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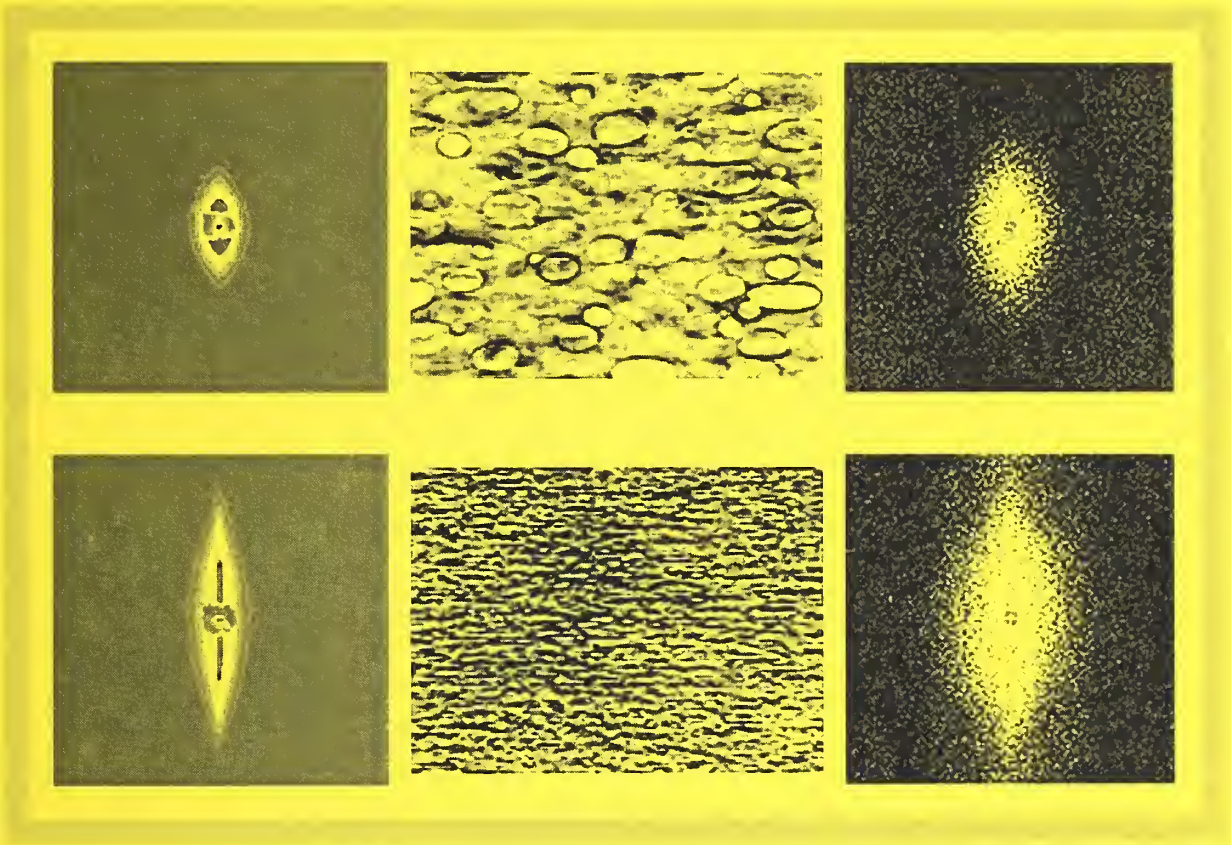
Materials Science and Engineering Laboratory

POLYMERS



NISTIR 5749
U.S. Department of Commerce
Technology Administration
National Institute of Standards
and Technology

Technical Activities 1995

Polymers Division

Light scattering, phase contrast optical microscopy and Fourier transforms of the optical images (left to right) for a phase separated blend of polystyrene and polybutadiene showing the deformation and breakup of polystyrene droplets under shear rates of 2 s-1 (top) and 20 s-1 (bottom). These studies allow characterization of morphology in multi-phase polymer blends to optimize flow and temperature conditions for process design.

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

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

INTRODUCTION

Leslie E. Smith, Chief
Bruno M. Fanconi, Deputy Chief

This report gives a description of the principal technical activities of the Polymers Division during the 1995 fiscal year. It is organized according to the program structure by which we plan our work. This organization of the report provides the reader with the management context in which we view individual projects in order to make our motivation for the work clearer. We also hope this will encourage our customers to offer comments and advice on ways we can be more effective in our work.

The Polymers Division is responsible for providing standards, measurement methods, and fundamental concepts of polymer science to assist those U. S. industries that produce or use synthetic polymers in essential parts of their business. We plan our programs primarily to develop improved measurement capability for broad sectors of the industrial community. We rely heavily on advice from industrial and technical communities to set our priorities. This advice stems both from formal workshops, some of which are briefly described in this report, and from extensive informal visits to and from our customers.

In all these programs, collaboration with others continues to be the most effective way to develop and transfer technology. In particular, industry collaborators who know both their business and technical needs are vital to planning and execution. Many of these interactions are briefly described in the section on Industrial and Academic Interactions in the Appendix to this report.

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

For example, workshops and discussions with electronics manufacturers have helped defined our program in electronic packaging. As a result, we have concentrated on the role of materials in electronic packaging and work to improve the measurement methods that provide the critical materials data used to evaluate process and product quality.

Fiber reinforced polymer composites have tremendous unrealized potential in industries beyond the aerospace industry if manufacturing costs can be reduced and production rates increased. We continue to work with the automobile manufacturers and their suppliers on measurement and simulation problems that can aid in the use of composite materials in that industry. We are also exploring the needs and opportunities for composites in other industry sectors such as off shore oil production.

Our most comprehensive program currently aims at the needs of the producers and processors of polymer blends. Here we hope to provide the measurement methods and fundamental understanding that will help producers develop new blend systems more quickly. Resin producers are primarily large, sophisticated companies that want to produce higher value-added materials that also have significant potential volume markets. They need, and can use to substantial effect, very general and fundamental concepts of polymer behavior that affect broad classes of materials.

The Division's program on polymer blends is designed specifically to respond to such needs by providing the scientific basis for phase decomposition after mixing, the effect of compatibilizing additives, and the morphology of blends. These concepts can be used by polymer scientists and engineers to design new blend materials and processes more efficiently. We are working with a consortium of interested companies to help guide our research efforts and to transfer our technology more quickly and efficiently to the companies ready to implement it. We continue to seek more participation in this activity.

The blends program aims to provide support also to the formulators and processors of blends by developing sensors and models of mixing phenomena that can be applied to process control. We have begun by adapting advanced measurement techniques involving microscopy and light scattering to practical mixers and extruders.

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

Electronics Packaging and Interconnects Program

- An improved technique for determining the coefficient of thermal expansion of polymer thin films based upon a capacitance measurement has been demonstrated.

- X-ray reflectivity measurements reveal that polymers which have a favorable interaction energy with a solid substrate can experience an elevation of the glass transition temperature of as much as 70°C in a thin layer (ca. 400 Å) adjacent to the interface.

- An improved method for determining the density of ultra-thin films on a substrate utilizing X-ray reflectivity at multiple wavelengths has been developed.

- Hygroscopic expansion coefficients of ultra-thin polyimide films on silicon have been determined from X-ray reflectivity measurements.

Polymer Blends

- Phase diagrams were determined for a pure blend of polystyrene and polybutadiene and also with block copolymers added over a wide composition range. Measurements on the effects

of added diblock copolymer in a blend demonstrate suppression of the phase separation temperature.

- The formation of a copolymer layer by transesterification in the interfacial region surrounding phase separated polycarbonate and polymethyl methacrylate rich droplets have been characterized in thin film blends by a combination of neutron reflectivity and atomic force microscopy.

- It was demonstrated that dielectric relaxation spectroscopy can be used to characterize different phase morphologies resulting from transesterification in reactive polymer blends as a complement to previous neutron scattering studies. Conversely, polymer blends with different phase morphology can provide various dielectric characteristics which could be important for electronic packaging applications.

- Fluorescence band broadening in perylene has been used for fluorescence based temperature measurements up to 290°C. The technique was demonstrated in real-time during extrusion of polycarbonate doped with perylene.

- In-line, real-time temperature measurements have been made during extrusion for carboset resin (a poly(methyl methacrylate) copolymer) doped with bis-pyrene propane (BPP) and polycarbonate doped with perylene.

- Pressure coefficients have been obtained for the temperature dependence of both BPP and perylene using an IR radiometer as a reference.

- Temperature profiles in a laboratory experiment have been measured using an optical technique.

- In-line, real-time operation of the polarizing optics sensor for measuring fluorescence anisotropy was demonstrated.

- In collaboration with Dynisco a pressure/optical sensor which can be used to measure fluorescence and pressure simultaneously was developed.

- The NIST-developed temperature measurement technologies based on fluorescence are being adopted by consortium members. 3M is using the technology in process modeling laboratories and Du Pont is working with NIST on the extensions to temperature profile measurements.

Polymer Matrix Composites Program

- Statistical methods have been used in a novel technique to predict the permeability for realistic materials which have significant variations in their microstructure.

- A 2.5D model has been developed to simulate mold filling for the "no-gap" case in injection/compression liquid composite molding. A cooperative effort with the Automotive Composites Consortium was established to apply this model in their truck box program.

- A cure sensor and process control system were developed in cooperation with industry and demonstrated in the fabrication of polymer composite plaques. Northrop-Grumman has transferred the technology to their laboratory where it will be implemented on prototype production equipment as part of an ARPA program.

- A laboratory scale system designed to simulate structural reaction injection molding has been developed and used to fabricate urethane test samples for the measurement of durability.

- The role of bonding between a coupling agent and glass in determining the strength and durability of single-fiber-composite specimens was quantified for a model glass-epoxy system.

- Stresses produced by swelling of the matrix material in single fiber composite samples do not play a dominant role in the moisture induced degradation of the fiber-matrix interface.

- A high refractive index fiber was used to demonstrate for the first time that a single fiber can be employed for cure monitoring with both fluorescence and near infra-red spectroscopies. The fluorescence work received a Best Paper award at the 1995 SPE/ANTEC Conference.

- The Polymers Division and the Electron and Optical Physics Division held a workshop on infrared microspectroscopy using a synchrotron source. Two of the areas identified where the technique could have impact were polymer composites and electronic packaging.

Viscoelasticity of Polymers Program

- Collaborated with Rheometrics Scientific, Inc. in the redesign of a force rebalance transducer to eliminate thermal effects that can result in spurious normal force measurements.

- In collaboration with Dow Chemical Company, established that the aging behavior of syndiotactic polystyrene above the glass transition temperature is significantly different from that of other semi-crystalline polymers .

- Established that 'efficient' methods for determining the material parameters required for the mechanical characterization of the nonlinear mechanical behavior of polymers can be used with polycarbonate.

- Organized a NIST - hosted Workshop on "Hygrothermal Effects in Polymers and Composites."

- Co-organized a workshop on 'Nonlinear, Time-Dependent Constitution of Engineering Polymers'

- Established the existence of an isochoric glass transition temperature.

- Developed a method to predict from single step stress relaxation experiments in uniaxial extension the viscoelastic response of polymer melts in complex deformation and at differing rates.

- Validated a total strain criterion for mode II fracture in epoxy adhesives with an elastic-plastic finite element analysis of an adhesive joint.

- Established that the effect of physical aging on craze initiation for polystyrene is different from that for a styrene-acrylonitrile copolymer.

Polymer Characterization Program

- Standard reference material, SRM 1473a, was recertified as a melt flow standard .

- The mass spectrogram of a poly(methyl methacrylate) SRM revealed features attributable to the polymerization chemistry.

- The presence of axial defects in the morphology of polyaramide fibers was established by solid state NMR.

- Solid state NMR studies of methylated poly(benzobisthiazole) revealed little evidence for cross-link formation upon heating. This procedure had been proposed as a means of improving the compressive strength of PBZT fibers.

- Determined that the apparent absence of x-ray scattering from the lamellar microstructure below the T_g of sPS is a consequence of the virtually identical densities of the "glassy" and "crystalline" phases.

Dental and Medical Materials Program

- In an effort to improve access to spiro orthocarbonate (SOC) monomers capable of double ring-opening polymerization with expansion, a simple one-pot synthesis of multifunctional SOC oligomers was developed from inexpensive starting materials.

- Prepared and evaluated several fluorinated urethane methacrylate monomers and oligomers for use as hydrophobic matrix materials for dental composite applications. Demonstrated

that these fluorinated materials have mechanical strengths equivalent to that of conventional composites with up to 20x less water uptake.

- Demonstrated that both aryliminodiacetic and alkyliminodiacetic acids effectively demineralize the surface of dentin, but only the aryl conditions can initiate the self-polymerization of dental monomers, resulting in significantly improved bond strengths of dentin bonding systems.

- Demonstrated that a dental composite with amorphous calcium phosphate as the filler phase can, under oral-simulating conditions *in vitro*, remineralize carious lesions in bovine enamel.

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ELECTRONIC PACKAGING AND INTERCONNECTS

Goals

The U.S. microelectronics industry, valued at over $300 billion in 1995, is confronted with technological changes at an unprecedented pace and urgency. This is partially due to increased consumer expectations, rapid product evolutions, and heightened international competition. In response to these pressures, the U.S. semiconductor and module interconnection industries, representing a combined value of over $54 billion in 1995, took the landmark steps of developing technology roadmaps that identify roadblocks and performance characteristics for the manufacture of globally competitive products[1,2]. Significant portions of these roadmaps address the packaging and interconnection of semiconductor devices, a technology which now amounts to over one-third the delivered cost of integrated circuits.

To assist this strategic and rapidly growing U.S. industry, the Materials Science and Engineering Laboratory's program in electronics packaging and interconnection develops and delivers to U.S. industries measurement tools and data for materials and processes used in **semiconductor packaging, module interconnection and component assembly**. The strategy used to implement this program is based upon three primary needs:

- Techniques and procedures for making *in-situ*, in-process and in-use measurements on materials and material assemblies having micrometer- and submicrometer-scale dimensions.
- Data on material properties at small dimensions and near interfaces.
- Fundamental understanding of materials behavior needed for future packaging, interconnection and assembly schemes.

This strategy is the outgrowth of two industry-led workshops conducted at NIST. The first, conducted in 1990, set the course for the Laboratory's emerging plans in packaging, interconnection and assembly. The second, conducted in early 1994, identified a series of cross-cutting barriers, critical technical challenges and opportunities for NIST in materials science and engineering deemed most needed by U.S. industry[3].

Now in its second year, the program has a portfolio of projects involving staff in the Metallurgy, Polymers, and Materials

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[1] *The National Technology Roadmap for Semiconductors*, Semiconductor Industry Association, San Jose, CA, 1994.

[2] *Technology Roadmap: The Future of the Electronic Interconnection Industry*, Institute for Interconnecting and Packaging Electronic circuits, Lincolnwood, IL, 1994.

[3] Michael A. Schen, ed., *Metrology and Data for Microelectronics Packaging and Interconnection*, Results of a joint workshop, May 5-6, 1994, NISTIR 5520, November 1994.

Reliability Divisions. During this period, the MSEL program has developed numerous single-company and consortia-based collaborations that involve over twenty-three U.S. companies; fifteen universities; four other government agencies or laboratories; and eight consortia, standards bodies and associations. These collaborations have resulted in forty-six technical publications, sixteen of which were published in 1995, and numerous individual accomplishments that directly impact industry's research and development needs.

FY-95 Significant Accomplishments

- An improved technique for determining the out-of-plane coefficient of thermal expansion of polymer thin films based upon a capacitance measurement has been demonstrated.

- X-ray reflectivity measurements reveal that polymers which have a favorable interaction energy with a solid substrate can experience an elevation of the glass transition temperature of as much as 70°C in a thin layer (ca. 400 Å) adjacent to the interface.

- An improved method for determining the density of ultra-thin films on a substrate utilizing X-ray reflectivity at multiple wavelengths has been developed.

- The thermal pulse instrumentation has been applied to obtaining thermal conductivity of polymer thin films on a silicon substrate.

- Hygroscopic expansion coefficients of ultra-thin polyimide films on silicon have been determined from X-ray reflectivity measurements.

- Working with the NCMS PWB Consortium and a leading U.S. materials supplier, NIST provided previously unattainable z-axis CTE data for candidate polymer thin films as part of an industry development effort to fabricate low cost, high density substrates for printed wiring boards.

Improved Metrology for the CTE of Polymers

M.A. Schen, F.I. Mopsik, S.C. Roth, G.T. Davis and W. Guthrie (882)

Objectives

Improve the quality of measurements and data employed by the U.S. microelectronics industry to describe the dimensional stability of polymer thin films by further refining a NIST designed capacitance cell that measures the out-of-plane coefficient of thermal expansion (CTE) of polymer thin films typically used in microelectronics packaging. Work with industrial consortia, firms and universities to apply this technique to industrially relevant problems and cooperate with standards organizations in the development of improved CTE test standards.

Accomplishments

Knowing and predicting the dimensional stability of materials, especially polymers, are critical to the performance and reliability of semiconductor packages and module interconnects. Not only is it necessary to

manage the three-axis strains associated with thermal cycling, but measuring and predicting film shrinkage and warpage is essential for robust manufacturing. Industry planning documents, including NISTIR 5520, *Metrology and Data for Microelectronic Packaging and Interconnection*, specifically identify dimensional stability of materials, especially polymers, as a critical technical challenge for the industry.

In this project, NIST is pursuing a dual strategy to improve the quality of measurement techniques and resulting data for characterizing the z-axis CTE of polymer films. The strategy consists of effecting evolutionary improvements in commonly used measurement techniques and standards for measuring CTE using the thermomechanical analyzer (TMA), and of introducing revolutionary improvements in measuring CTE by developing and applying a new NIST capacitance technique that has vastly improved sensitivity and accuracy over the TMA or existing capacitance-based approaches.

Although not designed for measuring the very small out-of-plane (z-axis) strains in polymer thin films, the TMA continues to see widespread use in the electronics industry for measuring CTE due to the convenience of the measurement and the ready availability of the instrumentation. In conjunction with the Semiconductor Research Corporation (SRC), IBM, Digital Equipment Corp., Dow Chemical Co., the National Center for Manufacturing Sciences (NCMS) Printed Wiring Board Consortium, the University of Maryland CALCE Center, University of Texas at Austin, Cornell University, NASA Jet Propulsion Laboratory and the Naval Surface Warfare Center at Crane, the project has been evaluating the limitations and errors associated with the TMA measurement[4]. A model that considers four primary sources of measurement error is assumed: baseline repeatability, absolute displacement of the linearly variable differential transformer (LVDT), sample temperature, and repeatability of the sample response have been proposed. Using a statistically designed experiment that consisted of a 2^3 factorial design with two center points, NIST conducted a thorough examination of the systematic errors that arise from measurement factors most likely to influence the baseline repeatability. Factors evaluated include heating rate, probe force, probe diameter, and heating number. In these experiments, the 'first heating' is defined as the first heating and cooling cycle of the sample chamber after the TMA probe has been lowered into position. Second and subsequent heating numbers are then conducted without having disturbed the probe position. Separate graphical and numeric analysis of the results showed that heating number and heating rate had the two largest first order influences on baseline repeatability. In addition, a large second order interaction between heating rate and probe diameter was also identified. Under the best case and worst case conditions, a point-by-point uncertainty between baseline

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[4] M. Schen, G.T. Davis, F. Mopsik, W. Guthrie, W.T. Chen, E. Livingston, L. Lee, W. Robbins, C. Lee, P. Henderson, M. Li, M. Pecht, C.Y. Lee, J. Dion, P.S. Ho, H. Li, J. Kelly, *An Industry / Government / University Partnership: Measuring Sub-micrometer Strain in Polymer Films*, Proc. of the Tech. Conf., IPC Printed Circuits Expo., April 24-27, 1994, Institute for Interconnecting and Packaging Electronic Circuits, Lincolnwood, IL, P4-3 (1994).

response of approximately 9 nm and 30 nm, respectively, was found.

These first measures of the systematic errors associated with the TMA measurement have numerous implications. First, the conditions found for maximizing baseline repeatability are unlikely to be the same when the repeatability of a sample response is evaluated. For example, results show that faster heating rates give more repeatable responses. With a specimen in place, higher heating rates increase the uncertainty in knowing the actual sample temperature. Second, baseline repeatability is but one of four possible sources of measurement uncertainty. Making the assumption that uncertainties of comparable magnitude are found for the remaining three sources of uncertainty, a cumulative point-by-point uncertainty of 40 nm to 120 nm can be expected in the TMA measurement. Striving for a measurement protocol that maintains an uncertainty no larger than 5% of the total signal response for polymer specimens with a typical CTE of 50 μm/m°C, total specimen displacements of 800 nm to 2400 nm over a typical 200 °C temperature scan are needed. This translates to minimum specimen thicknesses of 80 to 240 μm. NIST is continuing this work to evaluate the other sources of uncertainty and further refine the estimates of minimum initial film thicknesses for the TMA technique to be confidently applied.

In the second project thrust, NIST has built a capacitance cell to accurately measure the distance between two parallel plates with a sensitivity far better than that accomplished using the TMA. For an ideal parallel-plate capacitor, the capacitance, C, scales directly with gap spacing (d) for a given electrode area (A) as :

$$C = \epsilon_0 \epsilon A/d \qquad (1)$$

where ϵ_0 is the permittivity of free space and ϵ is the dielectric constant of the gap. The specimens to be measured are placed between the plates but outside the electrode area and thus define the gap but otherwise do not enter into the measurement of capacitance. Precisely knowing ϵ of air in the gap and electrode area allows for accurate determination of out-of-plane thickness for specimens used as spacers separating the electrodes. Key elements contributing to the ability of the technique to monitor the thickness of a film to better than 1 μm/m is ensuring removal of all stray capacitance from the measuring circuit, maintaining a constant electrode area over temperature and measuring the pressure, temperature and relative humidity of the air in the gap. Excellent agreement has been obtained between measured isothermal z-axis expansion of a 2.4 mm thick silicon single crystal from 40-150 °C with published standard reference data [5]. Thickness change for the silicon is comparable to that expected from a 100 μm-thick polymer film.

Using the cell, data have been generated from 50-140 °C for 51 μm thick unconstrained polyimide. At these temperatures which are well below the T_g of the polymer, the CTE steadily and repeatedly increased from approximately 62 to 95 μm/m°C. The technique was also able to document changes in material dimensions due to creep and loss or gain of moisture.

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[5] C.A. Swenson, *Recommended Values for the Thermal Expansivity of Silicon from 0 to 1000 K*, J. Phys. Chem. Ref. Data, 12(2), 179 (1983).

Today, most design and modeling approaches assume a constant CTE within the glassy phase of polymers, independent of temperature. To a large extent this is because existing industry test methods are poorly suited for measuring the small out-of-plane strains associated with thin films. For example, attempts to obtain reliable CTE measurements for identical polyimide films using existing industry standard test standards and the TMA were unsuccessful during a NIST-industry-university round robin measurement exercise. In those experiments, the CTE values between 50 and 200 ^{0}C ranged from 63 to 103 μm/m^{0}C depending on where the measurement was performed.

Currently, a new environmental chamber that allows temperature and humidity control is being installed for use with this new capacitance cell. In addition, studies are underway to further understand the impact of film thickness, interfacial constraints, and environmental elements, such as water, on the out-of-plane strain of polymer thin films. NIST is using this new method in conjunction with industry to examine candidate dielectric resins for high density electrical interconnect substrates.

Outputs

Presentations

M.A. Schen, F.I. Mopsik, G.T. Davis, W. Guthrie, W. Wu and W.E. Wallace *Measurement of Z-Axis CTE of Polymer Films*, National Center for Manufacturing Sciences Printed Wiring Board Consortium, Materials Quarterly Meeting, Tucson, AZ, 1995.

M.A. Schen, F.I. Mopsik, G.T. Davis, W. Guthrie, W. Wu and W. E. Wallace *Update: Evolutionary and Revolutionary Advancements in z-Axis CTE Metrology*, SEMI Packaging Standards Committee Meeting, April 17, 1995.

Ultra-thin Polymer Films as Models for Interfacial Regions

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Objectives

Deduce the properties of the extremely important interfacial regions of polymers on substrates by measuring the physical properties of thin films as a function of film thickness in the range of 50 to 1000 Å.

Accomplishments

Results from three areas concerning polymer/solid interfaces are reported: (1) glass transition temperature and polymer density at interfaces, (2) measurement technique for the work of adhesion between solids and (3) moisture at polyimide/silicon interfaces.

Glass Transition Temperature and Polymer Segment Density

Specular x-ray and neutron reflectivity measurements were conducted to determine the effect of interfacial energy on the glass transition temperature, T_g, and the density of polymer near interfaces. To approach the interface behavior, the film thickness used in this work was as low as 50 Å. T_g of thin films was determined by monitoring the film thickness as a function of temperature, and T_g was identified as the temperature where the thermal expansion coefficient underwent a sudden change. X-ray and neutron reflectivities were used to determine film thickness with a precision of a few angstroms.

The systems examined so far include polystyrene(PS)/silicon, poly(methyl methacrylate)(PMMA)/silicon and poly (2-vinyl pyridine, (P2VP)/silicon. For PS, PMMA, and P2VP, their glass transition temperatures, T_g, and the coefficients of thermal expansion (CTE) of polymer thin films on silicon wafers were determined in order to investigate the effect of the presence of a substrate on local polymer chain dynamics. Among these three polymers their interfacial energy or the work of adhesion with a silicon oxide surface can be ranked as P2VP > PMMA > PS.

For PS on surface oxidized silicon, with its initial thickness below 100 Å, a decrease in film thickness with increasing temperature was observed. This contraction of the polymer film took place at temperatures as low as 30°C and was found for all the PS molecular weights studied so far. If one regards T_g as the temperature where chains exhibit significant mobility, this result can be interpreted to mean that T_g starts at 30°C in thin PS films. In contrast, on a hydrogen passivated silicon surface the T_g of PS was significantly elevated; the extent of elevation depends on the original film thickness. The data suggested that the range of influence of the hydrogen passivated substrate reached 400 Å, a value far greater than any theoretical predictions. In summary, the above results on PS demonstrate conclusively the impact of substrate on the polymer interfacial properties, T_g can be shifted by 70 °C or more. Based on contact angle results at 150°C, the work of adhesion of PS/silicon oxide and PS/Si-H is 54.3 and 57.7 erg/cm^2 respectively, only a modest difference.

For PMMA with thickness between 75 and 600 Å, no change in T_g from its bulk value was observed. However, the thermal expansion coefficient of thin films was found to be lower than that predicted for constrained thin films using bulk properties. The P2VP results suggested that T_g of thin films below 100 Å was greater than 160°C which was the instrument limit. T_g of bulk P2VP is around 100°C. Once again the above results of P2VP on silicon oxide clearly demonstrate the impact of interfacial interaction on the properties of the adjacent polymer layer.

An energy dispersive x-ray reflectivity technique was developed to improve the accuracy of density determination by a factor of five compared to results from single wavelength measurements. Measurement error due to misalignment can be alleviated by using this newly developed technique.

