test method. A source of uncertainty other than that caused by the measurement of the diameter is present. Identifying this source may allow researchers to improve the specimen preparation process and thus, identify the sources of other components of uncertainty. The micro-shear test has recently been utilized to explore the regional effects of enamel structure and the direction of sectioning on bonding to this anisotropic substrate. For a conventional non-priming adhesive system, composite to enamel bond strengths were significantly higher perpendicular to the enamel prisms than they were parallel to the enamel prisms.

Planned Outcomes

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. To further commercialization a patent based on the synthesis of silylated resins has been filed (December 17, 1998).

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 aimed at reducing the uncertainties of the basic 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.
- Dental composites with enhanced durability under aqueous challenge were obtained when the glass filler phase was silanized with a hydrophobic silane coupling agent.
- Facile syntheses of n-decyl, various organofluorosilsesquioxanes and methacrylic organofluorosilsesquioxanes co-oligomers 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 and carboxylated monomers to their silyl derivatives were developed. These novel resins are expected to have self-adhesive properties and be suitable for potential applications in composites, coatings, sealants and adhesives.

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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 systems for bonding to dentin and other dental substrates. An ancillary objective is to elucidate the mechanisms involved in bonding to dentin and enamel with various types of *N*-aryl- α -amino 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 dental surface for subsequent polymerization of photoactivated adhesive resins. With this simple two step bonding protocol strong composite-to-dentin bonds were routinely obtained. However, PIDAA and analogous aryl- α -iminodiacetic acids, although excellent activators-initiators for interfacial polymerization of adhesive resins, do not etch enamel sufficiently to yield similarly strong composite-to-enamel bonds. We have adopted two strategies for developing self-etching primers that would be applicable to both dentin and enamel surfaces. One approach, the subject of a recent joint patent application with the American Dental Association Health Foundation's Paffenbarger Research Center, involves adding small amounts of certain strong acids (e.g. dilute nitric acid) to PIDAA or its analogs. With this approach it is now possible to successfully etch and bond to both dentin and enamel. The second approach involved the synthesis of aryl- α -amino acids based on phosphonic acids. The rationale for this strategy is that the phosphonic acid group would yield self-etching primers of greater acidity and chelation potential than analogous aryl- α -amino acids. The aryl amino phosphonic acids were soluble in aqueous organic solvents, had lower pH values (1.3 to 1.7) than similar PIDAA solutions, and, as shown by scanning electron microscopy, effectively etched both dentin and enamel. Unfortunately, composite bond strengths to these two substrates were quite low, probably because the presence of the phosphonic acids groups rather than the carboxylic acids groups significantly inhibits the activating-initiating capacity of the aryl- α -amino acid. A possible strategy to overcome this deficiency of aryl- α -amino phosphonic acids is to introduce into their structure a polymerizable functional group such as a methacrylate group.

In a related study, it was shown that PIDAA and *N*-phenylglycine were highly effective in mediating the bonding of a resin modified glass ionomer cement and a compomer to both enamel and dentin. Compomers are composites that contain acidic monomers in the resin matrix and an ion-leachable glass in the filler phase, and as such can be regarded as a hybrid version of composites and glass ionomer cements. The ability to bond effectively to enamel probably was due to the acidic nature of the cement and compomer. In this study an improved micro-shear test

was used in assessing bond strength to dentin and enamel. In addition, it was demonstrated that *N*-arylglycines such as *N*-phenylglycine and their sodium salts are effective in the stabilization of demineralized dentin and in promoting bonding to etched dentin. Interestingly, with nitric acid as a conditioner, the salt forms of the *N*-aryl- α -amino acids yielded higher composite-to-dentin bond strengths compared to the acid form of these primers. Finally, it was shown that different types of acid-base dental cements (zinc phosphate, zinc polycarboxylate and glass ionomer) demineralize dentin to different extents resulting in hybrid layers of varying morphologies. In this study both scanning electron microscopy and confocal laser scanning microscopy were used to characterize the cement-dentin interfaces. The surface analytical results obtained by these two methods were generally comparable, but the non-destructive nature of confocal laser scanning microscopy has obvious advantages.