Technique for Measuring the Work of Adhesion

Construction of equipment for measuring the work of adhesion, W_{ad}, has been completed. The principle of measurement is based on JKR theory (*Surface Energy and The Contact of Elastic Solids"* K.L. Johnson, K. Kendall and A.D. Roberts; Proc. Royal Soc. A, 324, 301 (1971)); the contact area between two solids is monitored as a function of applied stress and the work of adhesion can then be deduced. Great difficulty has been experienced by us and others in the field to implement the JKR theory; irreproducibility and an anomaly of the observed W_{ad} with applied load are just two examples. The anomaly is that W_{ad} is not expected to depend on the applied load. To overcome these difficulties, our instrument is now equipped to monitor the displacement or the deformation of samples concurrently with the contact area. Preliminary results from our measurements indicate that both the system modulus and deformation can now be determined; the se

quantities, rather than W_{ad} depend on the applied load. The anomaly can be accounted for by the above finding and the reproducibility is also enhanced.

Moisture Detection at Polyimide/Silicon Interfaces

We have pioneered the use of neutron reflectivity (NR) for detecting moisture at the buried interface between polyimide and a silicon wafer with a depth resolution of a few angstroms. For interfaces between polymer thin films and solid substrates, x-ray reflectivity (XR) is expected to be applicable. XR is a technique more accessible to general users.

Increases in polymer film thickness after exposure to moisture were determined for samples with different dry film thicknesses. By extrapolating this moisture-induced increase to the condition corresponding to zero dry thickness, one can deduce the interfacial layer thickness. The results of our XR work on polyimide thin films on silicon wafers is consistent with our NR results which implied a thin moisture-rich layer of 30 to 40 Å at the interface. In addition, the XR results suggest that the time constant for interface moisture accumulation is longer than that of moisture diffusion through bulk polyimide, indicative of moisture induced interface damage.

Outputs

Publications

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W. Wu, W.E. Wallace, and J. van Zanten, *Glass Transition Temperature of Ultrathin Polymer Films on Silicon*, in Low-Dielectric Constant Materials - Synthesis and Applications in Microelectronics, T-M. Lu, S.P. Murarka, T.S. Kuan, C.H. Ting eds., Materials Research Society Symposia Proceedings, Vol. 381, Pittsburgh, PA, 147-152 (1995).

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W.E. Wallace, W. Wu, and R.A. Carpio, *Chemical-Mechanical Polishing of SiO_2 Thin Films Studied by X-ray Reflectivity*", submitted to Thin Solid Films.

Presentations

W. Wu, W.E. Wallace, J.H. van Zanten, and B.J. Bauer, *Diffusion of Linear PS into Crosslinked PS* APS meeting, 3/95 San Jose, CA.

W. Wu, W.E. Wallace, and J.H. van Zanten, *Glass Transition Temperature of Ultrathin Polymer films on Silicon* MRS meeting, 4/95 San Francisco.

W. Wu, W.E. Wallace, and J.H. van Zanten, *Measurements of CTE of Polymer Thin Films Using X-ray reflectivity,* National Semiconductor Corp. 4/95 Santa Clara, CA.

W. Wu, *Application of NR for detecting Moisture at Buried Interfaces*, du Pont Polyimide Conference, 5/95, Wilmington, Delaware.

W. Wu, W. E. Wallace, and J.H. van Zanten, *Thermal Expansion Coefficient of Polymers near Solid Substrates*, du Pont Marshall lab. 6/95, Philadelphia, PA.

W. Wu , W.E. Wallace, *A NR and FRES study of Diffusion of Linear PS into Crosslinked PS*, Univ. Delaware, 8/95, Newark, DE.

W. Wu, W. E. Wallace, and J.H. van Zanten, *Glass Transition Temperature of Thin PS Films on Silicon*, Europhysics Conference, 9/95, Hamburg, Germany.

W. Wu, W.E. Wallace, and J.H. van Zanten, *Glass Transition Temperature of Thin Polymer Films*, Univ. Of Michigan, 10/95, Ann Arbor, MI.

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W.E. Wallace, W. Wu, and R.A. Carpio, *Surface Roughness of Chemical-Mechanical Polished Silicon Dioxide Measured by X-ray Reflectivity*, Mat. Res. Soc., Boston, MA, December 1994.

W. Wu, J.H. van Zanten, and W.J. Orts, *Glass Transition Temperature of Ultrathin Polymer Film on Silicon*, Int'l. Symp. On Microelectronics, ISHM, Boston, MA, November 1994.

W. Wu, J.H. van Zanten, W.J. Orts, and W. E. Wallace, *Glass Transition Temperature of Polymers Near an Interface*, ACS Polymer Surfaces and Interfaces Workshop, Brewster, MA, October 1994.

Merging Dielectric Measurements from Discrete Frequency Ranges into a Continuous Spectrum from DC to 1 GHz

F. I. Mopsik and S. Roth

Objectives

Develop sample and electrode configurations and sample holders to enable accurate determination of dielectric constant and loss of polymer materials, many of which can be obtained only in the form of thin films. Integrate output of high frequency instrumentation, precision LCR (Inductance,

Capacitance, and Resistance) meters and impedance analyzers with that of the Dielectric Spectrometer used for lower frequencies so that data can be merged, assessed and analyzed.

Accomplishments

The LCR meters have been fully integrated for both collection and control into the computer system that controls and analyzes the Dielectric Spectrometer. This allows the data up to 30 MHz to be collected in an automated system and stored in a format that is compatible with the lower frequency data. The analysis programs have been updated to read and combine all the sets of the data in a consistent manner so that the data ranges between the different systems can be consistently merged with optimal matching points to remove minor differences in instrumental calibration.

The thin film sample holder has been modified and tested for use with the LCR meters so that the same film sample can be used for measurements from 10^{-4} to 3×10^{7} Hz. Limits of accuracy were shown in the data above 5 MHz that are set by the LCR meter configuration which were consistent with limits stated by the manufacturer. Such uncertainties prevented determination of the sample loss at the higher frequencies. Furthermore, it was determined that these uncertainties can only fortuitously be calibrated out since irreproducible uncertainties prevented any further calibration.

The losses above 5 MHz were determined to be due to the attempt to use a four-terminal configuration, the nominal LCR meter configuration, at line lengths long compared to the wavelengths involved. An initial attempt was made to refer the measurement back to the instrument front panel terminals by using a four-terminal to coaxial adaptor and placing the sample at the end of a precision coaxial line. The LCR meter then was used to measure the values of capacitance and loss at a reference plane at the entry to the coaxial line and the measurement was propagated to the position of the sample. The results showed that the measurements were much more stable than using the full four-terminal method and had only small uncertainties that were capable of further analysis.

This work shows that using a lead-independent measurement with one sample holder will not be possible at frequencies much above 5 MHz. However, with further work, a second, coaxial holder using a similar, if not the same sample, should be usable to about 1 GHz once the impedance analyzer is brought on line. Only two sample configurations will be needed to cover a frequency range of 13 decades on a thin film.

Outputs

Publications

B.J. Factor, F. I. Mopsik and C.C. Han , *"Dielectric Behavior of a Polycarbonate/Polyester Mixture upon Transesterification"* Macromolecules, in press.

Polymer Films on Silicon Substrates: Residual Stresses and Thermal Conductivity

A.S. DeReggi, S.C. Roth, B. Dickens, G.T. Davis

Objectives

Evaluate measurement techniques for deducing residual stress in polymer films and silicon substrates and identify and investigate all factors required for the accurate modeling of the stress resulting from cooling polymer-coated substrates from high temperatures of cure. Adapt the thermal pulse instrumentation to measure thermal conductivity of thin polymer films on silicon substrates and identify interfacial barriers, if any.

Accomplishments

A careful investigation of problems met in modeling stress induced by dissimilar contraction of polymer films cured at high temperature on silicon and cooled to room temperature has identified key factors affecting the thermal and mechanical properties of the adhered materials along the processing temperature-versus-time path. Because polymers are apt to take up moisture, their thermal and mechanical properties below approximately 100°C may have a significant dependence on moisture content. The residual stress after processing thus depends on both ambient temperature and relative humidity. Laser optical measurements of wafer-bow are used to investigate the moisture effects on stress. For films of a common polyimide (PTDA/ODA/MPD), typically 6 μm thick, deposited and cured on Si 111 wafers, typically 350 μm thick, it has been found that the bow induced by differential cooling to room temperature after curing at 300°C under dry atmospheric conditions is reduced by approximately a third at 23°C when the relative humidity is increased from zero to 50 percent. These measurements show that data bases for thermal and mechanical properties should include both temperature and relative humidity dependencies in order to meet the requirements of modeling stress in microelectronics.

The problem of determining thermal diffusion characteristics of a thin polymer film adhered to a semiconducting substrate has been investigated. These characteristics depend on both the intrinsic thermal diffusivity of the material and on the mechanical constraints which are often unprecisely known and difficult to determine. There is, therefore, an urgent need within the microelectronics community for reliable methods to measure thin film thermal properties or apparent properties characterizing *in situ* thermal performance. A new method was developed for measuring the thermal diffusivity of thin polymer films adhered to heat sinking substrates. The method, called the pulsed electrothermal technique is based on inducing a pyroelectric response from the film by applying both a DC voltage bias and a short laser pulse to the electroded outer surface of the dielectric film while the substrate is at ground potential. The time dependence of the pyroelectric response can be expressed in closed form which involves a sum of exponential terms. Fitting the measured response to the theoretical formula for the response yields the characteristic time to *circa* 2 percent uncertainty and the thermal diffusivity to an uncertainty limited by the uncertainty in film thickness. The thermal conductivity may be obtained from the diffusivity to the uncertainty with which the thermal mass is known. The method has been applied to polyimide films, typically 6 μm thick, adhered to silicon wafers. The results show agreement within a few percent of manufacturer data when available although such data came from much thicker samples. These results suggest that film properties remain similar to bulk properties as long as film thicknesses remain greater than a few micrometers. The pulsed electrothermal method has also been applied to polyimide types differing in molecular conformation,

including a rigid rod polyimide used in microelectronics as a low stress polyimide. The low stress properties are due to rigid rod orientation in the plane of the film. The pulsed electrothermal results when combined with related measurements obtained elsewhere show a strong anisotropy in thermal properties of thin films due to the rigid rod orientation and a weaker though clearly detectable anisotropy believed due to the constraints imposed by the substrate.

Outputs

Publications

A.S. DeReggi and S. Bauer, *Adaptation of the thermal pulse method to the measurement of the thermal diffusivity of dielectric films on conducting substrates*, 1995 Annual Report, Conf. Electr. Ins. and Diel. Phenom., pp. 536-539, IEEE Publication 95CH35842.

The Nature of Water Absorbed by Polymeric Electronic Packaging Materials

Brian Dickens and G.T. Davis

Objectives

The objectives are to use near infrared spectroscopy (NIR) and other techniques such as NMR and gravimetry to follow the absorption and desorption of water in polyimides, epoxies, and their composites with silica and to deduce the mechanism by which water accumulates and is held in the structure, especially when used to encapsulate microelectronic components.

Accomplishments

Pop-corning during solder reflow in micro-electronics manufacturing is believed to occur only at interfaces and to require the presence of large amounts of absorbed moisture. At interfaces, the interfacial bond strength is not as high as the cohesive energies in the components of the interface and stress and voids (delamination) typically exist. The name pop-corning suggests that explosive release of water is the cause of the catastrophic delamination which sometimes accompanies the rapid heating (during solder reflow) of electronic components previously stored in high humidity. Water-filled voids at the interface and perhaps water absorbed in polymeric materials such as epoxy and polyimide have been suggested as sources of the water.

Near Infrared (NIR) spectroscopy has been used to examine water in several solvents. The most intense NIR absorption, the $\upsilon 2+\upsilon 3$ combination band, occurs over the range 5160 to 5260 cm^{-1} with absorptivity between 1 and 3.3 L/mol/cm, depending on the degree of hydrogen bonding to the water molecule. The absorptivity is needed to translate spectral absorbance into concentration. Most IR absorptions have constant absorptivity but in the case of water the absorptivity is affected by hydrogen bonding, which greatly complicates estimation by IR of the amount of water present. Initial observations had suggested a relationship between absorptivity and peak maximum for water in various hydrophilic polymers. If such a relationship could be used for a range of systems, estimation of absorptivity would be greatly simplified. Measurement of absorptivities is time-consuming at best and is difficult in the case of absorbed water, whereas peak maxima are more easily measured. However, it was established that, although there is some correspondence between the position of the $\upsilon 2+\upsilon 3$ absorption maximum and the apparent absorptivity of water in a particular environment, this correlation is not generally applicable to a range of environments and in

some cases the value of the absorptivity decreases without a noticeable change in the peak maximum of the absorption envelope.

The position of the υ2+υ3 absorption maximum at low water concentration is related to the group(s) to which the water is hydrogen-bonded. When the water exists as isolated molecules, as in toluene or dichloromethane, or is the donor in any hydrogen bonds, as for example in ethyl acetate, the υ2+υ3 absorption maximum is near 5260 cm^{-1} and the absorptivity is greater than 3 L/mol/cm.

For small traces of water in acetone, the υ2+υ3 absorption maximum lies at 5240 cm^{-1} and decreases with increasing water-content, for example to 5190 cm^{-1} for a 50:50 volume% mixture of water and acetone, as more of the water molecules accept hydrogen bonding. The average absorptivity decreases from over 3 L/mol/cm for no hydrogen bonding to the water molecules to 1.2 L/mol/cm for the 50:50% mixture (70 mole% water) of water and acetone as the concentration of water increases. An absorptivity of 0.99 L/mol/cm is found for liquid water.

The changes in absorptivity are due to the influence of hydrogen bonding on the dipole moment. For the strongest NIR absorbance of water, both position and absorptivity are a combination of the bond strength and dipole moment of two bands - the υ2 asymmetric stretching mode and the υ3 bending mode - which react differently to hydrogen bonding. Therefore, an overtone of the symmetric υ1 stretch, seen as a weak absorption at about 7000 cm^{-1} , was used to confirm the observations based on the υ2+υ3 band.

Clustering of water, i.e., water receiving hydrogen bonds in systems where only water can be the donor in hydrogen bonds, is presumably revealed by changes in the rate of change of absorptivity with mole fraction water. In solvents which are inherently hydrogen bonding, water molecules have spectra much closer to that of liquid water. In acetic acid, the peak maximum is at 5215 cm^{-1} and the absorptivity is about 1.36 L/mol/cm. Clustering may depend on the solvent system. There seems to be no clustering of water in toluene, for example, although there is some small amount of absorption/dissolution.

NIR spectroscopy and gravimetry were used to monitor water uptake from various humidities and from liquid water at room temperature in several unsilanized-silica/polyimide(PI) composite disks. NIR spectra show that most of the water is in the polyimide part, which constitutes most of the specimen. As the humidity is increased, appreciable growth in the amount of absorbed water can be seen in the spectrum and spectral absorbance increases at the position of water receiving hydrogen bonds. Soaking the disks in water greatly increases the water uptake.

NIR spectra taken on water-soaked 55 wt% filled composite specimens as they dry show a radical change in background scatter in the earliest stages of drying. This suggests that a drastic change in refractive index takes place, i.e., that on drying, voids lose water to form air gaps. Soaking in water apparently fills voids in these disks but exposure to high (84%RH) humidity at 25°C does not. These preliminary findings will have to be confirmed. Temperature/RH studies to increase the amount of water available for absorption have not yet been carried out but should provide specimens with total water

absorption near that found from soaking in liquid water.

Gravimetry of absorbed water has several problems, including that the specimens tend to change weight as they are weighed if they had been equilibrated at a significantly different RH and that the low molecular weight of water means that absorption of water that is appreciable in terms of molar content confers small changes in weight. Given these limitations, gravimetry showed that wt % uptake of water at lower humidities at 25°C was roughly independent of the (non-silanized) filler content of the disk over a filler range of 1 to 55wt % (vol fraction 0.02 to 0.42). This result means that a given volume of silica filler (including any resin-filler voids) absorbs about twice as much water as the polyimide at 20%RH (i.e., in inverse proportion to their densities). Simple arguments based on the particle size of the filler (estimated to be 6 μm) suggest that a water-like layer of roughly 20 nm on each filler particle would be sufficient to accommodate all the water absorbed at 20%RH. About three times as much water was absorbed at 84%RH.

To examine water-filled voids and effects of aggressive water depletion on epoxy resin, epoxy disks containing voids were made from an epoxy typical of those used in electronic packaging by dissolving the epoxide and hardener in acetone solution, which was then heat-cured at reduced pressure. Bubbles up to 1 mm in diameter were produced in the cured disks. Several such disks were boiled in water for 8 days, after which the bubbles near the surface of the epoxy contained liquid water. The disks were then subjected to rapid heating to about 190 °C. The only effect was bursting of those bubbles with the thinnest (100 micrometer or less) walls. The rest of the water-saturated epoxide appeared to be unaffected and in particular was not crazed or shattered by rapid release of water. That silica filler absorbs more water than the polyimide matrix suggests that the silica/polyimide interface is a preferred site for absorbed water. Although voids and interfaces are difficult to study, there is not yet convincing evidence that water-filled voids per se exist or are influential when electronic components have been exposed to high humidity. The main effect of absorbed water in pop-corning may be to reduce the surface energies of the components of the interfaces. This interpretation is well-accepted in the field of adhesion and the effect is known to be enhanced by raising the temperature and by the presence of stress. Typical remedial approaches are to roughen the interface to provide some mechanical interlocking and to apply a coupling agent/primer to produce an interface which is less affected by the presence of water than the original interface is and that has less delamination and is therefore stronger.

Outputs

Publications

B. Dickens, *Monitoring the cure of thin-layer polyimides on glass substrates with photo-acoustic spectroscopy*, Proc. Intnl. Symp. Microelectronics (ISHM), Nov, 501-506, 1994.

Industry-NIST Roadmapping and Coordination in Electronics Packaging

M.A. Schen

Objectives

Enhance NIST's national role in electronics packaging, interconnection and assembly

metrology by coordinating and cooperating with U.S. industry and other government agencies in technology planning, infrastructure research and development, implementation of industry established technology roadmap research priorities, and assessing the technology currently being used.

Accomplishments

The NIST advanced materials program in electronics packaging, interconnection and assembly has a national role in assisting the U.S. microelectronics industry develop and use improved materials technology in the design, manufacture and reliability assessment of new products and processes. As part of this role, NIST has taken an active role in working with industry and other government agencies in technology planning, infrastructure research and development, implementation of industry established technology roadmap research priorities, and assessing current industry practice (benchmarking.)

In November 1994, NIST published a new report documenting the results of a recent Industry - University - Government workshop on "Materials Metrology and Data for Commercial Electrical and Optical Packaging and Interconnection Technologies" conducted on May 5-6, 1994. Coming on the heels of the first national technology roadmaps for semiconductors and electronic interconnects, the report, NISTIR 5520, *Metrology and Data for Microelectronic Packaging and Interconnection*, identifies cross-cutting barriers, critical technical challenges and opportunities for NIST in metrology and data for electronic packaging and interconnection technologies. Specific barriers that apply to all product applications considered and all technical challenges identified include: (1) *in-situ*, in-use, and in-process metrology, (2) data and databases, (3) modeling, design, and manufacturing tools, and (4) technology environment. Technical challenges viewed to strongly impact the performance and reliability of electrical and optical packaging and interconnection materials and material structures include adhesion, moisture measurement and control, micro thermo-mechanical measurements, dimensional stability, failure mechanisms, high frequency electrical measurements, and interconnection.

In other technology planning activities, NIST has been working closely with the Institute for Interconnecting and Packaging Electronic Circuits (IPC), which represents the printed wiring board and assembly industries, in the roadmapping of their technology needs into the next century. At the invitation of the IPC, NIST joined the IPC Roadmap Steering Committee in 1995, was heavily involved in the March 1995 Roadmap Workshop, and contributed substantially to the final roadmap report; *The National Technology Roadmap for Electronic Interconnects*. The overall mission of the IPC roadmapping process is to guide manufacturing, process, material, equipment, and product research and development in order to establish and maintain leadership in electronic interconnection technology; integrate the development with partners in the electronic industry, academia, and government; and excel in the global market by implementing these developments and continuously improving customer satisfaction. NIST's involvement with the IPC Roadmap Steering Committee continues as the Committee focuses its 1996 activities on industry and improved assessment of industry practice.

To utilize more efficiently government resources and coordinate among agencies, NIST participates along with other government agencies that have activities in

electronic materials in the President's National Science and Technology Council's (NSTC) Electronic Materials Working Group (EMWG). Established to support the activities of both the Materials Technologies and the Electronics Subcommittees of the NSTC's Civilian Industrial Technology Committee, the EMWG has the objective of pursuing methods to team industry groups and government agencies to create a national strategy for federal investment in high leverage and/or critical materials and material processing technologies to significantly enhance U.S. competitiveness in electronics and supporting industries, and provide a forum, knowledge base and recommendations for coordinating efforts of appropriate government agencies. As part of this year's activities, NIST and the EMWG sponsored a workshop on electronic materials in Dallas, TX, on December 6-7, 1994. Convened to address short and long term industry material needs in microelectronics, photonics, RF & microwave technologies, mass storage, module interconnects, materials characterization, and research opportunities, the workshop attracted over 85 participants from industry, academia and various government agencies. A public document, NISTIR 5777, summarizes the findings of this workshop.

In the areas of infrastructure research and development and implementation of technology roadmap research priorities, NIST is cooperating with the Semiconductor Research Corporation (SRC) and SEMATECH in a number of ways to better link NIST's activities to industry's needs and SRC and SEMATECH activities. In the case of the SRC, NIST is a participating member of the SRC Packaging Science's Technical Advisory Board and has become a mentor for a number of their individual research projects in packaging. A visit to NIST by the SRC and its member companies is expected in 1996. NIST has also built new links to SEMATECH's Assembly and Packaging efforts through its involvement in the SEMATECH Liquid Encapsulation Enhancement project.

Outputs

Workshops

Materials Metrology and Data for Commercial Electrical and Optical Packaging and Interconnection Technologies, sponsored by NIST, Institute for Interconnecting and Packaging Electronic Circuits, Optoelectronics Industry Development Association, Semiconductor Research Corporation, May 5-6, 1994, Gaithersburg, MD

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Microelectronics Symposium, IEEE Catalog #95CH35779, Austin, TX, 1995

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

M.A. Schen, editor, *Mechanics and Materials for Electronic Packaging: Thermal and Mechanical Behavior and Modeling*, American Society of Mechanical Engineers, AMD-Vol. 187, 1994.

Presentations

M.A. Schen, *Results of the May 1994 NIST/IPC/OIDA/SRC Workshop on Electronics Packaging and Interconnection*, ASME Winter Annual Meeting, Chicago, IL, 1994.

M.A. Schen, *Results of the May 1994 NIST/IPC/OIDA/SRC Workshop on Electronics Packaging and Interconnection*, NIST- SANDIA Workshop on Concurrent Design of Advanced Interconnect Technology, Amelia Island, FL, 1994.

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

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

M.A. Schen, G.T. Davis, F.I. Mopsik, W. Wu, W.E. Wallace, J.R. Manning, C.A. Handwerker, and D.T. Read, *Electronics Packaging Materials Research at NIST*, Electronic Packaging Materials Science VIII Symposium, Materials Research Society, San Francisco, CA, Spring 1995.

M.A. Schen, *Packaging Priorities and Materials Implications*, SRC Topical Review Conference, University of Texas/Austin, September 1995.

Moisture Effects in Electronic Packaging Resins: Physical and Mechanical Properties

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Objectives

The objective is to improve the ability of the designers of electronic packaging to account for the presence of moisture in predicting performance during manufacture and use. Data will be generated to advance the development of a hygrothermal model of the stresses in a typical chip package.

Accomplishments

Experiments are underway to measure mass uptake, volume change and diffusion coefficient of filled and unfilled epoxy resins used in electronic packaging applications as a function of temperature and relative humidity. Additionally, the impact of moisture content on the viscoelastic response of the epoxy over

a range of temperatures will be characterized. A pressure vessel developed previously and modified to accept humidity-proof LVDTs is being used for the strain measurement on the packaging epoxy resin. This system will be used for multi-step creep compliance evolution of the cured epoxy at different aging times under a variety of humidity-temperature conditions at atmospheric pressure. Thin films of bubble-free epoxy are required in order to achieve rapid equilibrium sorption. Reasonably good films have been cast onto smooth FEP surfaces.

In sorption experiments, time dependent weight changes are measured to calculate the diffusivity coefficient by solving an inverse problem in which unknown parameters (e.g., diffusivity) in the partial differential equation (diffusion equation system) are found. A computer code for the inverse problem is being developed to take account of the uncertainty in the usual one-dimensional diffusion approximation with simple initial and boundary conditions. Using an extended set of unknown parameters in the partial differential equation system describing the small molecule sorption behavior, we can also probe the possibility of non-Fickian diffusion, dual mode sorption, and non-instantaneous equilibrium at the polymer-plasticizer fluid interface often reported in the literature.

Moisture Effects in Electronic Packaging Resins: NMR Investigation of Moisture Distribution in Packaging Resins

D.L. VanderHart

Objectives

Moisture absorbed by electronic components encapsulated in polymeric packaging materials often leads to cracking or "pop-corning" at solder reflow temperatures. Moisture can also lead to weakened interfaces, delamination and subsequent corrosion of the integrated circuit and its connections. The objective of this project is to provide information about the distribution of water in filled and unfilled epoxy resins to enhance the understanding of moisture-induced cracking in plastic encapsulated electronic components.

Accomplishments

Nuclear magnetic resonance techniques are used to study the presence of moisture and its distribution in filled and unfilled epoxy resins used as electronic packaging materials (EPM). Such resins are usually highly filled with silica in order to reduce the thermal expansion coefficient and thus reduce the high stresses associated with thermal cycling. Therefore, characterization of moisture in these materials is not only a problem of understanding absorption in the bulk phase of the matrix material but also a problem of understanding the behavior of water at the interfaces.

The hypothesis we are pursuing in our work is that, in contrast to the pure epoxy, there are 'voids' along the interfaces in the composites which voids could serve two functions: a) more water than would be absorbed by the matrix could be present, especially at high relative humidities and b) a path of lower resistance than expected would be available for transporting water to the large internal surface between the package and the encapsulated electronics. Failure of the EPM during soldering is often accompanied by bulging and separation at this large interface. Note that the package is already under stress because of the differences in thermal expansion coefficients between the package and the encapsulated materials. It is,

therefore, not only the vapor pressure of water at that interface which helps to drive the separation, it is also the rate of transport of water to this interface which would be important in maintaining a high vapor pressure during the soldering operation.

For the NMR characterization, we hope to key on the idea that the chemical shift of water in the composite is an indicator of its average environment. Water molecules, over the millisecond time scale of our experiment, may visit many different kinds of sites. Thus the chemical shift should correspond to the average shift over these many sites. For a given temperature and a given water-to-matrix weight ratio, any difference in the chemical shift of water between the composite and the pure matrix material would be an indication of a change in the distribution of available sites for water. Then, to the extent that such a chemical shift difference would be characterized by a shift, for the composite, closer to the shift for bulk water, one could surmise that water was seeing voids.