External Collaborations

- Dr. Eichmiller and Dr. G.E. Schumacher, American Dental Association Health Foundation (ADAHF) Paffenbarger Research Center are assisting in the evaluation of new adhesive systems for dentin and enamel.
- Drs. T. Nikaido and Y. Shimada from the Tokyo Medical and Dental University collaborated in the evaluation of new dental adhesive systems and mechanism studies.
- Dr. Chetan A. Khatri, University of Massachusetts, Amherst, MA is actively advancing the synthetic aspects of the adhesion studies.

Accomplishments

N-Phenyliminodiacetic acid (PIDAA), modified with small amounts of strong acids such as nitric acid, were shown to produce a dental primer with the ability to etch effectively and mediate bonding to both dentin and enamel. PIDAA also was shown to be an effective self-etching primer for glass ionomer cements and compomers. Several aryl- α -amino phosphonic acids were synthesized, characterized and evaluated for their efficacy as self-etching primers in mediating bonding to tooth structure. Modification of these novel amino phosphonic acids by introduction of polymerizable vinyl groups has potential for yielding self-etching coupling agents for mineralized tissues.

Outputs

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

Joseph Antonucci

Objective

The objective is to develop improved polymeric composites with remineralization potential using various resin systems and 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 BisGMA based resins and stabilized ACP powders gave sustained release of calcium and phosphate ions over extended time periods without serious deterioration in mechanical strength. Also, in an *in vitro* study it was shown that an ACP composite effectively remineralized caries-like lesions in extracted bovine enamel.

To assess the effects of the resin matrix and the type of ACP filler on the release of calcium and phosphate ions from ACP/methacrylate composites the following study was designed. Three types of visible light curable resins were prepared: BTHZ resin consisting of BisGMA, triethyleneglycol dimethacrylate (TEGDMA), 2-hydroxyethyl methacrylate (HEMA) and zirconyl dimethacrylate (ZrM); TP resin consisting of equal mass fractions TEGDMA and pyromellitic glycerol dimethacrylate (PMGDM); UH resins consisting of urethane dimethacrylate (UDMA) plus HEMA at three mass fractions (0 %, 6.6 % and 13.2 %, designated as U0H, U66H and U132H, respectively). A total of five photoactivated resins: BTHZ, TP, U0H, U66H and U132H were evaluated for the effects of chemical structure and compositional variations on the release of mineral ions from ACP-filled composites. Three types of ACP fillers

were employed: unhybridized, pyrophosphate-stabilized ACP (Pyro-ACP), silica hybridized ACP (TEOS-ACP) and zirconia hybridized ACP (Zr-ACP) (the later two ACPs were hybridized with tetraethoxysilane (TEOS) and zirconyl chloride (Zr), respectively). Elevated calcium and phosphate ion concentrations were sustained in the BTHZ and all the UH resins. However, over time the TP composites failed to maintain a favorable remineralization potential due to the resin retention of released calcium via ion binding with the carboxylic acid groups of PMGDMA. The ranking according to remineralizing ability for Pyro-ACP composites was: (BTHZ, U132H) > TP > (U0H, U66H). Composites based on the TEOS- or Zr-ACP, and U0H, U66H, or U132H had significantly higher ($p < 0.0013$) remineralization potential compared to similarly prepared Pyro-ACP/ UH composites, as determined by Ca and PO_4 release profiles measured by atomic absorption and UV/VIS spectroscopy, respectively. By contrast, hybridization of the fillers had no effect on the ion release from BTHZ composites. However, internal conversion of ACP to HAP was significantly reduced or almost completely inhibited in both the BTHZ and UH/hybridized ACP composites.

External Collaborations

Dr. E.D. Eanes of NIDCR and Drs. F.C. Eichmiller, G.E. Schumacher, and D. Skrtic of the ADAHF- Paffenbarger Research Center are actively assisting in the further development and evaluation of bioactive polymeric composites utilizing ACP as a remineralizing filler.

Accomplishments

It has been demonstrated that the remineralizing properties of ACP-based polymeric composites can be affected by both the chemical structure and composition of the resin matrix and by hybridization of the ACP fillers. High concentrations of the carboxylic acid monomer PMGDMA in the matrix resin phase of ACP composites were shown to adversely affect calcium ion release due to ion binding. Hybridization of ACP fillers with glass-forming agents such as tetraethoxysilane or zirconyl chloride stabilizes ACP against intra-composite conversion to HAP.

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Cure Monitoring of Dental and Medical Resins by Fluorescence Spectroscopy

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Objectives

The objectives are to monitor the cure of resins by fluorescence spectroscopy, to establish correlations between fluorescence properties and performance properties for curing resins, and to transition NIST expertise 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 is 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. Consequently, the change in the peak fluorescence wavelength of the probe is a measure of the degree of cure of the bonding resin. Once a correlation is established between the change in the peak fluorescence wavelength and the degree of cure determined by FTIR, an absolute value for the degree of cure can be obtained from the change in the peak fluorescence wavelength. Alternatively, the measured value of the peak fluorescence wavelength can be used to compare and maintain the degree of cure during the application of the bonding resin.

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 by which the setting of a particular sample is determined. 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.

A bone cement is made by mixing its liquid component [volume fraction of 97 % methyl methacrylate and 3 % *N, N*- dimethyl- *p*-toluidine] and its solid component [mass fraction of 15 % poly(methyl methacrylate), 75% styrene-methyl methacrylate copolymer, 10 % BaSO₄, and 2 % benzoyl peroxide], often at a mass ratio of 2:1, powder: liquid. After the mixing, the viscosity of the bone cement increases because of the dissolution of polymers in the liquid and the polymerization of methyl methacrylate. In this method, a trace amount of the wavelength-shift fluorescent probe is dissolved in the liquid component, and the fluorescence spectrum of the probe was recorded as a function of cure time. Because the polarity and the mobility of the bone cement change during the cure, the peak fluorescence wavelength of the fluorescent probe decreases with the cure time. Consequently, the change in the peak fluorescence wavelength of the probe is a measure of the viscosity, as well as the degree of cure, of the bone cement. Once a correlation is established between the decrease in the peak fluorescence wavelength and the viscosity, an absolute value for the viscosity can be obtained from the change in the peak fluorescence wavelength.

External Collaborations

Dr. Deborah G. Sauder, Hood College, Frederick, MD, Dr. Yasuhiro Hotta, Showa University, Tokyo, Japan and Dr. Koichi Komatsu, Nihon University, School of Dentistry at Matsudo, Chiba, Japan, have actively advanced 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

- *Cure Monitoring of Bonding Resin*: 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 found to be 716 nm for the uncured resin and 670 nm for the fully cured resin, when the excitation wavelength was 520 nm. The ratio of the fluorescence intensities at 670 nm and 716 nm increased with the degree of conversion (DC) of the resin, and was a piecewise-linear function of DC, with a glass transition occurring near 60 % DC. The Vickers hardness of the resin could not be measured when the DC was less 60 %, but varied linearly with the DC beyond the transition near 60 %.
- *Cure Monitoring of Bone Cement*: A non-toxic fluorescent probe was found to be suitable for cure monitoring of a bone cement, since its peak fluorescence wavelength decreased by 100 nm during the first 10 min of cure.

Outputs

Publications

F.W. Wang and D.G. Sauder, *Examination of Fluorescent Molecules as In Situ Probes of Polymerization Reactions*, In: 3rd International Symposium on Bio-related Polymers, Polymeric Drugs and Drug Delivery Systems, Ottenbrite, R., Ed. Washington, DC: American Chemical Society (1999).