At this preliminary stage in our work, the experimental work on EPM is just beginning. A bottleneck has been obtaining composite samples representative of the industrially relevant materials along with the proper control samples. We have only looked at one system, namely, a polyimide (BTDA-ODA) filled with 30 weight percent silica. This composite seems to take up about twice as much water as gravimetric studies indicate is true for the pure matrix material and its chemical shift is significantly closer to that of bulk water than was true for a saturated sample of DGEBA-MPA epoxy. These are preliminary but promising results in support of the hypothesis; however, we expect much more concrete results in FY96.

A paper was completed and published in FY95 in which proton NMR was used to characterize water in a pure epoxy consisting of DGEBA and metaphenylenediamine. In this paper, the chemical shift of water in epoxy samples of various water contents was measured and from those measurements, it was concluded that in the epoxy the number of voids which could contain several water molecules was insignificant. In other words, the fraction of time a water molecule spends participating in multiple hydrogen bonds, i.e. in a 'bulk-water' environment, is very small. In this study, we also performed a couple of experiments designed to reveal heterogeneities in crosslink density and these were not found. Thus, the picture that emerges is that water is uniformly and molecularly dispersed; moreover, it has sufficient mobility at 70°C to generate a rather sharp resonance (implying that its lifetime at any hydrogen-bonding site is much less than 1 μs). Finally, the higher the concentration of the water, the more freedom of motion each water molecule has. This means that there is more rotational freedom at each site and/or greater translational displacement per unit time. Or said negatively, it is incorrect to assume, based on an assertion that the free volume available to water is independent of the concentration of water, that the diffusion constant for water ought to be Fickian.

Outputs

Publications

R.J. Schadt and D.L. VanderHart, *Solid-State Proton NMR of a Glassy Epoxy Exposed to Water,* Macromolecules 28, 3416 (1995).

POLYMER BLENDS AND PROCESSING PROGRAM

Goals

Applications of polymer blends and alloys have enjoyed steady growth over the last decade in terms of market share, consumption and employment within the plastics industry. Polymer blends constitute over 30% of polymer consumption and over the past ten years have shown an annual growth rate of 9%, which is four times the growth rate of the polymer industry as a whole. This growth has challenged materials suppliers to respond quickly to customer needs by reducing their new product development cycle. In assessing these requirements, a 1992 article in *Plastics Technology* expressed the need in the 1990's to "scientifically understand ways to compatibilize resins and create predictable stable morphologies", in contrast to the largely unsuccessful trial and error "empirical blending frenzy" of the 1980's.

The NIST Polymer Blends and Processing Program began its efforts in the mid-1980's with clear scientific goals to establish expertise in static and kinetic aspects of phase behavior in polymer blends, effects of shear flows on mixing and demixing, and reactive processing to promote compatibilization. Recent programmatic objectives are to use the knowledge base and measurement expertise to develop tools needed by industry to process polymer blends more effectively. Accordingly, the program initiated development of measurement methods using fluorescence, light scattering, neutron scattering, and microscopy to aid in monitoring polymer blend processing. In addition, two NIST/Industry Consortia have been established to facilitate interactions in the areas of polymer blends and processing.

The objective of the first consortium is to develop new measurement techniques based on optical methods to monitor important polymer processing parameters. Two areas of measurement development are being stressed in this program: real-time measurements of polymer rheology and temperature. Our industrial consortium partners are: 3M Co., Dow Chemical Co., DuPont Co., Rohm and Haas Co., and Dynisco (Flow Vision).

The second consortium is in the general area of polymer blends, and includes: Aristech Chemical Corp., Armstrong World Ind., Inc., Goodyear Tire & Rubber Corp., Raychem Corp., Rohm and Haas, Sandia National Laboratories, 3M Company. In addition Exxon participates through a separate CRADA. Work in this consortium during the past year focused primarily on *in-situ* characterization of mixing/demixing processes by shear and on interfacial modification and blend compatibilization by graft or block copolymers. Collaborative efforts with individual consortium companies serve to transfer the NIST expertise and capability in measurement technology as well as to provide an emphasis on issues of practical importance to industry.

FY-95 Significant Accomplishments

- Phase diagrams were determined for a pure blend of polystyrene and polybutadiene and also with block copolymers added over a wide composition range. Measurements on the effects of added diblock copolymer in a blend demonstrate suppression of the phase separation temperature.

- Model compatibilizers of block, graft, and random copolymers were synthesized for miscibility/ compatibility studies with the newly acquired Haake mixer/extruder. Mixing studies on the polystyrene/polyethylene oxide systems have begun.

- The formation of a copolymer layer by transesterification in the interfacial region surrounding phase separated polycarbonate and polymethyl methacrylate rich droplets have been characterized in thin film blends by a combination of neutron reflectivity and atomic force microscopy.

- It was demonstrated that dielectric relaxation spectroscopy can be used to characterize different phase morphologies resulting from transesterification in reactive polymer blends as a complement to previous neutron scattering studies. Conversely, polymer blends with different phase morphology can provide various dielectric characteristics which could be important for electronic packaging applications.

- A new cell was designed and constructed which is suitable for small angle neutron scattering, light scattering, and birefringence experiments on the influence of pressure on order-disorder transitions in block copolymers and phase behavior for polymer blends.

- Temperature jump experiments were implemented on the small angle neutron scattering facility.

- Fluorescence band broadening in perylene has been used for fluorescence based temperature measurements up to 290°C. The technique was demonstrated in real-time during extrusion of polycarbonate doped with perylene.

- In-line, real-time temperature measurements have been made during extrusion for carboset resin (a poly(methyl methacrylate) copolymer) doped with bis-pyrene propane (BPP) and polycarbonate doped with perylene.

- Pressure coefficients have been obtained for the temperature dependence of both BPP and perylene using an IR radiometer as a reference.

- Temperature profiles in a laboratory experiment have been measured using an optical technique.

- In-line, real-time operation of the polarizing optics sensor for measuring fluorescence anisotropy was demonstrated.

- In collaboration with Dynisco a pressure/optical sensor which can be used to measure fluorescence and pressure simultaneously was developed.

- Consortium members have initiated preliminary studies utilizing the shear light scattering and microscopy equipment.

- The NIST-developed temperature measurement technologies based on fluorescence are being adopted by

consortium members. 3M is using the technology in process modeling laboratories and Du Pont is working with NIST on the extensions to temperature profile measurements.

- Two meetings of the Polymer Blends Consortium were held in October 1994 and June 1995. Industrial members from Raychem, Goodyear and Aristech presented talks as did NIST members. An interactive discussion of the processing of blends and the new extruder capabilities at NIST was held with the member companies.

Polymer Blends Consortium - Interfacial Modification by Block Copolymers

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Objectives

Work in the polymer blend consortium focuses on the physical and chemical modification of phase-separated multicomponent interfaces to better understand the compatibilization and stabilization of blends. The project develops characterization techniques and analysis methodology for the interfacial properties of multiphase systems and transfers this measurement technology through joint projects with member companies. The ultimate goal is to help shorten the process development cycle in the polymer blends and alloys industries.

Accomplishments

In-situ studies of blend morphology are made through thermodynamic and kinetic studies of phase separation using both quiescent measurements and steady shear measurements. Techniques include small-angle neutron scattering (SANS), temperature jump light scattering (TJLS), shear neutron and light scattering, shear optical microscopy and optical and transmission electron microscopy. Measurement techniques are combined with shear flow, when possible, to more closely simulate processing conditions.

The kinetics of phase separation in a model system of polystyrene-d8 (PSD, M_w = 1000 g/mole), polybutadiene (PB, M_w = 5000 g/mole) and a symmetric PSD-PB diblock copolymer (M_w = 10,000 g/mole) has been studied extensively by TJLS. The coexistence curve was measured for the pure blend and the critical temperature was 51 °C at a composition of 75% PSD. Upon addition of block copolymer, a linear shift in the phase boundary with diblock copolymer content was observed, as shown in Figure 1. In addition, the rate of phase separation decreased greatly and the exponent of the power-law time dependence of $I(q_m)$ varied from 3 for the pure

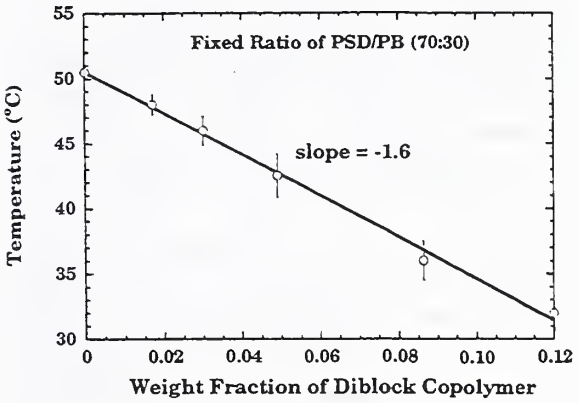

Figure 1 - Shift in Phase Boundary with Diblock Concentration

blend to 1 for the blend with 8.6 wt. % diblock copolymer. An additional slowing down was observed for deeper quenches as the T_g is approached within 20 °C. The T_g of the PSD-rich phase at this composition was ~10 °C.

The morphology of the blend was studied by transmission electron microscopy at a constant quench depth (ΔT = -1.6 °C) for blends (70 PSD:30 PB) containing up to 8.6 % diblock. The PB phase was stained dark using osmium tetroxide. For the pure blend, PB-rich domains of sizes between 0.5-2.0 μm were observed in a matrix of almost pure PSD. As block copolymer was added, the PB-rich domains became more dispersed and at 8.6 % diblock a very finely dispersed morphology was observed. The results appear to be consistent with compatibilization, and further TEM studies are planned to capture the morphology at an earlier stage in the phase separation process.

The capability of *in-situ* characterization using light scattering and optical microscopy on an extruder has also been added recently.

The introduction of diblock copolymers, having the same chemical composition as the homopolymers, to polymer blends is shown theoretically to lead to shifts of the phase boundary of blends depending on the molecular weight asymmetry of the diblock copolymer. A general tendency of asymmetric block copolymers to destabilize the blend phase stability (increase the critical temperature of the upper critical solution temperature) and symmetric copolymers to stabilize blends is found. The asymmetry of the blend homopolymer components, however, is indicated to be qualitatively unimportant factor in this stabilization-destabilization effect. Recent measurements on the shift of the phase boundary in a polystyrene-polybutadiene blend with diblock PS-PB additive which is nearly symmetric in the block molecular weights shows a stabilization effect in accord with theoretical calculations.

Outputs

Publications

L. Sung and C. C. Han, *Light-Scattering Studies on Phase Separation in a Binary Blend with Addition of Diblock Copolymers*, J. Polymer Sci.: Polym. Phys. Ed., Special Issue (1995).

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Interfacial Characterization and Phase Separation in Thin Film Polymer Blends and Block Copolymers

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Objectives

This study characterizes the interface between polymer phases in thin film coatings and investigates the kinetics of phase separation in polymer blends using state-of-the art neutron and x-ray reflection and optical and atomic force microscopy techniques. We investigate the interfacial activity of block copolymers in stabilizing the morphology of dispersed polymer phases. This project is aimed at quantifying phase separation and microphase separation of polymer blends and the interfacial activity of block copolymers in thin film coatings.

Accomplishments

Characterizing the interface between phase separated polymers in the form of thin film coatings is a difficult task due to the requirement of a high resolution technique to probe the interface. There is however significant interest in obtaining quantitative information on these systems. In addition, the interfacial activity of block copolymers in polymer blends is poorly understood. Issues related to changes in blend morphology, coalescence and changes in interfacial tension upon addition of block copolymer are technologically important in thin film coatings.

A combination of non-destructive high resolution techniques are used to profile depthwise the longitudinal distribution of phase separating polymer blends and microscopy techniques to characterize the transverse distribution. The depth profiling techniques include x-ray and neutron reflectivity while lateral scanning techniques include reflection optical microscopy and atomic force microscopy. The internal spatial distribution of blend components normal to the surface is obtained by specular neutron reflectivity. Phase separation is characterized by a "roughening transition" of the air surface measurable by x-ray reflectivity while the kinetics of phase separation is readily monitored by optical microscopy. Changes in blend film morphology as it affects surface composition is characterized by atomic force microscopy.

Phase separation was studied in thin films of two blend systems, one which exhibits a lower critical solution temperature (deuterated polystyrene/ polyvinylmethylether) (dPS/PVME) and another which exhibits an upper critical solution temperature (deuterated polystyrene/ polybutadiene) (dPS/PB). For both blend systems we utilize x-ray and neutron reflectivity and reflection optical microscopy as well as atomic force microscopy to examine phase separation in thin films of two component blends. Phase separation is found to be accompanied by topographical changes at the free polymer/air interface that reflect the underlying spinodal decomposition process within the film. This phenomenon was observed in systems where the same component segregated to the vacuum and substrate interfaces. In the dPS/PVME system, blend films with composition ranging between 0% and 100% dPS were investigated. The surface roughening phenomena was found to occur at all compositions. The magnitude of the interfacial tension relative to the surface tension is shown to set the size scale of the surface features. The observed structures are consistent with the aspect ratio estimated by

balancing the reduction in free energy from decreasing the coexisting phase contact area with the excess free energy due to increasing the polymer-vacuum interfacial area.

The kinetics of phase separation in thin film blends of deuterated polystyrene (dPS) and polybutadiene (PB) on a silicon substrate was examined by optical microscopy of the free polymer-air interface. Phase separation within the film induces pattern formation at the free boundary as in the dPS/PVME. The characteristic scale R(t) for the intermediate and late stage phase separation patterns is determined by Fourier transformation of the optical data. Importantly, the thickness range of the films is chosen small enough (thickness, L < 1000 Å) to suppress the development of surface directed concentration waves, but large enough so that a crossover from three-dimensional bulk-like to near two dimensional (thickness ~ 200 Å) phase separation kinetics can be observed. The

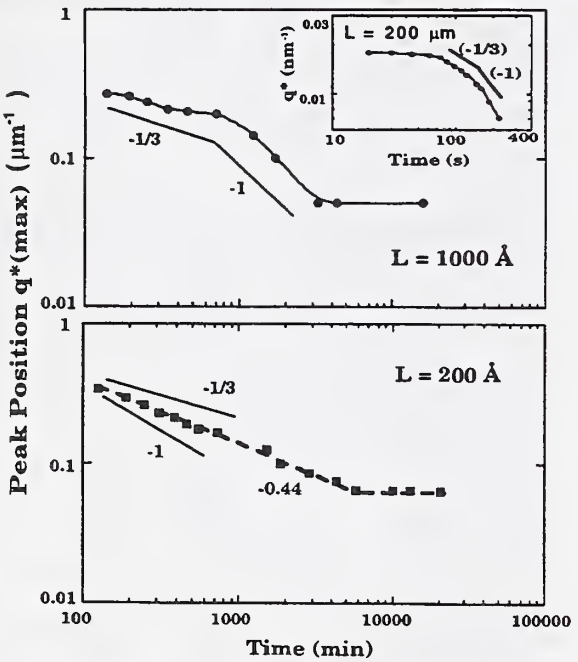

Figure 2 - Log-log plots characteriing the scale of the coarsening surface pattern in the thin and thick film, as compared to the bulk (inset).

exponent n, characterizing the coarsening ($R(t) \sim t^n$) in the viscous hydrodynamic regime, is found to equal 1.0 and 0.44 in the 1000 Å and 200 Å films, respectively (Figure 2). These observations are consistent with a dimensional crossover in the late stage phase separation kinetics. At a still later stage in the phase separation process the bicontinuous surface pattern breaks up and the pattern scale "pins;" an effect which seems to be associated with the finite film thickness. The addition of even 1% of a diblock copolymer of PS-PB to the blend dramatically slows down the kinetics of the process. The mechanism for this strong effect remains to be further investigated.

Outputs

Publications

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The Effect of Crosslinking on the Phase Behavior of Blends

Barry J. Bauer and Da-Wei Liu

Objectives

It is necessary to determine the effects of synthetic variables on the morphology of interpenetrating polymer networks (IPNs) for the purpose controlling the important physical properties. IPNs are commercially important types of blends that have many physical properties not available in standard polymers. The properties are dependent on the two phase morphology that develops during the polymerization process. Knowledge of the relationship between the synthetic variables and the resultant morphology will allow control of the physical properties.

Accomplishments

Small angle neutron scattering, small angle x-ray scattering, and transmission electron microscopy have been used to characterize the morphology of IPNs made by a wide variety of synthetic procedures. IPNs of organic-organic and organic-inorganic types were synthesized varying the relative rates of the two polymerizations, grafting between the phases, and crosslink density.

It has been demonstrated that many distinct morphological types can be obtained from the same set of ingredients by controlling factors such as relative polymerization rates and grafting reactions between the

components. Generic rules have been developed that apply to IPNs made by many chemistries.

In organic/inorganic IPNs made from an inorganic phase of SiO_2 formed by sol-gel chemistry and an organic phase made by polymerization of acrylates or methacrylates, four distinct morphologies can be made from the same polymers. When grafting between the phases is suppressed and the acrylic polymerization is much more rapid than the sol-gel reaction, a grossly heterogeneous structure results. When the sol-gel reaction is more rapid, a finely divided morphology results with interfacial mixing between the phases. Under conditions where the rates are similar, dendritic structures result. When the grafting reaction between the phases is promoted, phase separation is much weaker, and entirely suppressed in some cases.

IPNs made from SiO_2 and epoxies can be made by sequential or simultaneous polymerizations. The sequential polymerizations give strongly phase separated morphologies with broad interfacial areas between the phases. The simultaneous polymerizations inhibit phase separation yielding single phase materials.

IPNs made from two different polymers are destabilized with respect to blends of the same materials. Increased crosslink density causes phase separation in IPNs made from polymers that are miscible as simple blends. This is true for both semi and full IPNs

Linear chains in polymer networks are seen to diminish in size with increased crosslink density until they collapse into aggregates, even at extremely low linear chain concentrations. Such instabilities affect the homogeneity of polymer networks.

Phase diagrams have been established for the polymerization of styrene-divinyl benzene into a network. The system is treated as pseudo-ternary, made up of monomer-sol-gel. Previous work that measured the size of an individual chain in a network can now be extended to measure the size of a chain in a partially formed network to determine when the shrinkage and aggregation of the chains occur.

Outputs

Publications

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The Compatibilization of Polymer Blends by Strong Interactions and Reactions

Alamgir Karim, Jack F. Douglas, Yi Feng, Bradford J. Factor, Frederick I. Mopsik, and Charles C. Han

Objectives

Chemical reactions such as transesterification play an important role in many commercially important blend processes. Strong physical interactions such as hydrogen bonding and ion complexation are also important from an industrial perspective for their influence on the stability of polymer blend mixtures. We investigate these effects with the ultimate goal of creating polymer blend materials with controlled morphology and stability through precise control of relevant molecular parameters.

Accomplishments

It is usually difficult to produce thermodynamically stable polymer blends of high molecular weight polymers, since the entropy of mixing for these systems is very small because of chain connectivity. As a consequence, commercial blends are often prepared in a nonequilibrium state by mechanical mixing. It has long been appreciated that these mechanically mixed systems may be compatibilized by adding copolymers having the same chemical composition as the homopolymer blends. However, one difficulty that arises with this approach is that the copolymers do not easily reach the interface in a reasonable time because of their high viscosity. Thus it can be advantageous to produce copolymer *in-situ* by a chemical reaction between the blend components. Alternatively, it is possible to promote compatibilization through strong interaction between the blend components. We investigate these two approaches.

We study using neutron reflectivity the interfacial development of structure in bilayers of polymers which are compatibilized by strong interactions. A combination of neutron reflectivity and atomic force microscopy are used to characterize the growth of a transesterified layer and associated coalescence of droplets respectively. Transesterification in the bulk was characterized by dielectric spectroscopy. The interfacial structure and kinetics of mixing of two polymers that exhibit strong exothermic heats of mixing, poly (N,N' - dimethylethylene sebacamide) (mPA) and the Lithium-salt of a lightly sulfonated polystyrene ionomer containing 7.4 mol% sulfonate groups (Li-SPS), were characterized by neutron reflectivity measurements. Blends of Li-SPS and mPA are miscible below *ca.* 150 °C as a result of the formation of an ion-dipole complex between Li^+-sulfonate and amide groups. Neutron reflectivity measurements were carried out on spin-coated bilayers of the polyamide and a deuterated sample of the ionomer. The films were annealed for various lengths of time at 96 °C, which is above the melting temperature of the mPA (T_m=75 °C), but below the glass transition temperature of the ionomer (T_g=120 °C). The interface between the two films exhibited an asymmetric concentration profile

due to a large viscosity mismatch between the two polymers, since the polyamide was in its melt state and the ionomer was a glass. The interfacial mixing kinetics could not be explained by either strictly Fickian or Case II diffusion. A kinetic model that combines Fickian diffusion with a suppression of mobility due to intermolecular crosslinking adequately represents the experimental data.

The phase separation of the reactive blend polycarbonate (PC) and deuterated poly methylmethacrylate (PMMA) was found to be significantly different than in unreactive thin film blends. Samples annealed at 180 °C where the transesterification reaction occurs slowly show a conventional spinodal decomposition process at earlier stages, but the late stage coalescence of droplets is found to be quite different from the usual coalescence process. Neutron reflectivity provides evidence for the block copolymer layer and the atomic force microscope (AFM) images reveal a strongly inhibited droplet coalescence in the late stage phase separation which is presumably due to the presence of the block copolymer. Apparently the spinodal decomposition process becomes arrested and the usual spinodal structure breaks up at a characteristic scale due to the reaction. The copolymer layer leads to an effectively emulsified layer of droplets which accords with findings of emulsified particles in reactive blends subject to vigorous flow conditions.

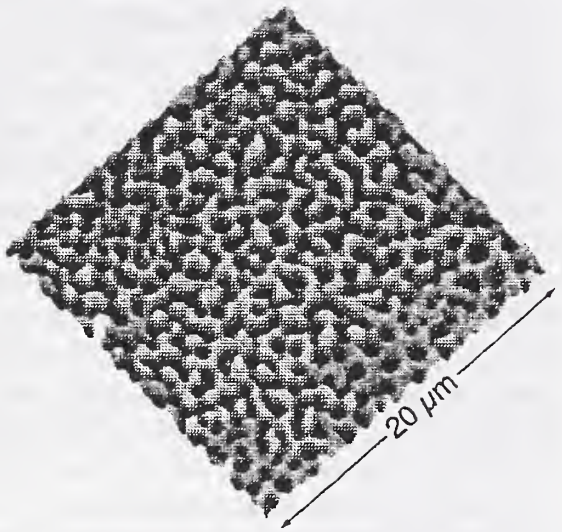

Figure 3 - AFM image of spinodal surface pattern formation in a thin film reactive blend sample at crossover stage between phase separation and transesterification dominated regimes.

Bulk mixtures of bisphenol A polycarbonate (PC) and poly - (oxymethylene-1,4-cyclohexylene methyleneoxyterpthaloyl)$_x$ - co -(oxyethyleneoxyterephthaloy)$_y$ (PET-PCHT) polyester copolymer with x:y = 64:36 were prepared. Bulk films of thickness approximately 0.3 mm were investigated by dielectric spectroscopy. Large changes in the dielectric constant, $\Delta\epsilon$ of PC / polyester mixtures are observed upon transesterification. Our measurements of $\Delta\epsilon$ permit a more comprehensive interpretation of specimen homogeneity than from a determination of T_g alone. In combination with the structural information from SANS, our results yield a consistent physical picture where $\Delta\epsilon$ increases or decreases as the phase structure becomes homogeneous or heterogeneous, respectively. Thus, the dielectric response can be effectively used to characterize phase morphologies.

Outputs

Publications

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Shear Mixing/Demixing of Polymer Blends

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Objectives

The development and application of measurement techniques for characterizing polymer blend behavior under shear flow is the primary goal of this work.

Accomplishments

The ultimate properties of polymer blends are related to the underlying morphology and microstructure of the materials. Polymer blend morphology, in turn, is strongly influenced by deformation history and the extent of deformation. Shear flow can also produce mixing or demixing behavior in polymers. This project seeks to quantify the relationship between polymer blend morphology and shear behavior and adapts the results for utilization in industrial processing equipment.

Instrumentation has been constructed for *in-situ* shear light scattering and shear small angle neutron scattering (SANS) measurements. Two light scattering instruments have been constructed with the second instrument also having phase contrast optical microscopy and fluorescence microscopy capabilities. Previously, shear effects on the phase behavior of polymer blends, semi-dilute polymer solutions, and block copolymers have been examined. This work includes the steady shear behavior of the materials as a function of temperature and shear rate, and the phase separation kinetics in homogenized systems following cessation of shear. Work has been initiated on three component compatibilized blends to examine the effects of compatibilizing agents on the shear behavior and subsequent morphology development.

The shear rate and temperature dependence of droplet break-up in a solution of a polymer blend [polystyrene (PS) and polybutadiene (PB) in dioctyl phthalate] and a low molecular weight polymer blend (PS and PB) have been examined by phase contrast optical microscopy and light scattering (Fig.4). The behavior is more complicated than the early predictions of droplet break-up proposed by Taylor and Tomotika. Besides regimes of droplet deformation (2 s^{-1} in Fig. 4) and breakup before homogenization, (20 s^{-1} in Fig. 4) at high shear rates and temperatures just within the two-phase region,a string-like phase has been observed (200 s^{-1} Fig. 4). The left hand column in Fig. 4 shows the light scattering patterns as a function of shear rate while the center column shows the corresponding microscopy pictures (flow direction horizontal). The right column shows the Fourier transform of the optical image and confirms the scattering patterns shown on the left. At high shear rates and temperatures

well into the two-phase region, small ellipsoidal domains with the long axis oriented normal to the flow direction instead of parallel to the flow direction have been also observed.

The phase separation kinetics of a pure

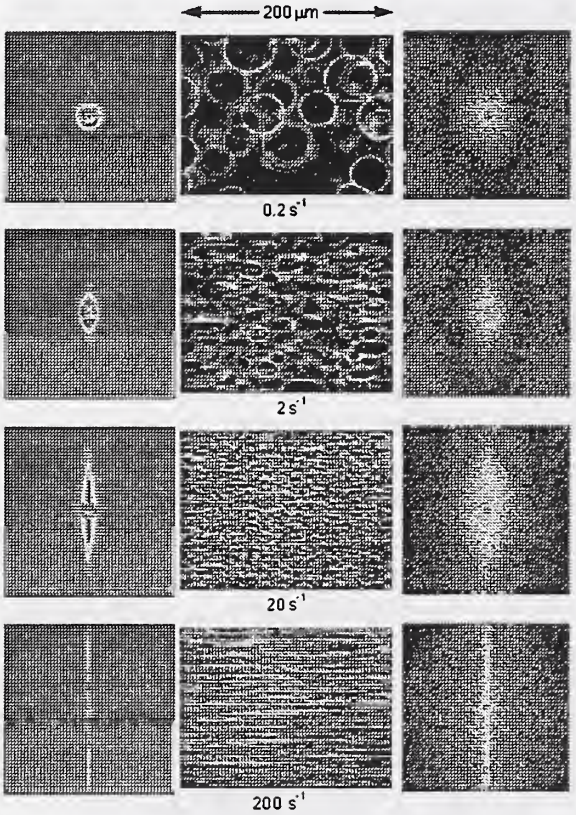

Figure 4

polymer blend during shear as a function of quench depth is in progress. Subsequently similar studies will be performed to examine the effect of block copolymer concentration.