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Presentations

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Support for the Biomaterials Integrated Products Industries (BIPI's)

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Objectives

The objectives are to manage Orthopaedic CRADA consortium on accelerated testing of new orthopaedic joint materials, liaison with FDA and NIH, American Academy of Orthopaedic Surgeons and Biomaterials Integrated Products Industry (BIPI), assess NIST ability to help meet technical needs of BIPI's and explore new CRADA partnerships via workshops, industrial visits and conferences/ meetings participation. In addition, personal research is conducted for improved materials for health care delivery and to provide greater visibility of NIST to BIPIs. Expected outputs include: test methods, standards/reference materials and materials properties useful for quality assurance, good manufacturing practices, product improvement, and submissions to national and international regulatory bodies/agencies.

Technical Description

Objectives are attained through technical research in support of issues identified by industry as important, by holding workshops to help identify issues, by participation in the activities of standards organizations and meetings of scientific organizations, and by holding leadership positions related to standards and scientific organizations. Some personal research is also conducted to assist in providing visibility to the biofunctional materials industry.

External Collaborations

- Biomet Inc. (Warsaw IN.), Depuy- Johnson & Johnson (Warsaw, IN.), Stryker Howmmedica-Osteonics Inc. (Allendale, NJ.), and Zimmer, Inc., (Warsaw, IN.), are members of the Orthopedic CRADA Consortium, for investigations into the effects of wear processes on the structures and properties of orthopedic implant joint bearing surfaces.
- Steve Li, Hospital for Special Surgery (HSS) has provided valuable historical input on UHMWPE reference bars that the HSS supplied to the industry over the previous immediate past four years.
- Poly Hi Solidur (Fort Wayne, IN.) will contribute materials (market value = \$45,000) toward NIST development of UHMWPE reference bars.
- American Association of Orthopedic Surgeons, Hip and Knee Society for release of public information of NIST CRADA Research.

Planned Outcomes

One goal is to develop basic information on the structure and properties of orthopedic joint bearing materials, as influenced by wear-load conditions that will be useful to the NIST Orthopedic CRADA Research Consortium for improving orthopedic joint implants. This includes the development of test methods that will be useful to industry and in the development of national and international standards for medical materials and devices. Related to the latter, another goal with impact is the development of reference materials that will be useful for biofunctional materials research, product development, and for use in international standards. It is also anticipated that research that develops the fundamental science and technology of materials that have potential for ameliorating known, published deficiencies in biomedical applications will help to lead to improved products and health care delivery.

Accomplishments

- Quarterly meetings were held with the Orthopedic CRADA Research Consortium, reports issued, and issues defined. Accelerated measurement technology was further developed and structure/wear property measurements and development of material wear maps is in progress.

Papers on wear testing, molecular orientation, and orientation technology were presented to industry and a unique variable in analysis of wear was developed.

- The first known measurements of molecular orientation of Medical Grade Ultra High Molecular Weight Polyethylene (UHMWPE) wear surfaces were made using polarized soft x-ray absorption. These kinds of measurements are essential for understanding the wear processes in artificial orthopedic joints that employ UHMWPE and, hence, should help lead to improved orthopedic implants.
- Workshops on Reference Materials (RMs) and Mechanical Heart Valves were held. The RM workshop identified the need for UHMWPE Reference Material for Orthopedic Applications. As a result of the NIST workshop on Reference Materials, work was initiated on development of UHMWPE Reference Material. This material will be used by the orthopedic industry and for round-robin testing in ASTM committees. Highlights of the Reference Materials workshop appeared in the Biomaterials Forum and an extended text is in press for J. Biomed. Mats. Res.
- The Orthopedic CRADA Consortium Research was featured in articles appearing in USA Today and in Orthopedics Today.
- Dr. John Tesk received the ASTM Committee F04 MOSES Award "for many years of outstanding service and participation in the work of the committee".

Outputs

Publications

J.A. Tesk, Christian E. Johnson, Stephen Hsu, Drago Skrtic, and Ming Tung, *Amorphous Alloys Containing Cobalt for Biomedical Applications*, Program Abstract for ASTM Symposium on Cobalt Based Alloys for Biomedical Applications, November 3-4, The Norfolk Waterside Marriott, Norfolk VA., 1998.

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H-W. Fang, M.C. Shen, U.Cho, J.Tesk, A. Christou, and S.M.Hsu, *Generation of Different UHMWPE Particle Shape by Wear through Surface Texturing*, 25th Annual meeting of the Society for Biomaterials, Providence RI, April 30, 1999.

Reference Materials

...addressing important needs for standards

NIST Workshop Examines Needs for Reference Biomaterials.

Priorities for reference biomaterials (RBMs) were established at a recent workshop held at NIST. The priorities strongly reflect the current status of materials selections within three applications of biomaterials - orthopedic, cardiovascular and tissue engineered products. A high priority RBM for the orthopedic industry was identified as particulate Ultra High Molecular Weight Polyethylene (UHMWPE) with size, shape, and morphology typical of wear debris found around orthopedic implants. UHMWPE is widely used in artificial joints, but demands for longer use life and higher performance drive the need for improvements in this material.



The cardiovascular industry representatives expressed support for the current reference material development efforts, but were also concerned about the need to identify more clearly the important properties and to formulate a clear rationale for additional RBMs. They also expressed a variety of opinions on the needs for additional RBMs for cardiovascular materials, reflecting the diversity of materials under consideration. The newly emerging tissue-engineering arena is at an embryonic state relative to its requirements for specific RBMs, and so there was no consensus on needs beyond a definite interest in reference tissue cell-lines. A commercial source for providing standard reference cells was identified in the discussions.



... impetus for such materials arises from defined needs as they appear in national/international consensus standards.

The workshop was sponsored by NIST, with cooperation of the NIH, FDA, and the Society for Biomaterials. About 40 participants registered for the workshop, with 16 representatives from industry. The workshop was motivated by ongoing discussions on RBMs at meetings of the National Institutes of Health (NIH), The American Society for Testing and Materials, and the Society for Biomaterials. There also has been a recently signed agreement (1997) between the NIH, NIST and the Food and Drug Administration (FDA) for cooperation on the development of needed RBMs.

The workshop featured speakers from the NIH, FDA, and the Orthopedic, Cardiovascular and emerging Tissue Engineered Products industries. Although the workshop was able to identify a few specific needs, including a stable, non-biased sources for RBMs, it also clearly demonstrated the importance of a continuing dialog to identify new RBMs, with the impetus for such materials seen as arising from defined needs as they appear in national/international consensus standards.

Measurement Science

... addressing important needs in physical measurements

NIST Workshop Identifies Needs for Heart Valve Research

A workshop hosted by NIST on December 2, 1998 identified three issues that heart valve manufacturers viewed as critical for more rapid introduction of improved prostheses: 1) measurement of residual stresses in mechanical heart valves, particularly as these stresses affect long term reliability, 2) accelerated testing for wear and durability and 3) in-vitro imaging of blood flow for both mechanical and bioprosthetic valves. The meeting was in response to the recommendations of an earlier workshop, held at NIST on February 23, 1998, to evaluate the current measurement methods and explore the possibility of cooperative research. Hence, the December 2 meeting emphasized reviews and critiques of the current methods employed for reliability analysis, accelerated test methods for wear and durability of mechanical heart valves, fluid mechanics analyses and imaging of fluid flow. Speakers from industry, the Food and Drug Administration (FDA), NIST,



The workshop has led to initial investigations on residual stress measurement and flaw detection.

and the National Institutes of Health (NIH) presented critiques and NIST led the discussions. Some issues common to both mechanical and bioprosthetic valves were raised by participants. The workshop has led to initial investigations within MSEL and the Automated Production Technology Division of MEL, on residual stress measurement and flaw detection, and ties have been established with the Fluid Mechanics Group of CSTL. The workshop also identified a strong interest in establishing a relationship between industry members, with NIST acting as the unbiased coordinator. The purpose would be to hold regular industry forums on industry-wide issues, with the possibility of future cooperative work as NIST capabilities for providing technical assistance become identified. The workshop was planned with the cooperation of the NIH and the FDA.