Finally, the orientation of a liquid crystalline The fluorescence microscopy attachments have been utilized to examine the distribution of labelled polystyrene in a blend solution of the labelled polystyrene and polybutadiene in dioctyl phthalate. At low shear rates, droplets of the labelled polystyrene are observed under the fluorescence microscope. With increasing shear rate, the labelled polymer becomes uniformly distributed throughout the sample, indicating that along with droplet break-up, the concentration difference between the two phases decreases.

polymer solution in steady shear has been examined by SANS as a function of temperature and shear rate. Three different flow regimes were identified which were delineated by two critical shear rates, $\dot{\gamma}_1$ and $\dot{\gamma}_2$. These two critical shear rates correlate well with the first two characteristic relaxation times of a rodlike polymer in concentrated solution.

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Structure Change and Alignment of Block Copolymers under Shear

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[2]University of Alabama, Birmingham, AL
[3]University of Massachusetts, Amherst, MA

Objectives

To study the effect of shear on block copolymer morphology and the ordering temperature of these materials and gain insight into processing characteristics of commercially important thermoplastic elastomers.

Accomplishments

Using a combination of *in-situ* SANS in a couette shear cell in the melt and SANS and transmission electron microscopy on sheared and quenched specimens, the shear rate and temperature dependence of the order-disorder transition temperature and morphology of block copolymers are investigated.

A unique change is observed in the equilibrium morphology of a cylindrical triblock copolymer of polystyrene-d8(PS)/polybutadiene(PB) /polystyrene-d8 through the application of steady shear near the order-disorder transition temperature, T_{ODT}. The change observed in the size and

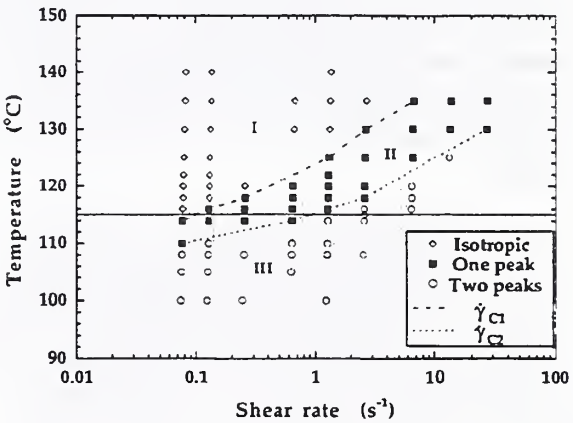

Figure 5 - Shift in the ordering temperature, $\dot{\gamma}_{C1}$, with shear rate for a triblock copolymer. Solid line shows the rheologically determined ODT temperature.

packing symmetry of the microphase separated cylinders is akin to "martensitic transformations" observed in metals. Also observed is a large shift in the "ordering temperature" of the block copolymer during shear. A scaling argument is used to

successfully treat the data as well as data published in the literature. The universality of this scaling approach will also be investigated with other copolymers as research in this area continues for new samples of a cylindrical diblock copolymer, a lamellar triblock copolymer, and a lamellar diblock copolymer. The samples have been synthesized and initial characterization of the quiescent microstructure in cast films was done with optical microscopy and TEM.

Outputs

Publications

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Polymer Processing Consortium, Sensor Development

Anthony J. Bur and Kalman Migler

Objectives

The objective of this consortium project has been the development of optical based sensor technology to measure, nondestructively and in real-time, polymer processing parameters. The sensor technology is based primarily on fluorescence spectroscopy and is designed to monitor rheology and temperature of polymer resins during processing.

Accomplishments

The U. S. polymer processing industry needs improved in-line, real-time measurement technology for processing and manufacturing polymer products. This need has arisen because of increased marketplace demands on the performance of polymer products and because of increased international competition. Tighter controls on processing conditions, improved characterization of resins during processing in conjunction with process models are needed to improve performance and increase productivity.

Fluorescence spectroscopy and optical fiber cables, which are inserted into process equipment using existing instrumentation ports, are the main tools that are being used to attain the measurement objectives. Temperature sensitive fluorescent dyes, doped into the polymer resin at parts per million concentration, are used to obtain resin temperatures. This method of measuring temperature is superior to using thermocouples because the thermocouple measurements can yield the temperature of the processing machine, rather than that of the resin. Measurements of temperature profiles across resin flow lines are also being developed using fluorescence and focusing optics.

A project goal of the past year has been to find temperature sensitive fluorescent dyes which survive at high temperatures (300 °C) without degrading. One such dye is perylene which, when doped into polycarbonate, displays stable fluorescence spectra at 290 °C for 10 hours. Considering that most processing is carried out on the order of 10 minutes, perylene is an excellent candidate for temperature monitoring at high temperatures.

The need for improved real-time temperature measurements can be demonstrated by observing the effect of shear heating during extrusion. A single screw extruder was instrumented with an optical fiber sensor placed in a standard 12.7 mm diameter (1/2") instrumentation port and with a thermocouple as illustrated in Figure 6. The optical fiber is a bundle of 100 μm diameter fibers half of which go to the light source while the other half transmit the fluorescence light to the detector. In

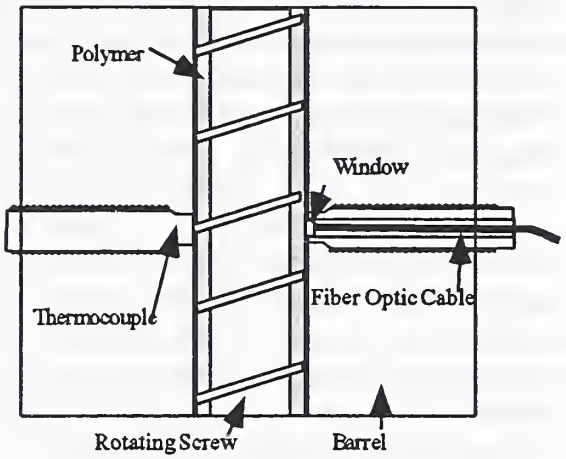

Figure 6 - The barrel of an extruder is shown with standard instrumentation ports containing a thermocouple and a fiber optic sensor. The design of the fiber optic sensor is such that it can access the extruder via existing ports.

Figure 7 is shown a plot of temperature versus time for both thermocouple and fluorescence temperature measurements during the extrusion of polymethylmethacrylate doped with bis(-pyrene) propane. During this experiment the extruder screw rpm was increased from 0 to 20 to 60 and back to 20 rpm as indicated. It is seen that the temperature measured by the thermocouple does not respond to the change from 0 to 20 rpm and

shows an increase of only 2 °C for the change to 60 rpm, whereas the overall change in temperature due to shear heating as measured by fluorescence was 20 °C. Clearly, the fluorescence measurement, which reflects the true temperature of the resin, is needed in order to properly describe the shear heating effect.

The fluorescence temperature measurements shown in Figure 7 are averages over the depth of view of the sensor which, in this case, is the thickness of the resin. During extrusion, the maximum shear occurs at the interface between the screw flight and barrel creating a hot spot in that area. Thus, the temperature distribution is not uniform. In order to fully characterize the thermal condition of the resin it is necessary to obtain the temperature profile. To do this, optical elements are designed which focus light to the point of measurement. By moving the position of focus over the thickness of the resin, a temperature profile can be obtained. Confirmation of this technique has been demonstrated in the laboratory and the sensor design for real-time measurements of temperature profiles is being carried out.

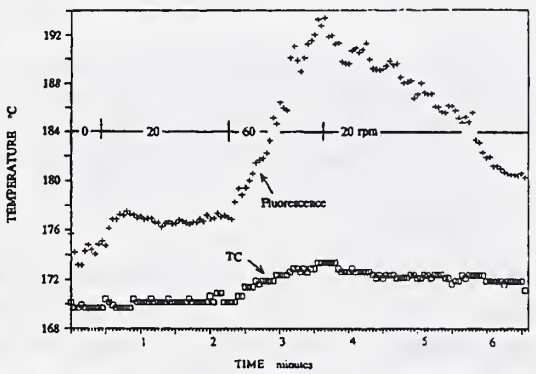

Figure 7 - Temperature is plotted versus time for an extruder run at 0, 20, 60 and 20 screw rpm. Temperature measurements were obtained from a fluorescent dye and a thermocouple (TC). The data shows the effects of shear heating.

An optical sensor which utilizes polarizing optics has been designed, constructed and successfully used to obtain real-time measurements of fluorescence anisotropy during extrusion of polycarbonate doped with perylene. The anisotropy sensor was placed in a slit die rheometer which was positioned at the exit of a single screw extruder. In addition to the anisotropy sensor, the rheometer contains instrumentation ports for pressure and fluorescence temperature measurements. Flow rate measurements are also made by weighing the extrudate. Measured anisotropy will be correlated to molecular orientation, and therefore to the magnitude of stress applied to the flowing resin during extrusion. The rheometer is being used to obtain a stress/anisotropy calibration function.

Modeling the response of the fiber optic sensor, used to monitor polymer injection molding, has been carried out. The sensor was used for light transmission and fluorescence measurements during injection molding of polyethylene, polypropylene and polystyrene. The data were analyzed by constructing a model of light transmission and fluorescence detection in crystallizing or glass forming resins. The calculations yield information about the time of crystallization and glass formation, the effects of pressure on crystallization kinetics, the thermal resistance at the resin/mold interface, and volume relaxation in a quenched glass forming resin.

Outputs

Publications

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Characterization of Polymer Blends during Processing

Barry Bauer, David Johnsonbaugh, D. W. Liu, and Kalman Migler

Objectives

We plan to transfer the technologies of light scattering and microscopy from the laboratory environment to the processing environment. This will enable us to carry out real time characterization of structure and morphology of polymer blends during mixing/extrusion. We are synthesizing and testing a variety of model compatibilizers to assess their relative merits in stabilizing immiscible polymers.

Accomplishments

Blends of immiscible polymers often require the addition of a polymer that improves the dispersion and adhesion of the phases. Such "compatibilizers" are widely used but poorly understood in the manufacture of polymeric materials.

The processing of polymer blends involves the application of complex shear, temperature and pressure profiles to polymeric resins. While most experiments isolate these effects in controlled laboratory conditions, we need to understand the mixing and morphology under actual processing conditions.

Optical microscopy and light scattering are useful tools in the characterization of polymer blends. Recently, the Polymer Blends Group developed an instrument for real time microscopy and light scattering in simple shear flow. The next step is to transfer this technology onto a laboratory scale polymer processing device. This will allow measurements of how actual processing conditions affect the morphology, the mixing and the phase behavior. Furthermore real time measurements of the effects of model compatibilizers in the processing of polymer blends will be carried out.

To test the relative advantages of compatibilization strategies, a variety of model compatibilizers were synthesized. The mixer/extruder will be used to test these compatibilizers in mixtures of immiscible polymers. Both on-line testing, via the microscope and light scattering apparatus, as well as off-line testing, via physical properties and scanning electron microscopy will be employed. The model system chosen includes polystyrene (PS), poly(methylmethacrylate) (PMMA), poly(methacrylic acid) (PMAA), and poly(ethylene oxide) (PEO).

The design and construction of the slit die / optical flow cell was completed. The die features an open optical pathway through the slit which allows either light scattering or optical microscopy to be carried out. The die is temperature controlled through cartridge heaters located in the body. The width of the die is adjustable between 0.2mm - 1.0mm. There is a bypass valve which allows adjustment of the flow rate of polymer through the slit. Also completed is the optical setup which features both phase contrast microscopy and light scattering. Switching from one mode to the other is carried out via translation of an optical element.

Quantities of PMMA-g-PS, PMMA-r-PS, PMAA-g-PS, and PMAA-r-PS (g, r designate graft and random, respectively) have been synthesized and blended into mixtures of PS and PEO. This will elucidate the relative merits of two important compatibilization strategies, graft vs random and weakly vs strongly interacting. Small angle neutron scattering has proven that the combination PMAA-PEO has a much stronger interaction than PMMA-PEO. Blends have been made with and without these four compatibilizers and characterization is underway. Preliminary results indicate that the compatibilizers modify the resultant morphologies, giving better dispersions.

Pressure Dependence of the Phase Behavior of Polymer Blends

Kalman B. Migler

Objectives

The goal is to measure the effect of pressure and temperature on the thermodynamic behavior of polymer blends, including those with diblock copolymers.

Accomplishments

Polymers are typically processed under conditions of high temperature, pressure and shear. Temperature and shear can greatly affect the miscibility of polymer blends, but much less is known about the effect of pressure.

This project aims to make fundamental measurements of polymers and polymer blends under pressure, focusing on issues of miscibility, interaction parameters and radius of gyration. Experimental data are compared with existing theories to stimulate the creation of new theoretical models. The data are used to understand the behavior of polymer blends in typical processing conditions. In order to maximize the materials and length scales which can be probed, complementary techniques of small angle neutron scattering, optical birefringence and optical cloud point measurements are used.

The construction and testing of the multi-use pressure cell was completed. (See schematic

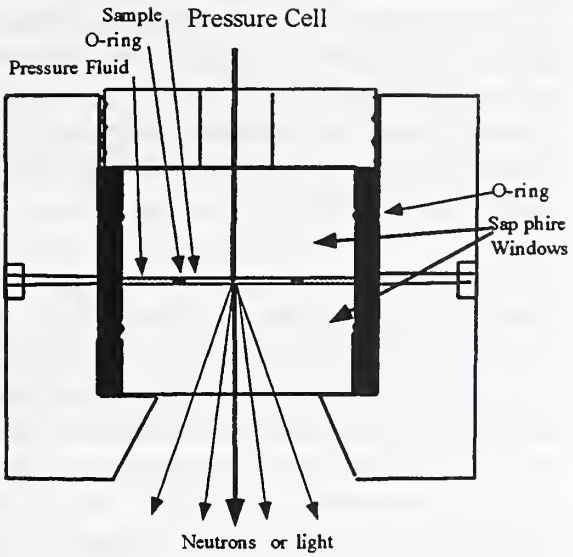

Figure 8 - Diagram of the pressure cell. The sample is contained within the o-ring that is sandwiched between the two sapphire windows. The pressure fluid squeezes the o-ring which pressurizes the sample.

in Figure 8) The pressure cell can withstand pressures to 100 MPa and temperatures up to 200 °C, which are typical processing conditions. The temperature and pressure controls are fully automated. The cell has been successfully tested in a preliminary run on the small angle neutron scattering facility. This experiment confirmed the enhancement of miscibility in the system polystyrene/ polyvinylmethylether.

Micellization of Model Ionic Graft Copolymers

C. L. Gettinger, C. L. Jackson, C. C. Han, M. Pitsikalis[1] and J. W. Mays[1]
[1]University of Alabama, Birmingham

Objectives

This project focuses on investigations of the solubility, thermodynamics and kinetics of the micellization process of model graft copolymers made up of neutral backbones and ionic grafts. The behavior of these materials are compared to that of similar linear copolymers in order to study the influence of structural architecture on the size and shape of micelles that form. These materials have potential applications in oil recovery, water treatment, and drug delivery.

Accomplishments

A series of model graft copolymers with polystyrene backbones and ionic grafts have been synthesized with varying molecular weights and grafting densities. These samples are being studied with techniques including dynamic light scattering (DLS), static light scattering (SLS), small angle neutron scattering (SANS), small angle x-ray scattering (SAXS) and transmission electron microscopy (TEM) in order to develop an understanding of how copolymer molecular weight, grafting density, relative volume fraction, and ion density affect the size, molecular weight and shape of the micelles that form in selective solvents.

Initial studies have focused on a copolymer consisting of a polystyrene (PS) backbone (M_W= 84,000 g/mole) with approximately 3 grafts of the sodium salt of polymethacrylic acid (PMANa) (M_W = 26,000 g/mole). This copolymer was dispersed in a 80/20 (v/v) water/tetrahydrofuran solvent and formed micelles that are approximately 120 nm in diameter as measured by DLS. In figure 9 a TEM micrograph of a precipitated sample of this copolymer is shown. In the photograph, the micelles are spherical and appear relatively monodisperse in size. In their solid form, the micelles are about 20-40 nm in diameter.

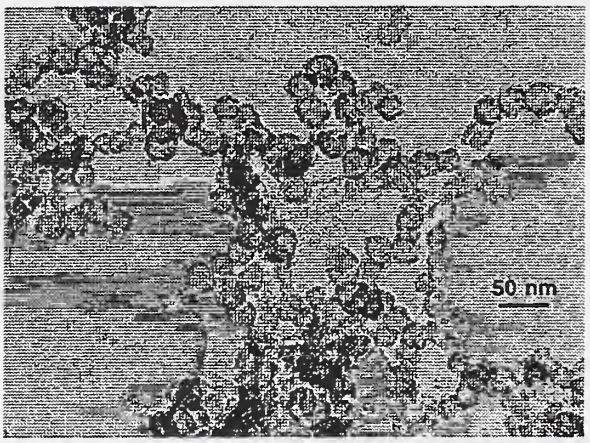

Figure 9 - TEM micrograph of graft copolymer PS-9-PMANa precipitated from 80/20 water/THF

Future experiments involve characterizing the molecular weight and shape of the micelles and measuring the interactions between the micelles using SANS. Of particular focus is the dependence of these measurements on changes of solvent, ionic strength and charge density.

Outputs

Publications

C. L. Gettinger, C. L. Jackson, C. C. Han, M. Pitsikalis and J. W. Mays, *Micelles Formed by a Model Ionic Graft Copolymer,* Polymer Preprints, in press.

Interactions between Ion Containing Polymers

Eric J. Amis, Brett D. Ermi[1], and Diane E. Valachovic[1]

[1]University of Southern California, Los Angeles, CA

Objectives

This project focuses on the physics of dynamic interactions between charged macromolecules in aqueous solution and in media of varying dielectric constant. The goal is to provide unique experimental methods and data which will lead to molecular interpretations for the unusual behavior which characterizes the structure and dynamics of polyelectrolyte solutions.

Accomplishments

Because of their significant scientific and technological importance, polyelectrolytes have been the focus of decades of theoretical and experimental efforts. Even so, there is still no clear molecular interpretation of many of their fundamental properties. In salt-free polyelectrolyte solutions, the presence of a dynamic attractive interaction between highly charged chains has been demonstrated. The resulting "dynamic domain structure" is interpreted as arising from a coupling between polyion and counterion motion. In order to clarify the molecular interpretation several special polymer types have been used to control chain conformation, charge density, backbone solvation, and hydrophobic interactions.

Static and dynamic light scattering has been used to investigate well characterized polyelectrolyte solutions including carboxylated poly(amido amine) half-generation dendrimers titrated to varying charge fractions in aqueous solutions and poly(N-methyl-2-vinyl pyridinium chloride) in solutions of varying dielectric constants. In all cases, under conditions of low concentration of added salt, these solutions show multiple diffusive relaxations in their dynamic light scattering correlation functions.

Dendrimers provide model polyelectrolytes as spheres which can be titrated by stoichiometric addition of base. By dynamic light scattering, a diffusive mode appears

which corresponds to that of the single dendrimer molecule. This mode is present throughout all degrees of charging including zero charge and in highly screened (high salt) solutions. For charged dendrimers in low-salt solutions a second slow diffusive mode appears which corresponds to a size of about 50 nm and agrees with the observation from the angular dependence of the scattering intensity. This slow mode, postulated as arising from coupled dynamic domains, was observed previously for linear polyelectrolytes but never before for non-entangling spherical macromolecules.

A recurring question in polyelectrolyte solutions is the quality of the solvent for the chain backbone in contrast to its quality for the charged polymer. In another unique experiment we made use to the fact that solvents with dielectric constants ranging from 37 (ethylene glycol and dimethyl formamide) to 182 (methyl formamide) are thermodynamically good solvents for poly(vinyl pyridine) and its quaternized polyelectrolyte analog. Since the neutral and the polyelectrolyte chains are both well solvated, the effects of charge interactions and charge screening can be investigated without the typical problem of phase separation of hydrophobic polymers dissolved in water. Two diffusive modes are observed when these solutions are prepared salt-free. The behavior of the slow and fast modes mimic the behavior observed for typical aqueous polyelectrolyte solutions.

The dominance of electrostatic interactions is also demonstrated in this system by performing dynamic light scattering on the neutral poly(2-vinyl pyridine), then on the quaternized polyelectrolyte version in both salt-free and high-salt solutions as shown in figure 10. Since the solvent quality is uniformly good for the neutral and polyelectrolyte, this figure demonstrates the effect of electrostatic interactions to split the single mode correlation function into fast and slow polyelectrolyte modes.

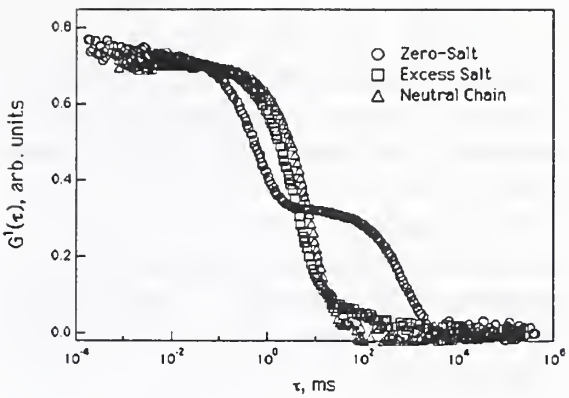

Figure 10 - Dynamic light scattering correlation functions for quaternized poly(2-vinyl pyridine) (or its neutral precursor) in salt-free or high salt solutions.

Outputs

Publications

E. J. Amis, D. E. Valachovic, and M. Sedlak, *Structure and Dynamics of Linear Flexible. Polyelectrolytes in Salt-Free Solution, Macro-Ion Characterization: From Dilute Solutions to Complex Fluids*, K. Schmitz, Ed., Amer. Chem. Soc., 322, (1994).

B. D. Ermi and E. J. Amis, *Model Solutions for Studies of Salt-Free Polyelectrolytes*, Polymer Preprints, **36**(1), 371, (1995).

D. E. Valachovic, D. A. Tomalia, and E. J. Amis, *Polyelectrolyte Dendrimers in Low-Salt Solutions*, Polymer Preprints, **36**(1), 373, (1995).

B. D. Ermi and E. J. Amis, *Model Solutions for Studies of Salt Free Polyelectrolytes*, Macromolecules, submitted.

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E. J. Amis, *Structure and Dynamics in Polyelectrolyte Solutions: What's Missing*, Department of Chemistry, Rutgers University, February 1995.

B. D. Ermi and E. J. Amis, *Model Polyelectrolyte Solutions for Salt-Free Studies*, American Physical Society National Meeting, High Polymer Physics Division, San Jose, March 1995.

D. E. Valachovic, E. J. Amis and D. A. Tomalia, *Polyelectrolyte Spheres in Low-Salt Solutions*, American Physical Society National Meeting, High Polymer Physics Division, San Jose, March 1995.

D. E. Valachovic, E. J. Amis and D. A. Tomalia, *Polyelectrolyte Dendrimers in Low-Salt Solutions*, American Chemical Society National Meeting, Anaheim, April 1995.

B. D. Ermi and E. J. Amis, *Model Solutions for Studies of Salt-Free Polyelectrolytes*, American Chemical Society National Meeting, Anaheim, April 1995.

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

POLYMER COMPOSITES PROGRAM

Goals

The polymer composites program seeks to facilitate the introduction of light-weight, corrosion-resistant composite materials into commercial applications by expanding the essential science base and generating test methods, reference data, and standard materials. The outstanding properties of composites mean they can be used to make products that are superior and more 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. A strong influence on the work is the automotive industry since this market probably has the biggest potential for near term impact. Nevertheless, the work also interacts with companies interested in off-shore oil platforms, infrastructure, aerospace, and a variety of other applications.

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

The work in the Durability Task focuses on composite degradation resulting from fluid attack, particularly moisture. The long term goals are to identify the chemical and physical mechanisms of degradation, to develop effective test methods, and to formulate reliable predictive models. The program focuses on glass fiber materials since they are the primary candidates for automotive applications. In addition, the work is beginning to look at graphite reinforced composites since these systems are important for marine and infrastructure applications. The usual approach in durability studies is to characterize the behavior of composite samples exposed to various environmental

conditions. Because a composite is such a complex system, however, the interpretation of the data is difficult. The work here uses two approaches to address this problem. First, composites are formulated with systematic variations in constituents and processing conditions. A comparison of durability data for the various samples can then provide insight into the possible sources of the differences in behavior that occur. Second, durability is measured on the individual components (i.e., the resin, the fiber, and the fiber-matrix interface) as well as the full composite. An understanding of how the component responses contribute to the behavior of the composite provides additional insights into the degradation mechanisms. There are currently three specific Projects in this Task.

FY-95 Significant Accomplishments

- Statistical methods have been used in a novel technique to predict the permeability for realistic materials which have significant variations in their microstructure.

- A 2.5D model has been developed to simulate mold filling for the "no-gap" case in Injection/Compression Liquid Composite Molding. A cooperative effort with the Automotive Composites Consortium was established to apply this model in their truck box program.

- A cure sensor and process control system were developed in cooperation with industry and demonstrated in the fabrication of a polymer composite plaques. Northrop-Grumman has transferred the technology to their laboratory where it will be implemented on prototype production equipment as part of an ARPA program.

- A laboratory scale system designed to simulate structural reaction injection molding has been developed and used to successfully fabricate urethane test samples for the durability program.

- The role of bonding between a coupling agent and glass in determining the strength and durability of single-fiber-composite, test specimens was quantified for a model glass-epoxy system.

- Results suggest that the stresses produced by swelling of the matrix material in single fiber composite samples does not play a dominate role in the moisture induced degradation of the fiber-matrix interface.

- A high refractive index fiber was used to demonstrate for the first time that a single fiber can be employed for cure monitoring with both fluorescence and near infra-red spectroscopies. The fluorescence work received a Best Paper award at the 1995 SPE/ANTEC Conference.

- The Polymers Division and the Electron and Optical Physics Division held a one day workshop on infrared microspectroscopy using a synchrotron source. Two of the areas identified where the technique could have impact were polymer composites and electronic packaging.

Liquid Composite Molding: High Speed Flow Behavior and the Development of Permeability Measurement Techniques and Data

R.S. Parnas, K.M. Flynn, D.L. Hunston, M.E. Dal-Favero[1]
[1]Standard Reference Data Program, NIST.

Objectives

The objectives are (1) to develop the technology for measuring permeability which is a critical input parameter for process simulation models, (2) to use this technology and establish a data base of values for industry, and (3) to define the limitations of such models.

Accomplishments

This is one of five projects in the Task on processing science of liquid composite molding (LCM), and the work here provides materials characterization data to the other efforts, particularly the project on the Development and Verification of Process Simulation Models. The focus is permeability which is a measure of the resistance to resin flow through the reinforcement materials that are combined to form the preform used in liquid composite molding (LCM). The approach is to study the nature of flow through porous media (i.e. the reinforcement) and to characterize the permeability in terms of the reinforcement's microstructure. By focusing on the microstructure, the factors that control permeability can be determined, and the effects of deformations in the reinforcement on permeability can be better understood. The deformation can arise either from the forces associated with fluid flow (hydrodynamically induced deformation) or the strains associated with fitting the preform into the mold (drape effects, etc.).

During the past year a data base format was developed in cooperation with the Standard Reference Data (SRD) Program. Based on that format, three years of permeability data generated at NIST were incorporated into a prototype data base which is now being testing. Moreover, agreements have been reached with other laboratories, including the Ford Scientific Research Laboratory, the University of Nottingham, and Ecole Polytechnique du Montreal--all of which have reliable permeability measurements--to contribute their results to the data base. In addition, several new reinforcements that are of interest to the Automotive Composites Consortium and the automotive industry in general have been characterized for inclusion in the data base.

Most permeability measurements are taken on flat undeformed samples of reinforcement. Previous work in this program has considered the problem of hydrodynamically induced deformation, and the results were reported in several papers last year. To address the other aspect of the deformation problem, work was begun to study the efforts associated with insertion of the preform into mold, i.e. bending around corners or draping in a variety of shapes to match the final part shape. The permeability of material deformed in this way can be significantly different than that of the undeformed material, altering the fluid flow behavior in the mold. The work, which involves a joint program with the Textile Research Institute, is conducting permeability measurements using molds that contain 90° bends with differing radii of curvature. Preliminary results from a non-woven fabric and a 3-D woven fabric indicate a substantial reduction of permeability in the bent region of the fabric.

NIST provides industry with permeability data and where appropriate transferring the measurement technology to industry. During the past year, several new reinforcement materials were characterized for the Automotive Composites Consortium. In addition, a staff engineer from ARDCO worked at NIST to generate permeability data on materials important to them using NIST's facilities.

Outputs

Publications

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Presentations

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R.S. Parnas, *Liquid Composite Molding: Experiments and Modeling*, Super Computer Institute, University of Minnesota, Minneapolis, MN, October 19, 1994.

R.S. Parnas, *Permeability Measurement*, International Conference on Automated Composites, Nottingham, England, September 5, 1995.

R.S. Parnas, C.R. Schultheisz, S. Ranganathan, *Hydrodynamically Induced Preform Deformation During High Speed Processing*, 4th International Conference on Automated Composites, Nottingham, England, September 6, 1995.

R.S. Parnas, *Experiments and Models for Liquid Molding*, Department of Engineering, University of Delaware, Newark, DE, November 1, 1994.

R.S. Parnas, K. Flynn, D.L. Woerdeman, *A Proposed Standard Reference Material for Permeability*, AIChE Annual Meeting, San Francisco, CA, November 17, 1994.

Liquid Composite Molding: Development and Verification of Permeability Prediction Models

F.R. Phelan Jr., S. Ranganathan,[1] and S.G. Advani[1]

[1]University of Delaware, Newark, DE

Objectives

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

Accomplishments

This is one of five projects in the task on

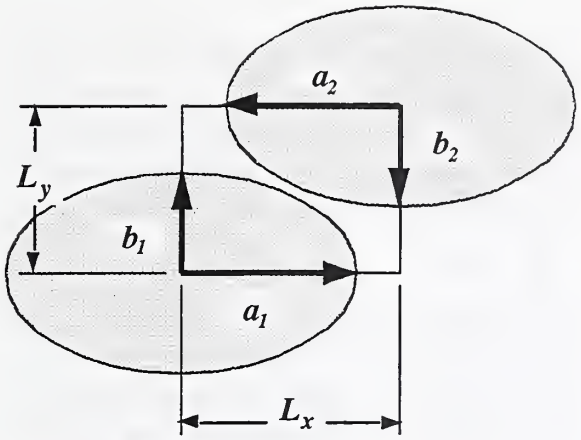

Figure 1: Unit cell for numerical calculations with dimensional variation in the tow structure.

processing science of liquid composite molding (LCM). The work benefits from the information generated in the Project on experimental measurement of permeability and will ultimately provide input data for the effort on process simulation. Permeability depends on the detailed microstructure of the reinforcement materials that make up the preform; the number of potential architectures and the range of possible volume fractions are very large. At present, the permeability must be measured in the laboratory, but the experiments are difficult and time consuming. Moreover, for some materials there is not an adequate means of getting the reinforcement material into permeability measurement molds without significantly altering the material microstructure. Consequently, the development of tools for predicting permeability as a function of microstructure is of great practical importance. It is also a first step in establishing processing/performance relations, since the composite properties also depend on the microstructure.

The textiles used as reinforcement in composite materials are typically made up of a network of fiber bundles called tows, where each tow contains hundreds to thousands of individual fibrils. In order to predict the permeability using flow modeling, both flow inside and outside the tows must be considered, as well as the complex geometry of the textile tow network. The approach taken here is to model the flow inside the porous fiber tows using the Brinkman equation given by

$$\mu \nabla^2 v - \mu K^{-1} \cdot v = \nabla P \qquad (1)$$

where v is the velocity, K^{-1} is the intra-tow permeability, P is the pressure, and μ is the fluid viscosity. The flow outside the tows is modeled using the Stokes equation. The Brinkman-Stokes approach allows intra-tow flow to be taken into account in a manner consistent with the proper tow-fluid interface boundary conditions. Analytical models based on flow in arrays of solid cylinders are used to predict the intra-tow permeability of the textile weaves needed in the Brinkman equation. Thus, this approach to permeability modeling enables predictions from first principles based entirely on the microstructure of the reinforcement. The equations are solved using a 3-D finite element simulation. The use of a finite element scheme makes it possible to obtain solutions for arbitrarily complex geometries (i.e. weave patterns).

During the past year, a novel new approach for applying these tools to the analysis of real reinforcement materials was developed. Most efforts at modeling the permeability of a porous medium are based on unit cell approaches in which it is assumed that the medium consists of a regular array of structures of uniform size, shape and position.

However, the microstructure of real materials

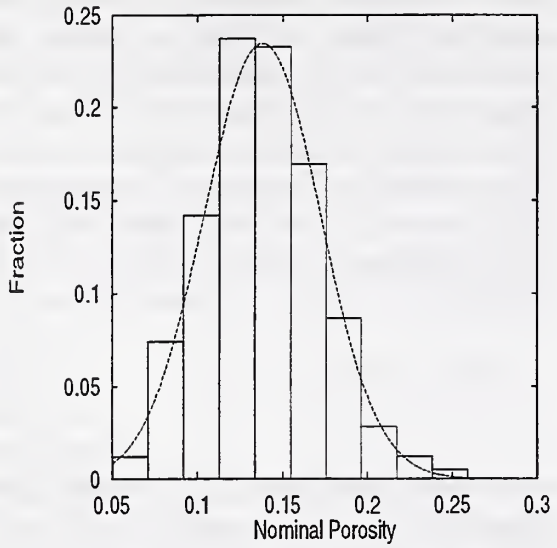

Figure 2: Porosity distribution for Knytex D155 material.

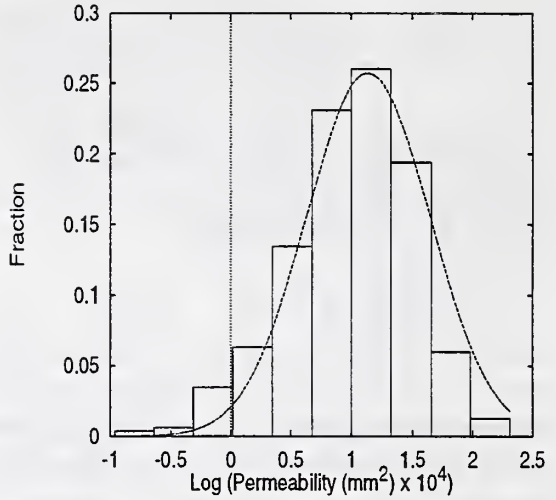

Figure 3: Permeability distribution for Knytex D155. The peak in the curve indicates the expected value.

has some degree of dimensional fluctuation about a mean. These variations from uniformity have an effect on the overall permeability, which in general, cannot be adequately accounted for in model calculations by defining unit cells based on average geometric properties. In this study, a method for incorporating the effect of variations in microstructure into model-based calculations of the permeability of a porous medium has been developed. For simple media, there are three main steps to the approach. First, numerical calculations are used to determine permeability as a function of porosity. Second, the microstructure variations of the media are characterized by obtaining a porosity micro-distribution for a given nominal porosity. Third, from steps (1) and (2), the permeability micro-distribution is calculated for the given nominal volume fraction. From the permeability distribution, an expected value and standard deviation of the permeability can be calculated.

The method has been used to model the permeability of a **Knytex D155** unidirectional material in a nested stacking sequence. The unit cell is shown in Figure 1. In previous

Geometry	a_1 (mm)	b_1 (mm)	a_2 (mm)	b_2 (mm)	ϵ	K(x 10^{-4} mm^2)
Max-Max	0.99	0.34	0.99	0.34	0.0193	0.078
Min-Min	0.765	0.235	0.765	0.235	0.355	19.4

Table I: Unit cell computations based on combinations of different tow dimensions found in Knytex D155 material. The geometry is given in Fig. 1.

work, the structural variations in the microstructure of this material were characterized; calculations show that these variations lead to large deviations in the "local" values of the permeability as sample data in Table I shows.

The porosity distribution for this material is shown in Figure 2. The effect of these structural variations were quantified using statistical analysis to obtain an expected value and standard deviation for the permeability from the data shown in Figure 3. Use of the method leads to a consistent comparison of experimentally measured and numerically computed permeability values.

Outputs

Publications

S. Ranganathan, G.M. Wise, F.R. Phelan Jr., R.S. Parnas, S.G. Advani, *A Numerical and Experimental Study of the Permeability of Fiber Preforms*, pp. 309-319 in Advanced Composites X: Proceedings of the 10th Annual ASM/ESD Advanced Composites Conference and Exposition (ASM International, Metals Park, 1994).

S. Ranganathan, F.R. Phelan Jr., S.G. Advani, *Microstructure Permeability Predictions for the Processing of Advanced Composites*, pp. 3035-3039 in Proceedings of the Society of Plastics Engineers ANTEC '95 (SPE, Brookfield, 1995).

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S. Ranganathan, G.M. Wise, **F.R. Phelan Jr.**, R.S. Parnas, S.G. Advani, *A Numerical and Experimental Study of the Permeability of Fiber Preforms*, 10th Annual ASM/ESD Advanced Composites Conference and Exposition (ACCE94), Detroit, MI, November 10, 1994.

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Liquid Composite Molding: Development and Verification of Process Simulation Models

F.R. Phelan Jr., and D.L. Hunston

Objective

The objective is to develop and apply models that can simulate the events which occur during the LCM process.

Accomplishments

This is one of five projects in the task on processing science of liquid composite molding (LCM). Input parameters for the models generated in this work are provided by the first two projects in this task while the sensor studies in the next two projects furnish feedback to test and improve the models. Simulations are important because optimized fabrication requires proper selection of the processing parameters for the particular part design and materials being used. Historically this has been done with time-consuming and expensive trial and error methods on full scale equipment. Simulation models can greatlyreduce the cost and increase the speed of this task. A wide variety of temperatures, pressures, injection ports, vents, etc. can be

inexpensively examined in a matter of hours using simulations. In addition, trade-offs such as the interaction between injection speed and pressure can be considered. As a result, processing conditions can be chosen to provide a highly efficient fabrication process.

The approach used in this project is to implement models based on Darcy's law in a finite element simulation for LCM and related processes. In previous years, a simulation was developed for the mold filling phase of simple LCM. This program enabled modeling of resin injection for either constant flow rate or constant pressure injection conditions, in geometries ranging from 2-D to fully 3-D.

The next phase of this project, which was started during this past year, is to extend the simulation to a second generation LCM process, called Injection/Compression Liquid Composite Molding (I/CLCM). This process has been selected by the automotive companies as the most promising method for fabrication of large structural parts. I/CLCM differs from conventional "injection-only" LCM in that subsequent to preform placement, the tool is only partially closed. An initial charge of resin--enough to partially fill the cavity--is then injected, followed by full mold closure. The final closing action of the mold compresses the preform to the desired net shape and volume fraction while distributing the initial shot of resin throughout the part. There are two main variants of the process. In the first and simplest case, the upper mold wall partially compresses the preform, and there is no gap between the preform and the mold wall during the initial injection phase. In the second, and more complicated case, the upper mold wall does not come into contact with the preform prior to injection, which leaves a gap for fluid flow between the preform and the mold wall.

The development of I/CLCM stems from the need to mold high fiber volume fraction components in applications with fast cycle times. In pure-injection LCM, such process constraints can result in excessively high injection pressures that induce undesirable fluid-structure interactions such as deformations of the preform, foam core, or tool.

In the past year, the LCM simulation has been extended to model the case of "no-gap" I/CLCM (see Figure 4). The simulation presently predicts flow front location, compaction pressure, and final fiber volume fraction for 2.5-D flows in multi-layer preforms. The simulation was tested by modeling flow in a flat plaque geometry using permeability-porosity data for a random mat material. A comparison of I/C simulations for the same initial fill fraction but different compression rates shows that the ultimate maximum pressure increases with increasing compression rate. I/C simulations were also compared with pure-injection simulations for which the processes being compared were

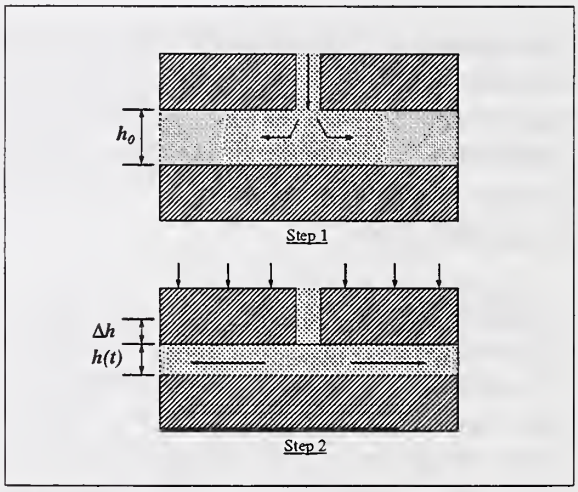

Figure 4: Schematic of injection/compression LCM for the simple "no gap" case.

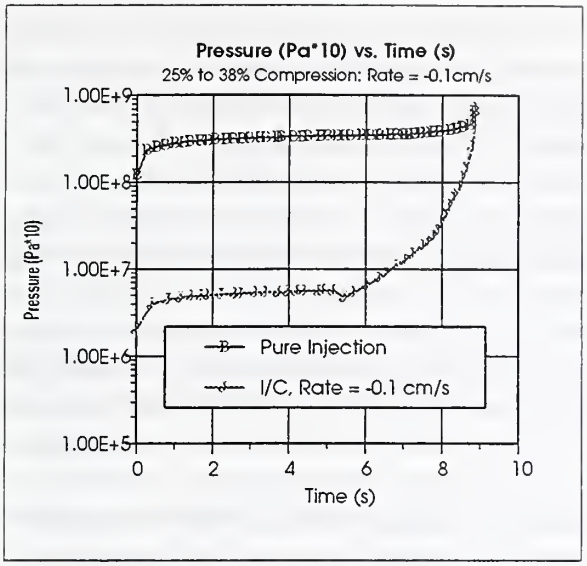

Figure 5: A comparison of maximum pressure vs. time for pure- injection and injection/compression with the same overall time to fill, and a compression rate = -0.01 (cm/s).

constrained to have the same overall fill times. These results show that I/C results in much lower pressures than pure-injection LCM throughout the majority of the process cycle--see Figure 5--but that the ultimate pressure in the system may be higher, depending upon the particular injection rate chosen. In future work, the simulation will be extended to fully 3-D flows, and the more complex case of an initial injection with a gap.

Outputs

Industrial Interactions

A CRADA between NIST and the Composite Civil Structures Consortium was signed. The flow simulation will be used by the consortium for the design of various components.

A contract was awarded to Structural Dynamics Research Corp. (SDRC) of Reston, VA to develop a graphical user interface enabling the interfacing of the NIST flow modeling software with their I-DEAS Master Series mechanical design software.

A number of companies continue to use the pure-injection LCM flow modeling program developed at NIST. They include the Automotive Composites Consortium (ACC), Northrop-Grumman Aerospace, Boeing Aerospace, and, a consortium involving AlliedSignal, Northrop-Grumman, and Allison Engine Company. Negotiations are currently underway with Lockheed .

Advanced Development Corp. to collaborate on vacuum-assist RTM (VARTM) for the manufacture of advanced aerospace parts.

A cooperative effort was established with the Automotive Composites Consortium (ACC) of Detroit, MI, to use NIST's model for injection/compression liquid composite molding in their ATP program to develop the technology for rapid, cost-effective manufacturing of a large truck box with this new process.

Publications

F.R. Phelan Jr., *Numerical simulation of injection/compression liquid composite molding*, p. 181 in Proceedings of the 11th Annual Advanced Composites Conference and Exposition, (ESD, Ann Arbor, Metals Park, in press).

Presentations

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F.R. Phelan Jr., *RTM Simulation of the Aerostar Cross Member Structure*, ACC Processing Group, Dearborn, MI, November

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Liquid Composite Molding: Development of Fiber Optic Sensors for Process Monitoring

R.S. Parnas, D.L. Hunston, J.P. Dunkers, D.L. Woerdeman[1], R.E. Lowry, K.M. Flynn, and K.N. Griffith[2]
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Objectives
The objective is to develop process monitoring sensors based on optical and spectroscopic measurement methods.

Accomplishments
This is one of five projects in the task on processing science of liquid composite molding (LCM). The work couples strongly with another project, Process Monitoring and Control of Pre-ceramic Polymers, that is implementing optical sensors for process monitoring and control in collaboration with industry. Ultimately, it should also assist the project, Development and Verification of Process Simulation Models, since the sensors can provide feedback for model verification and refinement.

The approach here is to develop optical fiber based spectroscopic methods for sensing behavior in the mold. Optical fiber sensors were chosen because they are very versatile and very small. Fiber optics can be used in many different ways to obtain information ranging from specific chemistries to mobility of probe molecules. Their small size means they can be placed within the molded part (even manufactured as part of the preform) and produce only a small perturbation to the processing or the properties of the final part itself. The application of this technology extends across a wide range of industries including the automotive market. During the past year, discussions were held with Ford and GenCorp about on-line process monitoring. Both indicated a strong interest in testing our sensors on the processing facilities associated with their projects supported by the Advanced Technology Program. This opportunity will be pursued in the coming year.

During the past year, an evanescent wave optical fiber fluorescence sensor has been developed and incorporated into a model preform. This optical fiber is inexpensive, possesses a refractive index above 1.61, and is transparent to visible and near IR light. The high refractive index allows the fiber sensor to be used in a surface-sensitive geometry (evanescent wave) to obtain information from several locations throughout the mold with a single fiber. A fluorescent probe has been obtained that not only functions well in epoxy systems, but also gives identical information in bulk and surface-sensitive sensing modes. The optical system requires less than 10 mW of power at 488 nm to provide excellent signal-to-noise ratio, and provides real-time spectral analysis for rapid measurements.

Several experiments have been conducted with an epoxy/amine resin system, glass fiber reinforcement, and a resin transfer molding apparatus to test the cure monitoring system under realistic manufacturing conditions. Professor Ben Wang and Julie Spoerre of the

Industrial Engineering Dept. at Florida State University provided valuable assistance in completing the experiments and in analyzing the parts for void fraction and interlaminar shear strength. Statistical analysis of the data indicates that the cure monitoring system provides an estimate of cure that is accurate to ± 5%. Improvements are being pursued with faster detectors, better optics, and more sophisticated signal processing techniques with the goal of reducing the uncertainty in the measured cure to less than 2%.

In related work, the fluorescence sensor is being improved to provide information from the 100 Å region adjacent to the fiber with the assistance of Professor Steven Pollack of Howard University. The idea is to bond the probe molecule to the surface of the glass fiber. A fluorescent silane material has been synthesized and is being studied to determine its surface properties. Coatings of the material on flat glass slides have demonstrated that the stilbene functionality of the probe molecule retains fluorescence on the surface and behaves identically to the precursor stilbene when dissolved in solution. A major benefit of such a surface coating on the optical fiber is that it eliminates the need to dope the bulk resin with a fluorescent dye. For applications in industry, this is a major advance.

Infrared sensing is also being pursued with two approaches. IR measurements provide unambiguous information on the reaction chemistry occurring at the sensor, but an optical fiber system similar to the fluorescence sensor is not practical at this time because of the high cost and toxicity of mid-IR transmitting fibers. The first approach is an attenuated total reflectance (ATR) surface sensor mounted in the mold wall, and that work is reported in the next project. The second approach is to use the near IR region of the spectrum and implement an optical fiber sensing element. Many optical fibers transmit well in the near IR region, and preliminary results indicate that the leaded glass fiber used in the fluorescence work will also be useful as a near IR sensor.

Once the sensor design is finalized and verified, it will be tested for process control capabilities. The model assisted feedback control algorithm that has been developed in the next project will be used. The control algorithm has been written to accommodate a wide variety of resin cure kinetics, and use in this project will demonstrate that a wide variety of molding systems can be controlled with a well formulated intelligent control system.

Outputs

Publications

D.L. Woerdeman, K.M. Flynn, J.P. Dunkers, R.S. Parnas, *The Use of Evanescent Wave Fluorescence Spectroscopy for Control of the Liquid Molding Process*, J. Reinforced Plastics & Composites, in press.

D.L. Woerdeman, R.S. Parnas, *Cure Monitoring with an Evanescent Wave Fluorescence Sensor*, p. 2805 in Proc. Society of Plastics Engineers/1995 ANTEC Meeting, Plastic Analysis Division (SPE, Brookfield, 1995). Received a best paper award for the 1995 ANTEC Conference.

D.L. Woerdeman, K.M. Flynn, R.S. Parnas, *Evanescent Wave Optical Fiber Sensor for Monitoring and Control of the Liquid Molding Process*, p. 315 in Proc. of the 4th International Conference on Automated Composites (The Institute of Materials, London, 1995).

D.L. Woerdeman, R.S. Parnas, *Cure Monitoring in RTM using Fluorescence*, Plastics Analysis, in press.

R.S. Parnas, D.L. Woerdeman, *The Use of Evanescent Wave Fluorescence Spectroscopy for Control of the Liquid Molding Process*, pp. 334-341 in ENERCOMP '95, (Technomic, Lancaster, 1995).

Presentations
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R.S. Parnas, J.P. Dunkers, K.M. Flynn, *The Use of Evanescent Wave Florescence Spectroscopy in Process Control of the Liquid Molding Process*, 1st International Conference on Composite Materials and Energy, Montreal, Quebec, Canada, May 10, 1995.

R.S. Parnas, *Cure Sensors for the Liquid Molding Process*, University of Delaware, Newark, DE, May 8, 1995.

R.S. Parnas, *Evanescent Wave Sensors for Molding Operations*, Workshop on Forming Advanced Composites, MIT, Cambridge, MA, July 11, 1995.

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D.L. Woerdeman, K.M. Flynn, **R.S. Parnas**, *Evanescent Wave Optical Fiber Sensor for Monitoring and Control of the Liquid Molding Process*, the 4th International Conference on Automated Composites, Nottingham, England, September 6, 1995.

Liquid Composite Molding: Process Monitoring and Control for the Manufacture of Pre-Ceramic Polymers

D.L. Hunston, J.P. Dunkers, R.S. Parnas, and K.M. Flynn

Objectives
The objective is to develop the tools to optimize the initial step of a process that makes a ceramic matrix composite. This first step is the fabrication of a polymer matrix composite by liquid composite molding.

Accomplishments
This is one of five projects in the task on processing science of liquid composite molding (LCM) and takes advantage of the output from the others. The work is part of a large external program involving industry, government, and academia sponsored by the Advanced Research Projects Agency (ARPA). The program is lead by Northrop-Grumman, AlliedSignal, and Allison Engine Company, but also involves a number of other participants. The goal is to reduce manufacturing costs for aircraft engine components made from a ceramic matrix composite. A commercial resin known as Blackglas® from the polydimethyl siloxane family will be used in the studies and by the companies to manufacture a demonstration part (turbine seal). The process involves first fabricating a polymer composite by LCM and then pyrolyzing it to produce the ceramic. The first step is known to be important because results have shown that the quality of the ceramic depends on the cure state in the polymer. NIST has contributed to

the program by providing process simulation models to Grumman, and they have used these models extensively to optimize mold design, preforms, and injection schemes. The results provide useful feedback for model testing and validation. NIST also provides materials characterization data, but the main focus in the current work is the development of a process monitoring and control scheme.

The approach in the work here is to examine the optical and spectroscopic monitoring techniques developed in the previous project and select the sensor that is most appropriate. This sensor is then coupled with on-line process control software specifically developed for this work. When implemented, this control system should reduce part cost by minimizing variability of the starting material for the pyrolysis and provide the tools for optimizing the cure cycle by reducing the time required to reach the desired cure state.

There were a number of important developments during this past year. A process control program was written. The infrared sensor selected by previous work in this program was used to generate isothermal kinetic data for the control program. The sensor was implemented on a model mold and coupled to the control program in the liquid molding facility assembled during the previous year. This facility was then used to demonstrate on-line process control in the fabrication of a number of sample test plaques.

The sensor system employs remote Fourier transform infrared (FT-IR) spectroscopy to follow the cure. The sensor is a prism mounted with one surface to the inside mold wall thus allowing non-invasive and optical contact with the resin. A surface sensor was acceptable because the demonstration part (turbine seal) is quite thin. An attenuated total internal reflection (ATR) infrared beam is used to probe the cure state of the resin. The beam exits an external port of the FTIR spectrometer and enters the prism face at near normal incidence using beam steering optics. The beam is then reflected at the prism surface that is in contact with the material of interest and is directed through beam steering optics to the detector which is also external to the spectrometer. The acquisition and processing of spectra are automated, and an index representing the degree of chemical conversion is sent to the process control computer. This sensor is reusable because of the non-stick nature of Blackglas® resin.

The process control software that has been developed here is based on a model-assisted feedback control algorithm. The model uses an empirical cure kinetic model with parameters determined from isothermal kinetic data generated by experiments with the cure sensor at various temperatures. During operation, the software uses the measured degree of chemical conversion and the processing time to calculate a temperature setpoint for the base-level temperature controller. This temperature is chosen to bring the degree of cure along a specified path. The control algorithm can be linked to any cure sensor that provides information on degree of cure. The kinetics model is of the form: $A = f(\mathbf{C},t,T)$, where A is the monomer concentration, $\mathbf{C}$ is a vector composed of model parameters, t is the time, and T is the temperature.