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 - o Light scattering and optical microscopy under shear
 - o Computer simulations
 - o Morphology of immiscible polymer blends under shear
 - o Phase separation near patterned surfaces

- Kim, Ginam⁺
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 - o Structure and morphology of polymers
 - o Transmission and scanning electron microscopy
 - o Cryo-electron microscopy

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Kolb, Rainer ⁺ rkolb@erenj.com	<ul style="list-style-type: none"> o X-ray reflectivity and scattering o Neutron reflectivity o Polymer crystallization
Komatsu, Koichi ⁺	<ul style="list-style-type: none"> o Fluorescence spectroscopy o Dental composites o Dentin adhesives
Kryder, Samuel J. ⁺	<ul style="list-style-type: none"> o Electronic circuit design and construction o Electronic troubleshooting and repair
Kueh, Sylvia ⁺	<ul style="list-style-type: none"> o Liquid molding o Optical fiber sensors
Lenhart, Joseph L. ⁺	<ul style="list-style-type: none"> o Sensors o Interphase structure
Li, Bizhong ⁺	<ul style="list-style-type: none"> o Polymer processing o Polymer blends o Polymer-clay processing
Liao, Kin ⁺ kin.liao@nist.gov	<ul style="list-style-type: none"> o Fatigue, damage, and NDE of composites o Environmental durability of composites o Behavior of ceramic composites
Liao, Nam S. [*] nam.liao@nist.gov	<ul style="list-style-type: none"> o Synthesis and testing of dental adhesives o Internal stress of compositon due to polymerization
Lin, Eric K. eric.lin@nist.gov	<ul style="list-style-type: none"> o Statistical mechanics o X-ray and neutron reflectivity
Liu, D.-W. da-wei.liu@nist.gov	<ul style="list-style-type: none"> o Polymer synthesis o Polymer characterization - thermal gravimetric analysis, differential scanning calorimetry, gel permeation chromatography, infrared spectroscopy, nuclear magnetic resonance, scanning electron microscopy, atomic force microscopy
Lynn, Gary W. ⁺ gary.lynn@nist.gov	<ul style="list-style-type: none"> o X-ray and neutron reflectivity o Optical microscopy
Mager, Carie ⁺ carie.mager@nist.gov	<ul style="list-style-type: none"> o Toughening Bioceramics o Fracture mechanics
Markovic, Milenko [*]	<ul style="list-style-type: none"> o Calcium phosphate chemistry

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milenko.markovic@nist.gov	<ul style="list-style-type: none"> o Biomineralization (normal and pathological) o Crystal growth and dissolution kinetics o Heterogeneous equilibria
Mathew, Mathai* mathai.mathew@nist.gov	<ul style="list-style-type: none"> o Crystallography o Calcium phosphate compounds
Maurey, John M.+ john.maurey@nist.gov	<ul style="list-style-type: none"> o Ultracentrifugation o Rayleigh light scattering o Osmometry o Densimetry o Refractometry o Intrinsic viscosity
McDonough, Walter G. walter.mcdonough@nist.gov	<ul style="list-style-type: none"> o Processing and cure monitoring polymer composites o Failure and fracture of polymers o Polymer composite interfaces
McKenna, Gregory B.+ greg.mckenna@coe.ttu.edu	<ul style="list-style-type: none"> o Failure, yield and fracture of polymers o Nonlinear viscoelasticity o Molecular rheology o Physics of polymer glasses o Rubber thermodynamics and mechanics o Mechanics of composites
Meredith, J. Carson james.meredith@nist.gov	<ul style="list-style-type: none"> o Biodegradable polymer blends o Phase-separation and wetting properties of thin films o Combinatorial methods for coatings
Migler, Kalman kalman.migler@nist.gov	<ul style="list-style-type: none"> 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 o Polymer slippage
Mischenko, Mykola I. + mykola.mischenko@nist.gov	<ul style="list-style-type: none"> o Neutron and x-ray scattering o Dendrimers o Polyelectrolytes o Physical gels
Miyagi, Zenichi+ zenichi.miyagi@nist.gov	<ul style="list-style-type: none"> o Adhesion o Polymer mechanics o Experimental design
Mopsik, Frederick L. +	<ul style="list-style-type: none"> o Dielectric measurements and behavior

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frederick.mopsik@nist.gov

- o Automated measurement design
- o Computerized data analysis and programming
- o Electrical properties of polymers

Mueller, Herbert J. *
herb.mueller@nist.gov

- o Dental Biomaterials
- o Interfacial interactions via electrochemical and infrared spectroscopies
- 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 acquisition
- o Patent process (in electronic packaging)

Park, Joon-Yang⁺
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- 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 Evanescent wave optical fiber fluorescence monitoring
- o Control of the liquid molding process

Parry, Edward E. *
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- o Dental appliance and crown and bridges fabrication
- o Machine shop applications

Pfeiffer, Carmen⁺

- o Dental resins

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carmen.pfeiffer@nist.gov	o Monomer synthesis
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 ⁺ pochan@udel.edu	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 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
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
Schmidt, Gudrun ⁺	o Polymer blends o Liquid crystalline polymers o Polymer-clay interaction o Light and neutron scattering
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
Simon, Carl G., Jr.	o Biocompatibility

⁺Guest Scientist

^{*}Research Associate

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- o Cytotoxicity
- o Signaling in human platelets
- o Bone marrow cell lineage/trafficking

Skrtic, Drago*
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- o Calcium phosphates as dental materials
- o Liposome studies

Skordos, Alexandros⁺

- o Dielectric sensors
- o Composite processing

Snyder, Chad
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- o Polymer crystallization
- o WAXD and SAXS of polymeric materials
- o Thermal expansion measurements
- o Thermal analysis of polymers

Stansbury, Jeffrey W.
jeffrey.stansbury@nist.gov

- o Synthetic chemistry
- o Polymers and polymer composites
- o Polymerization of expanding monomers
- o Fluorinated polymers
- o Polymerization kinetics

Starr, Francis
francis.starr@nist.gov

- o Dynamics of filled polymers
- o Slow dynamics in soft condensed matter
- o Molecular dynamics simulations and parallel computing

Takagi, Shozo*
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- o Crystallography
- o X-ray diffraction
- o Calcium phosphate biomaterials
- o Topical fluoridation
- o De- and remineralization

Tanaka, Jiro⁺
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- o Dental composites
- o IR & NIR spectroscopies
- o Mechanical properties

Tesk, John A.
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- 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

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Tung, Ming S.*
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- o Chemistry of calcium phosphate compounds
- o Remineralization studies
- o Standard reference materials

VanderHart, David L.
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- 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

Viers, Brent
brent.viers@nist.gov

- o Polymer gels
- o Rubber elasticity
- o Inorganic organic hybrids
- o Dendrimer networks
- o Polymer stars
- o Hydrogels

Vogel, Gerald L.*
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- o Dental plaque chemistry, chemistry of calcium phosphates
- o Microanalytical techniques

Wallace, William E.
william.wallace@nist.gov

- o Surface and interface behavior
- o Ion beam and electron spectroscopies
- o X-ray and neutron reflectivity
- o MALDI mass spectrometry

Wang, Francis W.
francis.wang@nist.gov

- o Photophysics and photochemistry of polymers
- o Fluorescence spectroscopy
- o Cure monitoring of polymerization
- o Tissue engineering

White, Christopher
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- 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