A number of isothermal control experiments were performed using a model sensor to demonstrate the effectiveness of the cure controller. A sample experiment is shown in

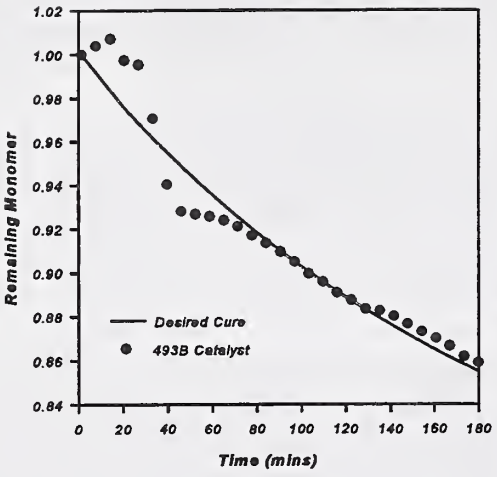

Figure 6: Control experiment showing desired and actual cure for the 493B catalyst.

the Figures 6. The cure labeled desired cure is the result obtained with the recommended isothermal cure temperature of 55°C and a fresh batch of commercial catalyst. When these same conditions are used with another sample of catalyst (labeled 493B), the cure behavior is quite different despite the fact that the two catalysts are supposed to be the same. The cure with 493B is much slower as might be the case with catalyst poisoning. The points in the Figure represent data for a material with the 493B catalyst but where the process control program has been activated. As seen in the Figure, the control program is able to adjust the temperature to achieve the desired cure path. Similar results have been obtained in other experiments, for example: cure at 75°C with the 493B and commercial catalysts, and cure at 55°C with excess commercial catalyst to mimic catalyst overload.

Outputs

Industrial and Academic Interactions

Through the Joint Venture supported by ARPA, NIST has established a collaboration involving Northrop-Grumman, AlliedSignal, Allison Gas Turbine, Atlantic Research Corporation, Synerials, and the Naval Air Warfare Center as well as Rensselaer, Drexel, and Rutgers Universities.

At the request of Northrop-Grumman, the technology developed here is being transferred to their laboratory where it will be implemented on prototype production equipment as part of the ARPA program.

Publications

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Presentations

J.P. Dunkers, R.S. Parnas, *An Infrared Attenuated Total Internal Reflection Cure Monitor for Control of the Liquid Composite Molding Process*, 19th Annual Conference on Composites, Advanced Ceramics, Materials, and Structures-A, Cocoa Beach, FL, January 10, 1995.

J.P. Dunkers, D.L. Hunston, R.S. Parnas, *Progress on the Development of the Mid-IR ATR Surface Sensor and Process Control*, Meeting for the Low Cost Ceramic Composite Program, Rensselaer Polytechnic Institute, Troy, NY, August 3, 1995.

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Precursor, 2nd International Conference on Composite Engineering, New Orleans, LA, August 21, 1995.

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Environmental Durability Studies: Effect of Fiber Coatings and Interfaces

D.L. Hunston, K.S. Macturk, J.P. Dunkers, C.L. Schutte, G.A. Holmes, and C.R. Schultheisz

Objectives

The objective is to investigate the effects of fiber surface treatments and coatings on the durability of composites. The focus is moisture attack on the fiber and interface in glass fiber/epoxy systems.

Accomplishments

This is one of three projects in the Durability Task. It uses the single fiber fragmentation (SFF) test and relies on the results from the next project which is establishing a correlation between SFF data and tests on full composites. The approach is to prepare samples with systematic variations in the fiber surface treatment and then characterize the interface strength as a function of exposure to water for various lengths of time.

The focus during the past year was on the role of coupling agents. The specimens were made with E-glass fibers and an amine cured DGEBA epoxy. Owens Corning and OSi are collaborating by providing advice and materials. To vary the chemical nature of the interface region and the degree of covalent bonding between the fiber and the epoxy matrix, samples are prepared using silane coupling agents individually and in mixtures. To study the effects of bonding, two silanes were used: 3-aminopropyltriethoxysilane (APS) which can bond with both the glass and the epoxy, and n-octadecyltrichlorosilane (ODS) which reacts with glass but not with epoxy. A 50-50 mixture of the two silanes was used to obtain an intermediate level of bonding. Unfortunately, the experiment is complicated since both the bonding and the chemical nature of the interface region change. Contact angle measurements on surface treated fibers show that APS surface is fairly hydrophilic, while ODS is more hydrophobic. The 50-50 mixture is also hydrophobic. It might be argued that a hydrophilic interface region would produce a higher local water concentration and therefore be more likely to degrade. To examine the role of hydrophobicity, tests were made using fibers treated with 3-glycidoxypropyl-trimethoxysilane (GPS) which can react with epoxy but is expected to be more hydrophobic than APS. For comparison, experiments were also performed on samples made with no silane surface treatment. Some samples were tested in the dry state while others were immersed in distilled water at 75°C. After various periods of time (up to 1800 hours), samples were extracted and measured. The analysis developed in previous work was used to determine the strengths of the fiber and the interface.

Results from the fragmentation test on dry samples were consistent with literature results from similar experiments on flat plaques. The strength of the interface increased significantly with increased covalent bonding between the silane and the epoxy, while the hydrophilic/hydrophobic nature of the silane had little effect. APS and GPS gave the

strongest interfaces, while ODS gave the weakest. A 50/50 mixture of APS and ODS gave intermediate interface strengths. Interestingly, the unsized samples gave interface strengths comparable to the 50/50 mixture. This is also similar to earlier results on flat plate systems.

In the durability experiments to date, samples treated with silane gave interface strengths that did not show significant degradation even after being subjected to 1800 hours in hot water. In contrast, samples containing unsized fibers experienced drastic losses in interface strength. What is perhaps surprising is that all of the silane treatments had this beneficial effect, even the system that did not have bonding between the silane and epoxy and gave relatively poor interfacial strength when dry. One possible explanation is that the silane bonding to the glass shifts the locus of failure away from the moisture-sensitive glass interface to the silane-epoxy interface. Work is continuing to more fully investigate these results and better understand their scope.

Another important aspect of the work is the effort to characterize the nature of the surface treatment and the conditions in the interface region during processing and environmental exposure. One promising tool is infrared microspectroscopy. During the past year, the Polymers Division and the Electron and Optical Physics Division held a one day workshop on infrared microspectroscopy using a synchrotron source. The synchrotron is very bright compared to other infrared sources, and this enables the study of sample areas approaching the diffraction limit of the infrared light. Two areas of important impact identified in the workshop were polymer composites and electronic packaging.

Outputs

Industrial Interactions

The project interacts closely with Owens Corning and OSi who are providing materials and advice on the fibers and fiber surface treatments, because the results have direct relevance to their technical problems.

Publications

K.S. Macturk, C.R. Schultheisz, C.L. Schutte, *Preliminary Results on the Role of Coupling Agents in Composite Interface Strength and Durability*, Proc. Society of Plastics Engineers/ANTEC (SPE, Brookfield, 1995).

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C.L. Schutte, *Use of the Single-Fiber Fragmentation Test to Study Durability of Model Glass Fiber/Epoxy Interfaces/Interphases on Exposure to Water*, AIChE Annual Meeting, San Francisco, CA, November 18, 1994.

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D.L. Hunston, *Overview of Composites Activities at NIST*, Owens Corning Research Center, Granville, OH, July 26, 1995.

K.S. Macturk, *The Role of Coupling Agent in Composite Durability*, OSi, Tarrytown, NY, April 14, 1995.

K.S. Macturk, *Investigation of the Relationship Between Interphase and Composite Durability*, EXXON Research Center, Annandale, NJ, May 24, 1995.

K.S. Macturk, *Investigation of the Relationship Between Interphase and Composite Durability*, Owens Corning Research Center, Granville, OH, July 26, 1995.

K.S. Macturk, *The Influence of Coupling Agent on Composite Durability*, Middle Atlantic Regional Meeting of the ACS, Washington, DC, May 26, 1995.

D.L. Hunston, *Characterizing the Fracture Behavior of Structural Adhesive Bonds*, 10th ASM/ESD Advanced Composites Conference and Exposition, Dearborn, MI, November 8, 1994.

D.L. Hunston, *The Use of Fracture Mechanics to Characterize the Strength of Adhesive Joints*, Department of Measurement systems, National Research Laboratory for Metrology, Tsukuba, Japan, February 23, 1995.

D.L. Hunston, *Fracture Behavior of Structural Adhesive Bonds: Structure-Property Relationships*, University of Tokyo, Japan, February 24, 1995.

D.L. Hunston, *Polymer Composites Activities at NIST*, Drexel University, Philadelphia, PA, April 10, 1995.

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

C.R. Schultheisz, W.G. McDonough, G.A. Holmes, J.P. Dunkers, K.S. Macturk, D.L. Hunston, C.L. Schutte, and S. Kondagunta[1]
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Objectives

The objective is to establish the relationship between durability results for the single fiber fragmentation test and similar experiments on full composites. The work also provides insight into the role of different resins and fiber surface treatments on durability.

Accomplishments

This is one of three projects in the Durability Task. It utilizes both the single fiber fragmentation test and experiments on full composites. The work relies on the results of the previous project to establish the experimental protocol for the fragmentation test. The advantage of micro-measurements such as the fragmentation test is that they have the potential for combining simplicity with a relative direct measure of constituent properties such as the fiber and interface strengths. To be useful, however, the results must be relevant to the behavior of full composites. A number of authors, particularly the papers from Drzal's group at Michigan State University, have shown this connection for dry samples. The work here seeks to do the same for durability, i.e. samples exposed to water and other fluids.

The approach in this project is to generate single fiber fragmentation specimens and full composites from a variety of fibers, matrices, and surface treatments; test these specimens after exposure to fluid for various lengths of time; and compare the results to develop correlations. In support of this work, a number of companion studies are investigating the mechanistic aspects of fluid attack and failure behavior in these samples. Most of the work here utilizes a glass-epoxy system which is well characterized and thus, serves as an excellent model. In addition, a urethane is under development in the next project so the studies can be extended to materials of interest for automotive applications. New experiments are also exploring the behavior with graphite-fiber composites because such materials are important to the off-shore oil industry and infrastructure applications. Work during the past year falls into three areas. In the first, both the micro- and macro-tests are done at NIST; the second focuses on the mechanistic aspects of the problem; and the third involves collaboration with industry to obtain materials and macro-test data which can be correlated with the micro-test data generated at NIST.

In the first area of work, NIST has fabricated single fiber fragmentation samples and test plaques for full composite experiments using a model epoxy and E-glass system. For this work, Owens Corning provided fibers with two surface treatments that should have different bonding and durability characteristics. The samples are tested in a dry state and after varying times of immersion in 25°C and 75°C distilled water. Since previous results in this project have shown that both the fiber and the interface are attacked by moisture, the composites tests were chosen to be sensitive to one or the other of these changes. The selected tests are: compression strength and interlaminar fracture behavior (Mode I and Mode II) which should reflect degradation at the interface, and tensile strength which should reflect degradation of the fiber. Measurements on the single fiber fragmentation specimens have been completed in the dry state and after immersion in 25°C and 75°C distilled water for up to 5000 hours. Although there is considerable scatter in the data, degradation of both the glass fibers and the fiber/matrix interface is apparent. The pattern of degradation in fiber strength, initially rapid and then slowing, suggests that the stresses produced by swelling of the matrix material

are not an important factor. The water alone (zero-stress aging) appears to be the major driving force.

In other tests, tension and Mode I fracture experiments on the resin alone have been performed, and full composite experiments have been completed in the dry state. As expected, the results show a good correlation between results for micro- and macro-tests in the dry state. Before the end of the coming year, measurements on the immersed composites will be completed and correlations with the micro-tests developed.

To assist with data interpretation, a number of studies are focusing on mechanistic aspects of the problem. First, the same model materials used above are being measured in collaborative experiments by Professor Walter Bradley at Texas A&M University. He is performing micro-testing in a scanning electron microscope where the local strains and failure mechanisms can be identified and studied. Second, a model for the degradation of the glass fibers is under investigation. Third, experiments have been initiated to study the path of water infiltration into the composites. It is often suggested that water is transported preferentially along the fiber/matrix interface. If so, this makes end effects very important. A new effort is using Fourier Transform Infrared Spectroscopy (FTIR) to evaluate the presence of water in the bulk matrix material and at the interface as a function of exposure time. This should establish the path of water infiltration.

The third area of work involves a number of cooperative programs. A collaboration with the Automotive Composites Consortium (ACC) was initiated to investigate the effects of water and other fluids (notably windshield washer and brake fluids) on candidate E-glass/urethane materials of interest to the automotive industry. Utilizing the processing method being developed in the following project, NIST will fabricate and test fragmentation samples. The results can then be compared with data from macroscopic composites tests performed at Oak Ridge National Laboratory. Second, a collaboration to study the use of composites in infrastructure applications (such as bridges and roads) has begun with Northwestern University's Basic Industrial Research Laboratory, University of Kentucky, Morrison Molded Fiber Glass, and a number of State Departments of Transportations. NIST's role is to define the current state-of-the-art in durability prediction for the companies interested in infrastructure applications. An initial literature survey on this topic is underway, and experiments are planned to investigate the durability of composite materials appropriate for these applications. Finally, NIST is working with industries involved in off-shore oil applications of composites. Hercules, who is participating in several projects on composites for off-shore oil structures supported by NIST's Advanced Technology Program, has agreed to help in selection of model systems involving graphite fibers and to provide materials for testing. In addition, Exxon has agreed to collaborate in a program where NIST performs micro-mechanical durability testing for comparison with measurements at Exxon on macroscopic samples of filament-wound tube.

Outputs

Industrial Interactions

Industrial interactions for this project include collaborations with the ACC and Dow in the automotive field, Exxon and Hercules for oil applications, and Morrison Molded Fiber Glass in the infrastructure area.

Publications

C.R. Schultheisz, C.L. Schutte, W.G. McDonough, K.S. Macturk, M. McAuliffe, S. Kondagunta, D.L. Hunston, *Effect of Temperature and Fiber Coating on the Strength of E-Glass Fibers and the E-Glass/Epoxy Interface for Single-Fiber Fragmentation Samples Immersed in Water*, in ASTM Symposium on Fiber, Matrix and Interface Properties, ASTM STP 1290 (ASTM, West Conshohocken, PA, in press).

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C.R. Schultheisz, C.L. Schutte, W.G. McDonough, K.S. Macturk, M. McAuliffe, S. Kondagunta, *Effect of Temperature and Fiber Coating on the Degradation of Glass Fiber/Epoxy Single-Fiber Fragmentation Samples Immersed in Water*, Society for Experimental Mechanics Spring Conference, Grand Rapids, Michigan, June 13, 1995.

C.R. Schultheisz, *Durability of Composites*, Exxon Research and Engineering Company, Annandale, New Jersey, May 24, 1995.

C.R. Schultheisz, *Effect of Temperature and Fiber Coating on the Degradation of Glass Fiber/Epoxy Single-Fiber Fragmentation Samples Immersed in Water*, Owens-Corning Science and Technology Center, Granville, Ohio, July 26, 1995.

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

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

Objectives

The objective is to develop new processing procedures that will enable the preparation of urethane test specimens that can be used in the durability program and which are equivalent to

materials made in industry by structural reaction injection molding (SRIM).

Accomplishments

This is one of three Projects in the Durability Task. The work here relies on the other two Projects for establishing the test methods and developing comparison data. The durability work in those Projects involves epoxies, but the automotive industry is interested in urethane composites. It is desirable, therefore to include this material in the durability studies. A major tool in these Projects is the single fiber fragmentation experiment, and, unfortunately, the usual preparation procedure for fragmentation samples does not produce useable specimens with the urethanes that are of most interest to the automotive companies. Consequently, new preparation procedures are necessary.

To achieve this goal, a joint effort with the Automotive Composites Consortium (ACC) was established. The Dow Chemical Co. is also participating by providing resin systems and advice on their preparation. The long term aim is to understand the response of automotive composites to fluids that they are commonly exposed to such as windshield wiper fluid, brake fluid, water, motor oil, etc. Certainly, much useful information can be gained by directly exposing bulk composites to automotive fluids and monitoring how the composite properties such as shear, tensile, and compressive strengths change as a function of exposure time. Unfortunately, such tests are expensive, time-consuming, and even impractical when one considers the large number of combinations of resins and fibers that are possible. Furthermore, it is sometimes difficult to separate out the failure modes due to the complex nature of the composite. Since there is considerable evidence that the fiber-matrix interface is a key area for durability, one approach to this problem is to use the single fiber fragmentation test which provides a simpler and more direct measure of the fiber-matrix interface strength.

The work here involves three phases. First, a processing method to prepare void free samples must be found. Two approaches are being tried. The first uses reduced catalyst concentrations to slow the reactions and an autoclave to apply pressure that reduces the foaming. The second seeks to develop an injection process that more closely simulates SRIM. Once void free samples are prepared, the specimens must be shown to have sufficient extensibility to permit single fiber fragmentation tests to be performed. Finally, the laboratory samples that are made with these techniques must then be compared with SRIM materials generated by the ACC to be sure that they are equivalent. Mechanical characterization, spectroscopy, and swelling experiments are being used for this purpose.

Previous work has shown that the first processing approach can produce void free samples, that these samples can be successfully tested in the single fiber fragmentation experiment, and that mechanical and spectroscopic measurements appear similar to results from SRIM materials. Although the comparison results are encouraging, they are not sensitive to the detailed network structure so additional comparisons would be useful. In response to this need, swelling experiments which are very sensitive to the network structure have been initiated. The swelling fluids were chosen to be materials that the automotive industry finds of interest.

Although the first fabrication method seems to be a viable route for making fragmentation

samples, it is difficult to prove that they are equivalent to SRIM materials. Consequently, a second method is also being pursued. A mold from the Liquid Composite Molding Projects was modified by adding an insert that contained dog bone shaped cavities. When resin is injected, the cavities produce multiple fragmentation samples. A specially designed injection system was made to simulate the SRIM process. The isocyanurate resin is put into one chamber and the polyol/catalyst mixture is put into another chamber, and during processing, the liquids are combined together in a static mixer and injected into the mold. Preliminary trials with this system are very encouraging. If successful, this procedure will produce samples very quickly which is important for durability studies where a large number of specimens are needed.

Outputs

Industrial Interactions

This project involves active collaboration with the Automotive Composites Consortium and Dow Chemical Co. The data generated here will help these companies introduce urethane materials into automotive applications.

Publications

W.G. McDonough, C.L. Schutte, C.K. Moon, C.R. Schultheisz, *Processing and Testing Issues for a Model Polyisocyanurate/Glass Single Fiber Composite*, p. 535 in Proc. 10th Annual Advanced Composites Conference and Exhibition (ASM, Metals Park, 1994).

G.A. Holmes, W.G. McDonough, C.R. Schultheisz, *Comparison of Polyisocyanurate Networks Using Swelling Tests*, p. 425 in Proc. of the 11th Annual Advanced Composites Conference and Exposition (ESD, Ann Arbor, in press).

W.G. McDonough, C.K. Moon, J.P. Dunkers, C.R. Schultheisz, C.L. Schutte, Evaluating a Polyisocyanurate/Glass Fiber Composite for Interfacial Studies, p. 497 in Proc. of the 2nd International Conference on Composite Engineering (ICCE/2, New Orleans, 1995).

Presentations

W.G. McDonough, C.L. Schutte, C.K. Moon, C.R. Schultheisz, J.P. Dunkers, *Processing and Testing Issues for a Model Polyisocyanurate/Glass Single Fiber Composite*, 10th Annual Advanced Composite Conference and Exposition, Dearborn, MI, November 9, 1994.

W.G. McDonough, C.K. Moon, C.R. Schultheisz, C.L. Schutte, J.P. Dunkers, *Developing a Model Glass/Polyurethane System for Durability Studies*, Materials Research Society's Fall Meeting, Boston, MA, December 1, 1994.

W.G. McDonough, C.K. Moon, J.P. Dunkers, C.R. Schultheisz, C.L. Schutte, *Evaluating a Polyisocyanurate/Glass Fiber Composite for Interfacial Studies*, Second International Conference on Composite Engineering, New Orleans, LA, August 22, 1995.

W.G. McDonough, *Evaluating Polyisocyanurate Composites for Interfacial Studies*, OSi Research Center, Tarrytown, NY, April 24, 1995.

VISCOELASTICITY OF POLYMERS PROGRAM

Goals

The goals of the Viscoelasticity of Polymers Program are motivated by the rapid growth in polymers in engineering applications, including wholly new uses. The efficient development of new applications for polymers requires improved design methods for estimating dimensional stability and long term performance. Technical factors include dimensional tolerances, process-induced residual stresses and fatigue behavior in complex thermal, stress and humid environments during use.

The goals of the Viscoelasticity of Polymers Program are to develop measurement strategies that produce mechanical properties data in efficient ways and concurrently to build methodologies that can be applied in the design and development of finished polymers. The approach uses the theoretical frameworks of continuum constitutive equations and micro- to meso-scale physical models to interrelate the mechanical responses under different loading conditions and to test model predictions using available measurement methods. The work involves the first major effort to measure the mechanical and rheological responses of a single class of solid polymer in multiple geometries of deformation and modes of loading as well as in different temperature histories. The combination of experiment and modeling results in both improved models and the development of new experimental methods for measuring material property parameters. Furthermore, the measurement and modeling requirements are renewed continuously by coordinating the efforts through collaborations with and support activities for other Programs in the Polymers Division including the Polymer Characterization Program, the Polymer Theory and Modeling Program, the Electronic Packaging and Interconnects Program, as well as other agency and miscellaneous projects that result from the Program's activities.

In addition, the Program seeks actively to work with Industrial research programs. Activities such as workshops and special symposia that improve the interaction of the Program with outside industry and the general technical and scientific communities are also fostered.

FY-95 Significant Accomplishments

- Collaborated with Rheometrics Scientific, Inc. in the redesign of a force rebalance transducer to eliminate thermal effects that can result in spurious normal force measurements.
- Collaborated with General Motors/General Electric to provide thermo-viscoelastic input data for their finite element analysis.
- In collaboration with Dow Chemical Company, established that the aging behavior of syndiotactic polystyrene above the glass transition temperature is significantly different from that of other semi-crystalline polymers .
- Established that 'efficient' methods for determining the material parameters required for the mechanical characterization of the nonlinear mechanical behavior of polymers can

be used with polycarbonate (GM/GE ATP Program)

- Co-organized a workshop on 'Nonlinear, Time-Dependent Constitution of Engineering Polymers'
- Established the existence of an isochoric glass transition temperature.
- Used the Purdue University thermo-viscoelastic constitutive equation to explain multiple time scales in volume recovery and mechanical evolution of polymers near to the glass transition.
- Established that the 'Strain Energy Clock' constitutive equation cannot describe the multiple step stress relaxation response of polycarbonate at room temperature.
- Torsional Dilatometry experiments established that the structural shift factor, a_{δ}, is less than the shift factor for physical aging, a_{te}.
- Developed a method to predict from single step stress relaxation experiments in uniaxial extension the viscoelastic response of polymer melts in complex deformation and at differing rates.
- Validated a total strain criterion for mode II fracture in epoxy adhesives with an elastic-plastic finite element analysis of an adhesive joint.
- Established that the effect of physical aging on craze initiation for polystyrene is different from that for a styrene-acrylonitrile copolymer.
- Organized a NIST/Academe/Industry Workshop on "Hygrothermal Effects in Polymers and Composites."

Sub-Yield Behavior of Solid Polymers: Material Clock Constitutive Models

G.B. McKenna, D.M. Colucci, E.A. DiMarzio, J.J. Pesce, and P.A. O'Connell, J.M. Caruthers.

Objective

The objective is to evaluate the range of applicability of material clock constitutive equations for amorphous polymers in time, temperature and deformation space. The project evaluates the set of material clock nonlinear viscoelastic constitutive equations that are proposed in the literature for describing the sub-yield behavior of solid polymers. Such data can also be used in finite element analyses of residual stresses that are critical for predicting dimensional stability and warpage of molded polymers and composites.

Accomplishments

During both processing and use, polymers experience large deformations and large changes in temperature and pressure. Progress to improve the design and reduce rework of processing equipment, such as molds for injection molding, is hampered by a lack of adequate material constitutive models. Current models for the solid-like behavior of post-molded parts have been relatively poorly evaluated, yet such models are often used to determine the suitability of a material for a specific application.

During the past year efforts have focused on the evaluation of two constitutive models

based on material clock or pseudo-time concepts. In addition, two equation of state models for the glass transition behavior under isobaric and isochoric conditions have been evaluated.

Material Clock Models: Experiments have been performed using a thermoplastic polycarbonate. Single and two-step stress relaxation data have been obtained in torsion, tension and compression and the current work is focused on evaluating the ability of the 'strain energy clock' form of the Bernstein-Shokooh nonlinear constitutive equation to describe the two step behavior. In addition, the thermo-viscoelastic constitutive model developed by Caruthers and co-workers at Purdue University, which uses a configurational entropy-based material clock, is being evaluated using tension and compression data. Eventually both constitutive equations as well as several others from the literature will be evaluated with the same data.

Because the PVT behavior of the polymer during processing is important in the development of residual stresses, equation of state models and the thermo-viscoelastic constitutive model of Caruthers are being evaluated in terms of the isobaric and isochoric behavior of polycarbonate.

Isotropic Deformations (PVT behavior): Current polymer equation of state models can be classified into two categories: (i) free volume and (ii) configurational entropy models. Each of the models chosen is used to predict both isobaric and isochoric (constant volume) PVT experimental results. The free volume Simha-Somcynsky theory and the configurational entropy Gibbs-DiMarzio theories are being applied to the experimental results. Preliminary analysis shows that both models describe the isobaric behavior. During the coming year the Caruthers model will also be considered and all three models will be evaluated in the context of the isochoric glass transition temperature results.

Anisotropic Deformations: The 'strain energy' clock model and the configurational entropy clock model nonlinear viscoelastic constitutive models both fall into the general class of reduced time models, where the time scale of relaxation is altered by a shift factor which can be a function of, stress, deformation, or thermodynamic state. Results show that in two-step stress relaxation in polycarbonate, the 'strain energy' clock model does not correctly describe the second step response for polycarbonate in torsion. It is a good descriptor of the nonlinear single step response in torsion for both the torque and the normal force. The configurational entropy based clock model from Purdue predicts previously unobserved features of the volume changes in compression.

Outputs

Publications

G.B. McKenna, *On the Physics Required for the Prediction of Long Term Performance of Polymers and Their Composites*, Keynote Lectures in selected Topics of Polymer Science, ed by E. Riande, Dodecaedro, S.A., Santa Clara, Spain, 1995, 139-172.

W.K. Waldron, G.B. McKenna, and M.M. Santore, "The Nonlinear Viscoelastic Response and Apparent Rejuvenation of an Epoxy Glass," J. Rheology, **39**, 471 (1995).

J.J. Pesce and G. B. McKenna, *Non-linear Viscoelastic Response of Polycarbonate in Torsion,* Proceedings ANTEC, SPE,Vol. 2, 1932-1935 (1995).

J.J. Pesce and G.B. McKenna, *A Comparison of Torque and Normal Force Responses in Polycarbonate in One and Two Step Torsional Histories with a Material Clock Model*, ASME, Winter, 1995 Meeting Proceedings (In Press).

Presentations

G.B. McKenna, *On the Physics Required for the Prediction of Long Term Performance of Polymers and Their Composites*, Society of Engineering Sciences Annual Technical Meeting, College Station, TX, October, 1994.