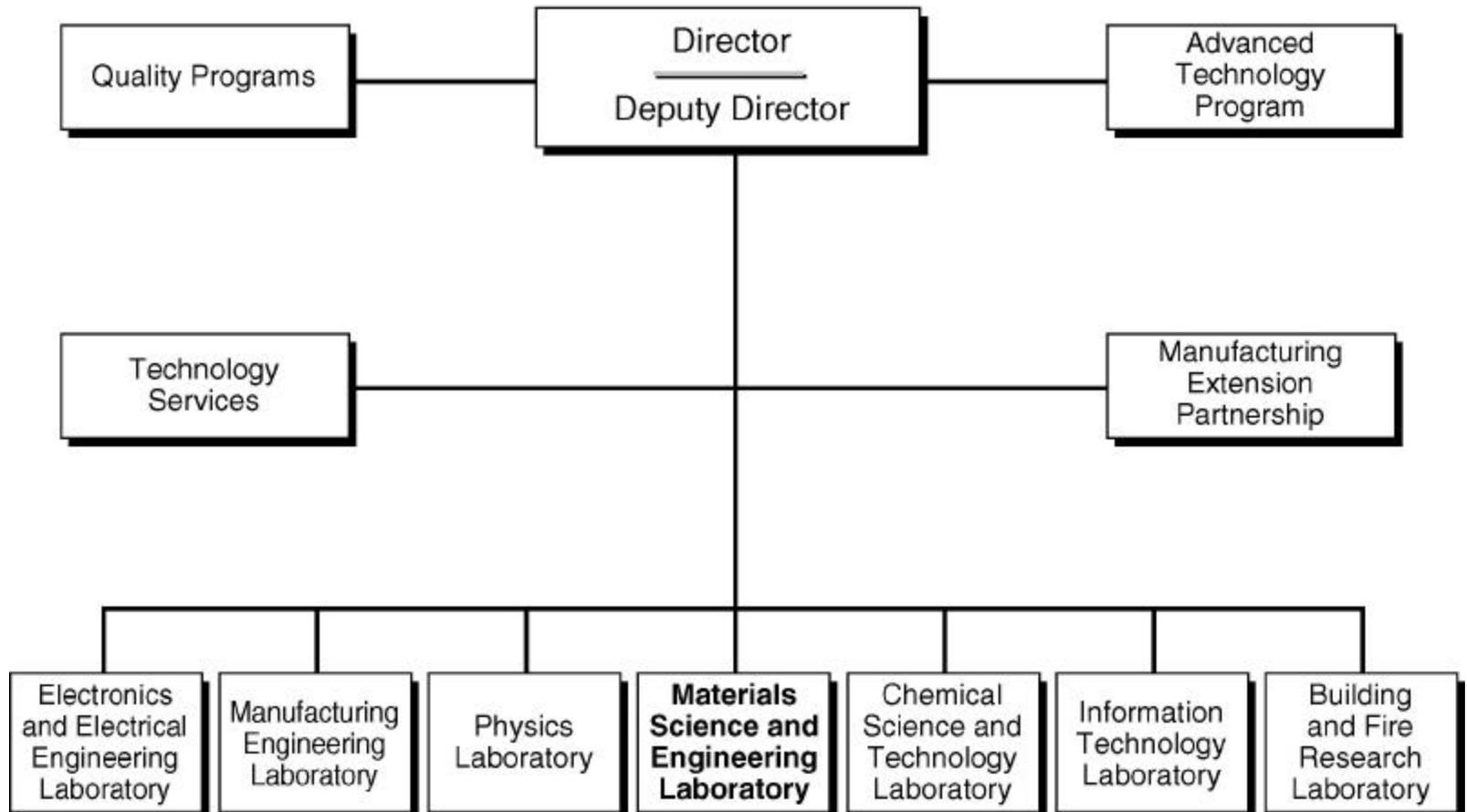
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*Research Associate

- o Mechanical behavior of polymers and composites
 - o Polymer surfaces and interfaces
- Xie, Baosheng⁺
- o Testing micro tensile and micro-shear bond strength
- 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⁺
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- o Dynamic light scattering
 - o Polyelectrolytes
 - o Small angle neutron scattering
- 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

National Institute of Standards and Technology

Organizational Chart



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ENGINEERING LABORATORY**

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D.E. Hall, Deputy Director

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