G.B. McKenna, *An Overview of NIST Activities in Collaboration with the Thermoplastic Engineering Design Program*, TED Semi-annual Review, Troy, MI, November, 1994.

G.B. McKenna, *On the Physics Required for the Prediction of the Long Term Performance of Polymers and Their Composites*, University of Maryland, College Park, MD, December, 1994

G.B. McKenna, *Volume Recovery, Nonlinear Viscoelasticity, and Other Long Time Processes in Polymeric Solids*, 3M Company Research Laboratories, St. Paul, MN, April, 1995.

G.B. McKenna, *Physical Aging in Polymeric Solids: The Impact of Structural Recovery on Mechanical Behavior*, University of Maryland, Baltimore Campus, Baltimore, MD, April, 1995.

G.B. McKenna, *Structural Recovery and Viscoelasticity in Polymers*, American Ceramic Society 97th Annual Meeting and Exposition, Cincinnati, OH, May, 1995.

G.B. McKenna, M.Y. Chiang, C.R. Schultheisz, P.C. O'Connell, J.M. Niemiec, *NIST Activities in Support of the Thermoplastic Engineering Design Program*, GE Plastics, Pittsfield, MA, May, 1995.

G.B. McKenna, J.-J. Pesce, *Non-linear Viscoelastic Response of Polycarbonate in Torsion*, ANTEC, SPE, Boston, MA, May, 1995.

G.B. McKenna, *The Glass Transition Event: Thermodynamics and Kinetics. An Overview of Phenomenology and Links to Nonlinear Viscoelasticity*, Institute for Mechanics and Materials Workshop on 'Nonlinear, Time-Dependent Constitution of Engineering Polymers,' La Jolla, CA, June, 1995.

G.B. McKenna, *Critical Tests of Nonlinear Constitutive Laws. Step Strain Experiments: Lessons from Melt Rheology*, Institute for Mechanics and Materials Workshop on 'Nonlinear, Time-Dependent Constitution of Engineering Polymers,' La Jolla, CA, June, 1995 (W. Knauss, California Institute of Technology and G.B. McKenna, co-organizers)

D.M. Colucci, J.M. Caruthers, *Prediction of Nonlinear Creep Using Several Constitutive Theories*, American Physical Society, Division of High Polymer Physics, March Meeting, San Jose, CA, March, 1995.

Sub-Yield Behavior of Solid Polymers: Efficient Determination of Material Parameters

G.B. McKenna, J.M. Niemiec, J.J. Pesce, P.A. O'Connell

Objective

The objective is to develop methodology that reduces the experimental time required to obtain nonlinear materials data and simplifies the geometrical complexity of the tests. The concepts from incompressible finite deformation theory of elastic bodies that allow the use of tests in a single deformation geometry for the prediction of behavior in other test geometries are extended to viscoelastic materials, including polymer melts and solutions as well as glassy polymers.

Accomplishments

Modeling the response of solid-like polymers is often difficult owing to the highly nonlinear behavior of the materials and problems obtaining relevant material data. In the development and use of the nonlinear constitutive models, it is essential that the material parameters used in the models be obtainable in the laboratory in a straightforward manner. A major problem is the need for extensive testing in multiple geometries of deformation, i.e., the material parameters that successfully describe shearing deformations may not be the same as those that describe tension or compression behaviors. This greatly increases the amount of experimentation required to obtain material parameters and consequently the difficulty and cost of using the powerful material clock constitutive models that show promise for material description.

The approach taken is to extend incompressible finite elasticity theory, that is successful for rubber, to viscoelastic materials and to the description of the behavior of compressible materials. The investigations focused on the non-linear constitutive description for a poly(vinyl chloride), PVC, melt based on methods that have been successful in the description of rubber-like materials to melt behavior through the formalism of the BKZ constitutive equation. A simple method is found of obtaining the material functions for the BKZ constitutive equation from a single deformation geometry. Single step stress relaxation experiments were carried out in uniaxial extension using a commercial PVC above the glass transition temperature. From these data, assuming time-strain-temperature separability, a Valanis-Landel (V-L) type of strain energy function is calculated as the kernel for the BKZ theory. The BKZ theory is then used to calculate the constant rate of deformation response of the PVC in three different deformation geometries: uniaxial extension, equibiaxial extension, and pure shear. The model calculations are compared with experimental results obtained on the same lot of PVC by Sweeney and Ward with a reasonable agreement.

The use of finite elasticity concepts to describe the single step stress relaxation response for a polymer glass (polycarbonate) far below its glass transition is examined. Torque and normal force measurements are used to obtain isochoric values for the derivatives W_1 and W_2 of the strain energy density function in terms of the deformation invariants. These values of W_1 and W_2 are used to determine isochronal values of the V-L function $w(\lambda)$ and to predict the tension and compression responses for different deformations λ below yield. It is found that, for the conditions examined, the tension and compression responses are well described within the V-L framework despite the fact that polycarbonate is a compressible material. Such results suggest that the major effect on the behavior of polymer glasses in the deformation range studied arises from similar considerations as those that lead to the ideas

in rubber elasticity that 'a stretch is a stretch' and which lead to the so-called Flory-Rehner hypothesis. Furthermore, it suggests that the set of experiments required to describe the nonlinear behavior of glassy materials may be smaller than previously thought.

Outputs

Industrial Collaborations

Rheometrics Instrument Co. participates to identify modifications to its rheometers that incorporate these research findings.

Publications

A.S. Wineman and G.B. McKenna, *Determination of the Strain Energy Density Function for Compressible Isotropic Nonlinear Elastic Solids by Torsion-Normal Force Experiments*, in Nonlinear Effects in Fluids and Solids, Plenum Publishing Corporation, Mathematical Concepts and Methods in Science and engineering series. (in press)

J.M. Niemiec, J.J. Pesce, G.B. McKenna, S. Skocypec and R.F.Garritano, *Normal Force Measurements Using a Force Rebalance Transducer*, Proceedings ANTEC, SPE, 2424-2429 (1995)

J.M. Niemiec, *Prediction of Multiaxial Deformation Response from Simple Stress Relaxation Tests*, University of Maryland, Masters Thesis, 1995

J.M. Niemiec, J.J. Pesce, G.B. McKenna, S. Skocypec and R.F.Garritano, *Anomalies in the Normal Force Measurement when Using a Force Rebalance Transducer*, J. Rheology (in press)

Presentations

J.M. Niemiec, J.J. Pesce, **G.B. McKenna**, S. Skocypec and R.F.Garritano, *Normal Force Measurements Using a Force Rebalance Transducer*, Society of Plastics Engineers, ANTEC, Boston, MA, May, 1995

J.M. Niemiec, J.J. Pesce, G.B. McKenna, S. Skocypec and R.F.Garritano *Normal Force Measurements Using a Force Rebalance Transducer*, Society of Rheology Annual Meeting, Philadelphia, PA October, 1994

J.M. Niemiec, G.B. McKenna, J. Sweeney and I. M. Ward, *Prediction of Multiaxial Deformation Response from Simple Stress Relaxation Tests*, University of Maryland, Department of Aerospace Engineering, April, 1995

J.M. Niemiec, G.B. McKenna, J. Sweeney and I. M. Ward, *Prediction of Multiaxial Deformation Response from Simple Stress Relaxation Tests*, Naval Surface Warfare Center, Bethesda, MD, May, 1995

Sub-Yield Behavior of Solid Polymers: Finite Element Analysis

M.Y.M. Chiang, G.B. McKenna and H. Chai

Objective

The objective is to determine the impact of specific parameters, e.g., deviations from material linearity, inhomogeneity of temperature, etc., on the residual stresses and resulting dimensional stability or warpage of polymer-based components. The project implements nonlinear viscoelasticity into finite element codes that are used to analyze the impact of thermal history on the residual stresses in printed wiring board type composites and injection molded parts.

Accomplishments

Many previous analyses used thermo-elastic models or, less frequently, thermo-linear viscoelastic models to describe residual stress development in polymeric materials subjected to thermal processes in which the glass transition is traversed. The approach taken here is to build on developments of nonlinear constitutive equations for glass forming polymers that implement thermo-viscoelastic models to describe material behaviors such as physical aging and nonlinear viscoelasticity.

Application to a printed wiring board inner layer subjected to different cooling rates showed the importance of accounting for the effect of time-dependent stress responses on dimensional change after the part is removed from the mold. Incorporation of a realistic time-temperature superposition (TTS) response at temperatures below T_g showed that these changes continue for long times after reaching ambient temperature. In addition, preliminary results showed that the value of the coefficient of thermal expansion (CTE) of the inner layer depends on thermal history during the measurement, and the final configuration of the inner layer is governed by the stress-free state of the substrate. Finally, these results revealed that dimensional stability is determined by the thermal history of the material.

The experimental part of the program is integrated into the modeling part by calculating the viscoelastic response of the polymer using viscoelastic data from T_g to room temperature. The time-temperature superposition principle is applied using a log (a_T) which is bilinear in temperature, as observed experimentally. Physical aging is treated by using an aging time shift factor a_{te} determined from laboratory measurements of the dynamic mechanical response of polycarbonate subsequent to temperature jump experiments. The latter has not previously been done, to our knowledge, for polymeric materials. The finite element method is used to solve the problem as a function of cooling rate and level of non-uniformity of temperature distribution. Of particular interest is the observation of plate warpage and its evolution with time after reaching room temperature.

In addition to considerations of time-temperature superposition behaviors, it has been observed that polymeric materials undergo a continuous evolution of properties below the glass transition temperature and that the changes in viscoelastic properties can be well represented by a time-aging time superposition principle as discussed in the following project. Now, rather than describing the material response at different temperatures T, we need to consider different aging times. Therefore, we chose a circular plate to predict the warpage caused by residual stresses, which are induced by the quenching from the temperature near T_g to room temperature. The plate, 100 mm in diameter and the thicknesses varied between 1.3 and 2.5 mm, is initially assumed to be stress free and viscoelastic. The analysis includes heat transfer and subsequent stress analysis.

Outputs

Industrial Collaborations

The Thermoplastic Engineering Design Program, carried out by GM and GE with NIST ATP support, is working to incorporate a non-WLF temperature dependence of the relaxation functions into their computer codes.

Publications

J.-J. Pesce, J. M. Niemiec, M.Y.M. Chiang, C. L. Schutte, C.R. Schultheisz, and G.B. McKenna, *Characterization of Polymers in*

the Glass Transition Range: Time-Temperature and Time-Aging Time Superposition in Polycarbonate, ASME Spring Meeting, Los Angles, 1995

M.Y.M. Chiang, G.B. McKenna and J. Yuan, "A Viscoelastic Micro-Mechanical Model for Dimensional Stability of a Composite Layer," Polymer Engineering and Science, 1994, 34, 1815-1822

Sub-Yield Behavior of Solid Polymers: Time-Temperature and Time-Aging Time Superposition in Thermoplastics in the Nonlinear Viscoelastic Range

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

Objectives

The objectives are to establish the range of validity of time-temperature and time-aging time superposition principles of a polycarbonate thermoplastic in the large deformation, non-linear viscoelastic regime and to determine the applicability of accelerated testing based on superposition concepts, valid in the linear viscoelastic regime for polymer melts, to areas of nonlinear viscoelasticity below the glass transition.

Accomplishments

Current research is investigating the effects of temperature and deformation on the mechanical response of polycarbonate. The linear and nonlinear viscoelastic response at temperatures ranging from room temperature to T_g are considered using tensile, compressive and shear deformations. At large deformations in compression, the volume exhibits a local minimum and, after a critical deformation corresponding to the yield point, begins to increase rapidly.

The results of static shear stress relaxation experiments performed in torsion over temperatures ranging from room temperature to just below T_g and at specific aging times were analyzed using time-aging time superposition. It was found that the effect of physical aging on the mechanical response varied greatly with applied strain and temperature. The time-temperature and time-aging time superpositions work well over the temperature range from 30°C to 140°C. However, the conventional analysis using a stretched exponential relaxation function was inadequate to describe the relaxation master curve. In addition, time-strain superposition can be applied to form a strain shifted reduced curve. However, the reduced curve for the time-strain superposition is different from that obtained from time-temperature and time-aging time superposition. These results demonstrate that reduced time concepts can be used for accelerated testing purposes when the reducing variables are aging time or temperature. However, there is a need to exercise caution when using such concepts as strain-time superposition.

Outputs

Publications

J.J. Pesce and G.B. McKenna, *Non-linear Viscoelastic Response of Polycarbonate in Torsion*, Proceedings ANTEC, SPE, Vol. 2, 1932-1935 (1995)

Presentations

J.J. Pesce and **G.B. McKenna** *Non-linear Viscoelastic Response of Polycarbonate in Torsion*, ANTEC, SPE, Boston, MA, May, 1995

G.B. McKenna, *The Glass Transition Event: Thermodynamics and Kinetics. An Overview of Phenomenology and Links to Nonlinear Viscoelasticity*, Institute for Mechanics and Materials Workshop on 'Nonlinear, Time-Dependent Constitution of Engineering Polymers', La Jolla, CA, June, 1995

G.B. McKenna, *Critical Tests of Nonlinear Constitutive Laws. Step Strain Experiments: Lessons from Melt Rheology*, Institute for Mechanics and Materials Workshop on 'Nonlinear, Time-Dependent Constitution of Engineering Polymers,' La Jolla, CA, June, 1995

Physical Aging of Polymers: Structural Recovery of Polymer Glasses

G.B. McKenna, C.R. Schultheisz and D.M. Colucci

Objectives

The objective is to determine the Tool-Narayanaswamy model parameters for polycarbonate for input into viscoelastic finite element codes that include the effect of structural recovery on residual stress development in non-isothermal histories typical of processing in composites and in molding operations. Structural recovery measurements are also performed on semi-crystalline polymers and the results compared with the mechanical responses in physical aging experiments.

Accomplishments

Structural recovery is a contributor to changes in residual stresses and performance in polymers and composites. The data obtained in this project, therefore, can serve as the basis of improved estimates of dimensional stability and warpage during processing as well as the evaluation of long term durability of polymers. Results from experiments on a model epoxy indicated that the volume and mechanical response change at different rates and with different dependence on temperature. These experimental results were analyzed assuming time-aging time superposition to determine the rate at which the "clock" that governs the mechanical properties operates. In addition, a program was written to reduce the volumetric recovery data using the Tool-Narayanaswamy-Moynihan-Kovacs model to provide a measure of the rate at which the "clock" that governs the volume response operates. The experimental results have also been analyzed using a more recent thermoviscoelastic constitutive model developed in Caruthers' group at Purdue University. Simulations of aging experiments on PVAc indicate similar disparities in the rates of volume recovery and mechanical relaxation to those found in the experiments; however, this model employs only a single "clock," and the difference in time scales originates from the nature of the model formulation.

Aging measurements on the dynamical mechanical response of polycarbonate have been completed over a temperature range from room temperature to 145°C at aging times from 0.5 to 32 hours. Torque and normal force measurements have been incorporated in a Bernstein-Shokooh nonlinear viscoelastic model modified to use a strain energy clock; results from such measurements have also been used to evaluate parameters in a Valanis-Landel model, which was then compared to stress relaxation experiments in tension and compression. The tension and compression experiments on polycarbonate (and polymethyl methacrylate) have also provided additional evidence for the

usefulness of the thermo-viscoelastic constitutive model.

An apparatus was constructed to measure the volume changes in polycarbonate following changes in temperature. This apparatus used a measurement of length change, but the specimen was found to creep under the action of gravity near the glass transition. As a result, a more-traditional mercury dilatometer has been constructed for measuring the volumetric response of polycarbonate.

Outputs

External Collaborations

GM/GE Thermoplastic Engineering Design Program conducts complementary work on polycarbonates.

Publications

G.B. McKenna, Y.L. Leterrier and C.R. Schultheisz, *The Evolution of Material Properties During Physical Aging,* Polymer Engineering and Science, 35, pp. 403-410, 1995

C.R. Schultheisz, G.B. McKenna, Y.L. Leterrier and E.A. Stefanis, *A Comparison of Structure and Aging Time Shift Factors from Simultaneous Volume and Mechanical Measurements*, Proceedings of the 1995 Society for Experimental Mechanics Spring Conference and Exhibit, pp. 329-335, Grand Rapids, Michigan, June 12-14, 1995

C.R. Schultheisz, D.M. Colucci, G.B. McKenna and J.M. Caruthers, *Modeling the Differing Time Scales of Structural Recovery and Mechanical Relaxation Observed in Aging Experiments*, in Mechanics of Plastics and Plastic Composites, 1995, ed. by M.C. Boyce, American Society of Mechanical Engineers, 1995, MD-68 and AMD-215, 309-336

Presentations

C.R. Schultheisz, *A Comparison of Structure and Aging Time Shift Factors from Simultaneous Volume and Mechanical Measurements*," 1995 Society for Experimental Mechanics Spring Conference and Exhibit, Grand Rapids, MI, June, 1995

Physical Aging of Polymers: Time-Temperature and Time-Aging Time Superposition in Amorphous Thermoplastics in the Linear Viscoelastic Range

G.B. McKenna, J.M. Niemiec, C.R. Schultheisz, M.Y.M. Chiang, J.-J. Pesce, C.L. Schutte, C. Williams

Objectives

The objective is to develop a data base of the time-aging time and time-temperature superposition shift factors for polycarbonate to be input into NIST and GM/GE finite element models of dimensional stability of molded parts. In this project dynamic mechanical measurements are performed to determine the time-temperature and the time-aging time superposition behavior of polycarbonate in the linear viscoelastic regime. Similar data on the behavior of other thermoplastics are being developed in collaboration with the Dow Chemical Company.

Accomplishments

Time-temperature and time-aging time superposition principles are excellent tools for estimating the behavior of polymeric materials at experimentally inaccessible times, for example short times typical of processing or extremely long times typical of long term applications. A data base of dynamic

mechanical properties is developed as input parameters into finite element computer codes for the GM/GE Thermoplastic Engineering Design Project.

Dynamic mechanical testing using a rotary rheometer to apply oscillatory strains to a cylindrical sample is performed in the frequency range from 0.001 rad/sec to 50 rad/sec and at temperatures from 30 to 145 °C. Aging times were investigated from 0.5 to 32 h. The data are reduced using the time-aging time and time-temperature superposition principles. Vertical and horizontal shift factors are tabulated and master curve representations for the loss and storage moduli are stored as functions of reduced frequency.

Outputs

External Collaborations

The master curves for the loss and storage moduli as functions of reduced frequency along with the vertical and horizontal shift factors have been provided to GM/GE.

Publications

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

J.-J. Pesce, J.M. Niemiec, M. Y. Chiang, C. L. Schutte, C.R. Schultheisz, and G.B. McKenna *Characterization of Polymers in the Glass Transition Range: Time-Temperature and Time-Aging Time Superposition in Polycarbonate*, Proceedings ASME Spring Meeting, Los Angeles, CA, June, 1995

Presentations

G.B. McKenna, *Time-Temperature and Time Aging Time Superposition in Polycarbonate Below the Glass Transition*, ANTEC, SPE, Boston, MA, May, 1995

G.B. McKenna, *NIST Activities in Support of the Thermoplastic Engineering Design Program*, GE Plastics, Pittsfield, MA, May, 1995

G.B. McKenna, *Characterization of Polymers in the Glass Transition Range: Time-Temperature and Time-Aging Time Superposition in Polycarbonate*, ASME Spring Meeting, Los Angeles, CA, June, 1995

Physical Aging of Polymers: Time-Temperature and Time-Aging Time Superposition in Semi-Crystalline Thermoplastics in the Linear Viscoelastic Range

G.B. McKenna, J.D. Barnes, J. Beckmann, I. Spinu

Objectives

The objective is to determine the creep responses below and above the glass transition for semicrystalline nylon 6-6, poly(ethylene terephthalate)(PET) and syndiotactic polystyrene(sPS) over a range of temperatures, aging times and stress levels and to delineate differences from corresponding data on amorphous polymers.

Accomplishments

The physical aging process was studied in sPS, nylon 6-6 and PET, all of which are semi-crystalline. Conventional aging behavior is expected for the nylon and PET. In sPS the amorphous and crystalline phases have similar densities and a different behavior is expected because constraints on the amorphous phase

would be less than those found in other polymers where amorphous/crystalline densities are significantly different.

When physical aging occurs in glassy amorphous polymers and below T_G in semi-crystalline polymers changes in viscoelastic response can be represented using a time-aging time superposition model. Here, creep experiments are performed and a viscoelastic spectrum described by retardation times τ_i was found. Each τ_i increases by a multiplicative factor a_{te} upon aging for a time t_e and it is observed that the creep compliance 'shifts' along the time axis by an amount a_{te}, also referred to as the aging time shift factor. Carrying out this data analysis leads to a 'master' curve in a fashion similar to time-temperature superposition.

Two important results emerged from the research: First, in the semi-crystalline nylon 6,6 aging proceeds faster in the temperature regime above the conventional glass transition. The aging behavior of PET is similar to that in the nylon.

In the sPS, on the other hand, aging above T_g is associated with only small vertical shifts of the data and with no change in the value of the τ_i of the retardation (creep) response. Such behavior is surprising and implies that the differences in the crystal-amorphous region in the sPS and the nylon lead to differing aging responses.

Outputs

External Collaborations

The work in this project area has been performed primarily in collaboration with DuPont (nylon and PET) and Dow Chemical Company (sPS).

Publications

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

Presentations

I. Spinu and G.B. McKenna, *Physical Aging of Thin Films*, SPE Annual Technical Conference, Boston, MA, May, 1995

I. Spinu and G.B. McKenna *Biaxial Testing, Aging and Moisture Effects in PET Films*, E.I. DuPont de Nemours Company, Circleville, OH, March, 1995

I. Spinu and G.B. McKenna *Moisture Effects in PET Films*, E.I. DuPont de Nemours Company, Circleville, OH, July, 1995

Physical Aging of Polymers: Impact of Plasticizing Molecules on the Aging Response

G.B. McKenna, P.H. Verdier, W.H. Han

Objectives

The objectives are to develop the techniques of pressure-jump and humidity-jump experiments and to establish methods of data analysis that account for the slow diffusion of plasticizing molecules into glass forming polymers.

Accomplishments

In this project, a method of evaluating the impact of plasticizer and changes in plasticizer concentration on the viscoelastic response of polymer glasses is developed using the framework of physical aging, but with partial pressure of the plasticizer over the polymer as the parameter to change the structure of the glass rather than the

temperature. Experiments are conducted using water as the plasticizer in epoxy resins. In the case of thermoplastics, the plasticizer is supercritical CO_2.

The object of this study is to establish the validity of the hypothesis that moisture acts as a simple plasticizer in epoxies and, consequently, changes in moisture content in polymer glasses can be treated in a similar way as changes in temperature. Similarly, supercritical CO_2, a critical solvent in novel separation technologies and a solvent/foaming agent in some manufacturing processes, shows unusually high diffusivity and solubility in polymers even at ambient temperature. While there has been research on equilibrium thermodynamics of supercritical CO_2 and polymers, virtually no study concerning the physical aging process of polymers upon the sorption or desorption of supercritical CO_2 has been reported.

(i) Humidity effect on the aging behavior of cured epoxy system
Preliminary results demonstrated the importance of understanding the coupling between moisture ingress in epoxies and the physical aging process. The past year has been spent modifying the equipment to improve the precision of the results. Stress and strain sensors more sensitive than those employed in the preliminary work have been installed on the tensile testing machine. The systems used to control relative humidity are also being improved. Meanwhile, data on moisture uptake and loss at various humidities are being obtained.

For the electronic packaging epoxy resin the pressure vessel system developed for the supercritical CO_2 experiments was adapted with humidity-proof LVDTs for strain measurements. The multi-step creep compliance evolution of cured epoxy system is measured at different aging times under a variety of humidity-temperature conditions at atmospheric pressure.

The moisture diffusion kinetics in the epoxy system are determined by sorption experiments. A computer code for extracting the diffusion coefficient was developed to take account of the uncertainty in the usual one-dimensional diffusion approximation with simple initial and boundary conditions. The analysis was extended to consider the possibility of non-Fickian diffusion, dual mode sorption, and non-instant equilibrium at polymer-plasticizer fluid interface often reported in the literature.

(ii) Thermoplastics in the supercritical CO_2
The aging process of a thermoplastic (polycarbonate) is monitored by accurate measurements of creep compliance and specific volume evolutions at different aging times under supercritical CO_2. Supercritical CO_2 conditions (P_c=73.8bar, T_c=304.25K) require that the existing pressure vessels be modified to withstand higher pressures. The modified experimental setup will also incorporate in-situ measurement of creep compliance of the thermoplastic samples using LVDTs connected to a PC.

Outputs
Presentations
A. Perez-Castorena, R. Grosfeld, P.H. Verdier and G.B. McKenna, *The Physical Aging Response of Epoxy in Relative Humidity Jump Experiments*, American Physical Society, March Meeting, San Jose, CA, March, 1995.

Failure of Solid Polymers: The Influence of Structural Recovery on Craze

Incubation and Growth in Amorphous Polymers

G.M. Gusler and G.B. McKenna

Objectives

The objective is to establish the validity of craze initiation and growth criteria by using structural recovery induced changes in mechanical properties as a means of changing material parameters that appear in the models, e.g., yield strength and relaxation modulus.

Accomplishments

In this project the response of craze initiation and growth processes in amorphous polystyrene (PS) and styrene acrylonitrile copolymer (SAN) to physical aging are being investigated.

In order to examine the craze response and compare it with models of craze initiation, experiments were performed in two different geometries of deformation. Biaxial tests were performed using inflation of a circular film; the criterion for craze initiation was the first visual observation of a craze using the naked eye. Uniaxial experiments were used to determine the critical strain at which crazing occurs by bending strips of material over a known varying curvature using a Bergen strain jig. The results show that the critical strain at craze initiation decreases as both the temperature and aging time increase. The general results are consistent with the expectation that the physical aging should decrease the strain at crazing and increase the time to craze. However, there is some evidence that in the equibiaxial stress tests there are two regimes of response and that crazing under constant stress conditions might be different from that under constant strain conditions. At low stresses aging has little effect on the time to craze and the stress dependence of the craze time is very strong. At higher stresses, the stress dependence becomes much less but aging seems to decrease the time to craze in PS, but increase it in the SAN. Consistent with expectations from Kambour's work, in constant strain experiments increasing temperature and aging time both decrease the strain for craze initiation.

Outputs

Publications

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

Presentations

G.M. Gusler and G.B. McKenna, *Effects of Physical Aging on Crazing Behavior in Polystyrene*, American Physical Society, Division of High Polymer Physics, March meeting, San Jose, CA, March, 1995

G.M. Gusler and G.B. McKenna, *The Effect of Physical Aging on the Crazing Behavior of Polystyrene*, American Chemical Society, Fall meeting, Chicago, IL, August, 1995

Failure of Solid Polymers: Finite Element Analysis

M.Y.M. Chiang and H. Chai

Objectives

The objectives are to incorporate material and geometrical nonlinearities into a finite element model to predict the deformation characteristics at the crack tip of an adhesive interlayer and to compare the model predictions with experimental data on the global response of an adhesive interlayer.

Accomplishments

The fracture response of thin layers is not well understood as measurements of fracture toughness can depend upon layer thicknesses. In this project experiments and finite element analysis are combined to focus on the local deformation at the crack tip in an effort to elucidate a fracture criterion which is independent of the specimen geometry. Adhesive bonding test specimens are used in this work to study the constrained interfacial crack propagation in bond thicknesses from 25 μm to 420μm. The initial cracks were either placed at the interface or close to the bond center. The adherends were 7075-T6 aluminum alloy while the adhesive was BP-907, a toughened, mildly ductile epoxy having a Young's modulus approximately 5% that of the aluminum adherends.

In the finite element analyses, a large strain incremental plasticity model was implemented to study the deformation and mechanism of fracture during the entire event of crack propagation, which includes the onset of crack propagation. The analyses of two different initial configurations of interfacial crack give different stress states which may lead to kink and void formation under certain circumstances. The fracture tests show that regardless of the initial crack position within the bond, the crack tends to propagate along either one of the two interfaces of the bond. The comparisons of local shear strain of finite element analyses and experimental results are reasonably successful. The analysis also provides quantitative insight into the mechanics of other failure modes observed in the experiments. The onset of a detrimental microdebond ahead of the crack tip is controlled by the bond-normal tensile stress. Hydrostatic tension seems responsible for the development of a large void at the crack tip which temporarily arrests the crack while the principal tensile stress at the crack tip seems to govern crack kinking. All of these failure modes are activated under large strains, which highlights the rule of plasticity in the fracture of polymer joints. Preliminary results suggest that there is a local material failure criterion, which is intrinsic and independent of bond thickness for the adhesive interlayer.

Outputs

Publications

Chiang, M.Y.M., *Modified Mohr-Coulomb Plasticity Model for Nonlinear Fracture Analysis of Polymeric Interlayer*, ANTEC, Society of Plastic Engineers, Boston, MA, May 1995

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

Workshop on Hygrothermal Effects on the Performance of Polymers and Their Composites

M.Y.M. Chiang, and G.B. McKenna

Objective

The objective is to hold a NIST/Industry/University "Workshop on Hygrothermal Effects on the Performance of Polymers and Their Composites". The workshop purpose is to obtain industry and academic input for the planning of future research in data and measurement needs regarding moisture effects in polymers and composites as well as identifying opportunities in development of theories and models of these effects.

Accomplishments

The workshop on "Hygrothermal Effects on the Performance of Polymers and Polymeric Composites" brought together investigators from academe, industry and NIST with the objective of identifying moisture issues in polymer materials and processes that are important to industrial competitiveness, defining scientific and technical needs and providing a research agenda for developing theories, building appropriate numerical models, and developing better measurement techniques to address these problems. Sponsorship was provided by the Center for Theoretical and Computational Materials Science in MSEL.

The workshop was divided into three sections: a) Academic Research, with four expositions of the academic perspective on hygrothermal problems; b) Industrial Perspective: Electronic Applications, with four expositions on challenges in the electronics and composites industries; c)Industrial Perspective: Automotive applications, with one exposition of the supplier's viewpoint (3M) and one of the end user (Ford Motor Company).

One of the goals of the workshop was to identify issues related to fundamental understanding or measurements of moisture effects on polymers and their end-use products and where NIST could potentially contribute to solutions. It was clear from the workshop that, while there are specific problems associated with moisture in each industrial sector, there are also areas of common interest. First, it was recognized that the impact of moisture on the mechanical response of polymeric materials is seldom fully characterized. Hence the perceived need for better measurement procedures to obtain data that are relevant to the estimation of long term performance. Some of the important common issues identified were the identification of changes in the glass-transition temperature with moisture uptake which affects service temperature because of changes in the viscoelastic response, changes in the fracture response due to plasticization or stress cracking effects and changes in the fatigue behavior of both polymers and composites. In addition, the representatives from the electronics industry were concerned about the reliability of electronic systems which can be degraded during processing and use by moisture absorption at the interface between the polymer and electronic components. Representatives from the composites industry demonstrated interest in interfacial effects and the automotive industry in adhesive fracture. Finally there was general agreement that some of the problems in estimating the impact of moisture, either in general or at interfaces, arise from contamination of materials and interfaces by substances that adsorb or absorb moisture. Few studies of such effects have been made as related to these industries.

The workshop ended with an extended discussion and agreement to form working groups that address two of the identified areas of research: 1) Effects of moisture on the mechanical response of polymers with initial emphasis to be placed on viscoelasticity and fracture; 2) Influence of contaminants in the materials on the uptake of moisture and consequent deleterious effects at interfaces.

Outputs

External Interactions

The workshop "Hygrothermal Effects on the Performance of Polymers and Polymeric Composites" drew forty nine (49) registered participants, including the ten (10) invited speakers, twelve (12) representatives from the

academic community and twenty two participants from the private sector representing seventeen (17) companies. Also, staff from several divisions at NIST participated actively in the workshop.

POLYMER CHARACTERIZATION PROGRAM

Goals

The Polymer Characterization program provides measurement methods, data, and standard reference materials needed by U.S. industry, research laboratories, and other federal agencies to characterize polymers for processibility, properties, and performance. Molecular weight and molecular weight distribution are the molecular characteristics of polymers that most affect their processing, properties and performance. Properties and performance may also vary widely depending on the solid state structure formed during processing. Therefore, the focus of the program is on techniques that measure molecular weight, its distribution and the solid state structure of polymers. Primary methods employed for molecular weight characterization are dilute solution light scattering and osmometry; chromatographic techniques, which require calibration by standards of known molecular mass, provide information on molecular weight distribution. Recent activities seek to exploit recent advancements in mass spectrometry using mass assisted laser desorption ionization (MALDI) to determine molecular weights of synthetic polymers. Other spectroscopic methods, solid state nuclear magnetic resonance (NMR) and infrared, as well as x-ray diffraction are developed and applied to elucidate the solid state structure of polymers.

The polymer industry and standard 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. Standards are produced for calibration of gel permeation chromatographs, the principal method used by industry for assessing molecular weight and molecular weight distributions, and melt flow standards that are used in the calibration of instruments used to determine processing conditions for thermoplastics.

FY-95 Significant Accomplishments

- Standard reference material, SRM 1473a, was recertified as a melt flow standard.

- Three linear polyethylene narrow molecular weight standards have been purified by recrystallization in preparation to light scattering measurements leading to their certification as molecular weight standard reference materials.

- The mass spectrogram of a poly(methyl methacrylate) SRM revealed features attributable to the polymerization chemistry.

- The presence of axial defects in the morphology of polyaramide fibers was established by solid state NMR.

- Solid state NMR studies of methylated poly(benzobisthiazole) revealed little evidence for cross-link formation upon heating. This procedure had been proposed as a means of improving the compressive strength of PBZT fibers.

- Determined that the apparent absence of x-ray scattering from the lamellar microstructure below the T_g of sPS is

a consequence of the virtually identical densities of the "glassy" and "crystalline" phases.

Standard Reference Materials

C. M. Guttman, J. R. Maurey, W. R. Blair, B.M. Fanconi

Objective

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

Accomplishments

Recertification of a SRM 1473a, a Melt Flow Standard

Melt flow rate is widely used in the polymer industry and in polymer technology as a product specification since its value gives an indication of the processing properties of the polymer. Industrial practice is to measure melt flow rates according to ASTM test methods and to use NIST standard reference materials to verify that the equipment is operating properly and that the test protocols are accurately carried out by the staff. Standard Reference Material (SRM) 1473b, a polyethylene resin, was recertified with a melt flow of 1.29 g/10 min at 190°C under a load of 2.16 kg using the ASTM Method D 1238-89.

New Polyolefin Molecular Weight Standards

Polyethylene and other polyolefins are the polymers of highest usage in the United States and the world. High temperature (150°C) Size Exclusion Chromatography (SEC), although a relative method requiring calibration, is the most commonly used method to establish the molecular weight of these polymers. Yet, few SEC calibration standards are available on the market for the calibration of high temperature SEC. Molecular weight fractions with M_w/M_n of less then 1.2 are the most useful materials for calibrating SEC. The only commercial supplier of sharp fractions of polyethylene offers repackaged NIST polyethylene standard reference materials. These SRM's will soon be out of stock.

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

SRM 1484, a sharp fraction polyethylene of molecular weight 120,000 g/mole, has recently been recertified. At the current sales rate of this SRM, this material will be exhausted in a few years.

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

All three fractions have been purified by recrystallization. Preliminary SEC analysis was conducted to check for homogeneity and a light scattering instrument was modified for high temperature operations. Molecular weight calibrations on the fractions should begin during FY96.

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

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

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

Outputs
Publications
Guttman, C.M. and Fanconi, B.F., *Polymers, Molecular Properties of,* Encyclopedia of Applied Physics, Vol. 14, 549 (1995).

Mass Spectrometry of Polymers

Charles Guttman, William Blair, William Wallace, Bruno Fanconi & David VanderHart

Objectives
Improve calibration standards for size exclusion chromatographs (SEC) to make these instruments, widely used by the polymer industry, more reliable for characterizing the molecular weight and distribution of polymers. Explore mass spectrometry as a method to measure the number average molecular weight and distribution of polymers that will become the next generation calibrants for SEC.

Accomplishments
Recent advances in Matrix Assisted Laser Desorption Ionization (MALDI) Time of Flight (TOF) Mass Spectroscopy (MS) allow the MS of whole undegraded polymer molecules with molecular weights up to 300,000 grams/mole. Collaborative work with Rohm & Haas and the Armed Forces Institute of Pathology (AFIP) is undertaken to explore the usefulness of this technique as a method to determine the absolute molecular weight of a polymer molecule for the production of molecular weight SRM's. A mass spectrogram of a NIST poly(methylmethacrylate), PMMA, SRM obtained by Paul Danis of Rohm & Haas revealed unusual features attributable to the polymerization chemistry. The MALDI-TOF-MS facility at the AFIP is used to examine current PMMA and polyethylene oxide, PEO, SRM's to gain experience in sample preparation, instrument operation fundamentals and data analysis.

Applicability of MALDI-MS to the determination of the absolute molecular weights and molecular weight distributions of synthetic polymer SRM's appears promising but several fundamental challenges remain to be addressed.

Chromatographic Techniques for Polymer Characterization

C. M. Guttman, W.R. Blair, E. A. DiMarzio, J. Douglas, & A. Yang[1]
[1]Armstrong World Industries

Objective
Provide the U.S. polymer industry with a simple chromatographic method to characterize the molecular weights of block copolymer. At present there are no satisfactory means to determine the individual

molecular weights of block copolymers. The approach involves chromatography at the adsorption transition and present efforts are to develop a data set for various homopolymers in mixed solvents which can be used to analyze chromatographic results on their copolymers.

Accomplishments

Chromatography of Polymers at the Absorption Transition

The size exclusion chromatographic (SEC) behavior of a polymer from the exclusion region into the adsorption range is modeled for chains with a variety of architectures and interactions with surfaces. Using the matrix method, arbitrary energies of adsorption of the individual monomers for the surface can be treated. Copolymers having linear, comb and star internal architectures have been modeled. Theoretical studies support the experimental work showing that diblock and triblock copolymers at the transition point of one of the blocks give chromatograms which display the SEC of only the other block. The theory promises to be of great utility in interpreting elution experiments on macromolecules of various architectures.

A chromatographic instrument was constructed to begin experimental studies to test theoretical predictions.

Effect of Heterogenous Energies on Absorption Properties of Polymer Chains

The presence of a few strong interactions in a chain with many weak interactions can change the properties of the polymer dramatically. For example, the presence of a few strong interactions will allow otherwise incompatible polymers to be compatible in a polymer blend. In recent experimental work related to the dilute solution characterization of polymers intended for use as an SRM, the association properties of the polymers were found to differ significantly due to the change of a few groups in the backbone. Currently, the interaction of polymer with a few strong interactions on a surface is studied by both numerical and analytical methods.

Outputs

Publications

Guttman, C.M., DiMarzio, E.A., *Chromatography of Macromolecules at the Absorption Transition,* ANTEC 95, Proceedings Society Plastics Engineers Annual Technical Meeting, May, 1995, pg 2551.

DiMarzio, E.A., Guttman, C.M., and Mah, A., *Effect of Heterogeneous Energies on Adsorption of Copolymers, Comb Polymers, and Stars onto a Surface,* Macromolecules **28**,2930 (1995).

Presentations

Guttman, C.M., DiMarzio, E.A., *Chromatography of Macromolecules at the Absorption Transition,* Society Plastics Engineers Annual Technical Meeting, May, 1995.

Characterization of Polymers by Spectroscopic Techniques

D. L. VanderHart and S.J. Kryder

Objectives

The objectives are to develop and utilize Nuclear Magnetic Resonance (NMR) techniques for characterization of molecular and microstructural level features that control the physical and mechanical properties of

polymers. Multiple-pulse proton spin diffusion techniques are applied to solid polymers in order to examine heterogeneities in composition, molecular order and dynamics. In addition, ^{13}C NMR is used in the characterization of liquid crystalline polymers, in the investigation of crystalline polymorphy, in the investigation of partitioning of comonomers between crystalline and non-crystalline domains, and as a means for following high-temperature chemical changes.

Accomplishments

Inhomogeneities in solid polymers characterized by multiple-pulse proton spin diffusion measurements

The objectives of this effort are to develop NMR measurement techniques which will yield information about small-scale (2 - 100 nm) spatial inhomogeneity in polymers. Moreover, in the event that chemical inhomogeneity is also present, another objective is to develop methods by which simultaneous information about chemical inhomogeneity can be obtained. Examples of inhomogeneities amenable to study are: a) polymer blends (intimacy of mixing in compatible blends; domain size and some information on domain stoichiometry in phase separated blends), b) size of crystalline and non-crystalline domains in semicrystalline polymers, c) spatial distribution of motional heterogeneity in glassy polymers and d) spatial distribution of motional heterogeneity in high strength fibers.

In these NMR studies spin diffusion techniques are combined with two other techniques, namely, multiple-pulse (MP) line narrowing and magic angle spinning (MAS). The simultaneous application of MP and MAS achieves a very modest (compared to liquid-state NMR) amount of chemical shift resolution. In polymer blends, the resolution is often sufficient to yield a contrast in the spectra of two polymers; hence, one can differentiate the signals arising from each component and deduce information about the phase dimensions. As part of this program, other methods, such as differential relaxation under MP, are investigated to establish polarization gradients based on differential molecular mobility. These experiments form the basis of the investigations into motional heterogeneity in glasses and defect structure in the interior of crystalline high-strength microfibrils. To aid in the data interpretation calculations are performed to relate spin diffusion data to different initial conditions and morphologies.

Most current work concerns polymer blends and utilizes MP techniques which require more experimental attention than other NMR techniques. The sensitivity of protons combined with the modest resolution achievable via MP methods make this technique widely applicable to the study of polymer blends. The measurement technique shows considerable promise for polymer blends, especially for those blends of glassy, high-T_g materials where thermal history and kinetics, in addition to thermodynamics, often dictate the level of mixing and the resulting domain sizes.

This year, three accomplishments can be cited. First, a draft of a general paper on the interpretation of spin diffusion data, especially for polymer blends, was written; the extraction of domain size and stoichiometric information was featured. This paper will be submitted to the journal, Solid State NMR.

The second accomplishment is the completion of experimental work that examines the

distance scale over which molecular motions are heterogeneous in a series of four highly-crystalline poly(p-phenylene-terephthalamide) samples: an as-precipitated powder, and Kevlar® fibers, Kevlar® 29, 49 and 149. Previous x-ray and electron microscopy studies concluded that the lateral crystallite size ranged from about 3.5 nm in the powder to 9 - 12 nm in the 149 sample with the 29 and 49 samples having intermediate values. In the fiber samples, these lateral crystallite sizes are associated with microfibril diameters. The approach was to measure the time required for spin diffusion to equalize local spin polarizations after spin polarization differences had been established based on differential relaxation (=differential molecular mobility) under multiple-pulse irradiation. The following observations were made: a) the fraction of protons associated with the faster relaxing sites decreased as the crystallite size increased and b) the distance scale over which this contrast in mobility is seen is about 5 nm and is independent of crystallite size. The latter observation contradicts the hypothesis that the faster relaxing chains are restricted to the surface of the crystallites, even if it is assumed that spin diffusion is not fully quenched under multiple-pulse irradiation. (The latter point is confirmed by computer modeling calculations.) These observations are consistent with a Kevlar® morphology defective in an axial direction and such a consideration may would be relevant to the mechanical properties. These morphological features may also explain why these fibers undergo biological degradation faster than expected.

The final accomplishment in this category is the completion of experimental work on a series of polymer blends consisting of an ionomer (a zinc-sulfonated derivative of polystyrene- 'ZnSPS(n)', where sulfonate groups have been attached randomly to the para-positions on 'n' mole % of the aromatic rings of PS), mixed with a methylated polyamide (mPA where all of the amide protons of the PA precursor have been substituted with methyl groups to reduce hydrogen bonding and slow down crystallization). Blends of pure PS and mPA are totally incompatible. It is the strong interaction between the sulfonate and amide moieties which generates a level of compatibility. Mixing was studied as a function of blend stoichiometry and n. A wide range of morphologies was observed. For example, for n=12%, mPA crystallization is inhibited and mixing is intimate so long as the weight fraction of ZnSPS(12) exceeds 0.45. Below this weight fraction, however, mPA crystallization is observed; yet the scale over which the sample-average stoichiometry is observed is in the range of 20-25 nm. In other words, crystallization seems to have developed from a somewhat mixed phase and the process of crystallization simply moves the ZnSPS into a more concentrated band surrounding the mPA crystals, even though there is also evidence that in the immediate vicinity around each mPA crystal, the concentration of ZnSPS is very low. It is interesting that this 20-25 nm distance scale is not a strong function of blend stoichiometry. Interesting also is the role of water exposure in changing this morphology. The ability of water to interfere with the hydrogen bonding seems to result in both an increase in the mPA crystallinity and an increase in the ZnSPS concentration in the mixed regions...both phenomena occurring without any appreciable change in the 20-25 nm distance scale. Hence, the overall scale of the morphology seems stable in the presence of water but water facilitates greater segregation within this scale. Presumably the segregation is driven, at least in part, by the favorable

thermodynamics of crystallization. The water simply provides a mechanism for more easily disrupting particular hydrogen bonds, given that the mPA has an excess of hydrogen bonding sites, so that the number of hydrogen bonds between ZnSPS and mPA does not diminish significantly as a result of the loss of certain mPA chains to the crystallization process. Other findings are consistent with intuition in the sense that mixing becomes more difficult as n decreases until, at some point, one observes 'large' (>150 nm) domains.

^{13}C NMR Characterization

Many of the accomplishments here were the result of final experiments on projects largely completed and reported on last year and the successful writing up of these results with acceptance by archival journals. The following summarizes new results and lists the resulting publications.

Co-crystallization of minority comonomers—

In ethylene/vinyl alcohol (EVOH) copolymers where the VOH comonomers are the minority and the crystal lattice is the polyethylene lattice, it was previously reported that the VOH residues are incorporated in the crystals in nearly stoichiometric numbers and short chain, aliphatic branches (mainly butyl branches) are largely excluded. Recent experimental work suggests that acetate branches (which remain as a result of incomplete saponification of the originally polymerized mixture of ethylene and vinyl acetate) are also largely **excluded** from the crystalline regions. Thus, a control over crystallite size and crystallinity can be exercised by controlling the concentration of acetate and aliphatic branches, rather than the concentration of the principal comonomer.

In the biologically synthesized and biodegradable copolymers of poly(4-hydroxybutyrate) (PHB) and poly(4-hydroxyvalerate) (PHV), there is a tendency to exclude the minority HV residues from the crystalline regions when those regions take on the PHB lattice. It is interesting that the ratio of the concentration of HV units within the crystals to that in the non-crystalline regions increases with the overall concentration of HV comonomer. In other words, it is easier to inject another VOH repeat unit into a crystal already containing many such defects than to inject it into a crystal with few defects. Also, experimental results are consistent with the segregation of chains of different average defect content during crystallization.

Characterization of liquid crystalline polymers (LCP)—

A second paper was published on a smectic LCP consisting of a bibenzoate polyester. Three preparations of the LCP were studied. All preparations show a tendency to crystallize, often very slowly. Interesting trends in these materials are the following:
-Crystallites are very thin, i.e. about 2-3 repeat units in thickness.
-Crystallinities tend to be low, i.e. 0.25 to 0.40 even when the precursor state is the smectic state. Hence, it is concluded that the formation of the smectic state in these LCP's does not involve any significant topological simplification, i.e. the smectic state can form and still leave the chains entangled and folded. Crystallinity is then limited by the 'defect' density of the non-crystalline regions.
-The similarity of molecular motions, as indicated via various relaxation times, in the non-crystalline regions of semicrystalline samples compared with the smectic regions of fully-smectic LC samples implies that a layered segregation of mesogens and spacers

may also characterize the non-crystalline state.

Crystalline polymorphy—

-Cellulose triacetates (CTA) possess at least two crystalline allomorphs. A paper, submitted for publication in *Macromolecules,* presents the NMR spectra of oligomers of CTA and shows that these spectra converge to the spectrum of CTA I, as opposed to CTA II. Also, included in this paper are some plausibility arguments on the chain polarity in these materials. An issue in CTA, as well as cellulose, is the crystal structure of the various allomorphs since large enough crystals for structural examination are impossible to grow. One implication of this work is that the structure of CTA I can be obtained by solving the crystal structure for any oligomer from the pentamer through the nonamer. Issues of chain polarity, to the degree they can be extended to cellulose, influence profoundly the understanding of the industrially important mercerization process.

High-temperature chemical changes—

-High temperature cross linking in fibers of a rigid rod polymer. Poly(benzobisthiazole) (PBZT) is a rigid rod aromatic polymer whose fibers are coagulated from a nematic, liquid crystalline solution. These fibers have very high tensile strength, but poor compressive behavior. In an attempt to improve compressive strength via cross-linking, the PBZT was modified by putting one methyl group on each phenyl moiety of the repeat unit. It was then supposed that by heating to a high enough temperature, the methyl groups would be the most reactive, thereby promoting the formation of methylene bridges between chains. Examination of heat treated MePBZT samples revealed evidence for the formation of methylene linkages, but these cross-links formed concurrently with a significant loss of other methyl groups and an overall deterioration of the mechanical properties. Hence, it is dubious that this strategy for improving compressive strength is viable.

Attempts to reduce flammability and increase char formation in poly(vinyl alcohol), PVOH, by the addition of a bis-maleimide—

The underlying hypothesis for improving char formation is that when PVOH is heated, water is first eliminated, leaving behind chain unsaturation. The bis-maleimide (BMI) molecule will react with unsaturation and form cross-links via a Diels-Alder reaction. It is proposed that the cross-linking, the existence of other unsaturated sites on the decomposing PVOH chain, and the presence of aromatic rings in the BMI will combine to enhance char formation. Pyrolysis of the pure PVOH powder and of mixed powders of PVOH and BMI showed that residue yields were increased in the presence of BMI for exposure temperatures in the 300 to 400°C range. However, there was no significant increase in char formation for high-temperature (700-800°C) pyrolysis. The NMR analysis quantified the decomposition of the PVOH and the reaction of the BMI. NMR also revealed substantial spatial heterogeneity of composition, including the level of PVOH decomposition. As a result, the following understanding for the increase in residue yields at lower temperatures was put forth: a) the PVOH and BMI phases remain largely separate and b) the BMI phase coats the PVOH particles and creates a barrier which leads to cross-linking at the surface of the PVOH particles and provides a membrane which serves as a trap for fragments possessing unsaturation as they escape from

the PVOH phase. This model also explains the puzzling finding that the NMR spectra of samples rich in each of the separated phases show more decomposition in the BMI-rich phase.

Outputs

Publications

E. Pérez, R. Benavente, A. Bello, J.M. Pereña, and D.L. VanderHart., *Solid State ^{13}C NMR Study of Thermotropic Polybibenzoates. II. Poly(triethylene glycol p,p'-bibenzoate)*, Macromolecules **28**, 6211 (1995).

D.L. VanderHart, *Proton Spin Diffusion Studies of Polymer Blends Having Modest Monomer Size: I. Poly(styrene)/Poly(xylylene ether)- A Miscible Blend*, Macromolecules **27**, 2837-2845 (1994).

D.L. VanderHart, R. St. John Manley, and J.D. Barnes, *Proton Spin Diffusion Studies of Polymer Blends Having Modest Monomer Size: II. Blends of Cellulose with Either Poly(acrylonitrile) or Poly(4-vinyl pyridine)*, Macromolecules **27**, 2826-2836 (1994).

J.A. Hyatt, D.L. VanderHart, and R.H. Atalla, *Relationship Between the Crystalline States of the Oligomers of Cellulose Triacetate and Its Two Allomorphs as Studied by Solid State NMR*, Macromolecules (Submitted).

J.W. Gilman, D.L. VanderHart, and T. Kashiwagi, *Thermal Decomposition Chemistry of Poly(vinyl alcohol): Char Characterization and Reactions with Bismaleimides*, ACS Symp. Ser. **599**, 161 (1995).

D.L. VanderHart, W.J. Orts, and R.H. Marchessault, *A ^{13}C NMR Determination of the Degree of Cocrystallization in Random Copolymers of Poly (β-hydroxybutyrate-co-β-hydroxyvalerate)*, Macromolecules **28**, 6394 (1995).

W.J. Orts, D.L. VanderHart, T.L. Bluhm, and Marchessault, R.H., *Cocrystallization in Random Copolymers of Poly (β-hydroxybutyrate-co-β-hydroxyvalerate) and its Effect on Crystalline Morphology*, Can. J. Chem. (in press).

D.L. VanderHart, S. Simmons, and J.W. Gilman, *Solid State ^{13}C NMR of Ethylene/Vinyl Alcohol Copolymers: Morphological Partitioning of Hydroxyls*, Polymer **36**, 4223 (1995).

Structural Characterization of Polymers by Small Angle X-Ray Scattering

John Barnes

Objective

The main objective is to maintain a state-of-the-art small angle x-ray facility, SAXS, that incorporates improvements in methods and instrumentation that expand the use of small angle x-ray scattering (SAXS) as a technique for characterizing materials and processes. SAXS is a complementary tool to small angle neutron scattering (SANS) because it utilizes different mechanisms for obtaining scattering contrast and because it is less subject to certain kinds of interferences. Hence, the availability of SAXS as a tool for probing microstructure in a wide range of materials in a form easily accessible to users, in spite of the complexities in instrumentation and interpretation, provides a resource to industrial clients as well as to internal research projects in the Polymers Division.

Accomplishments

Facility Development

There is a continuing effort to make the facility more accessible to its users through upgrades to the computer systems, the data handling software, and the x-ray camera itself. The improved user interface to the camera and the increased emphasis on remote data reduction have led to a need for improved user documentation. At the same time, the expansion of the user community within NIST has provided more opportunity for feedback and testing of written protocols. Therefore, the development of improved user documentation is the main thrust of efforts in FY 1996.

The addition of a modified microscope hot stage expands opportunities for high-temperature SAXS experiments. The normal procedures for collecting empty beam data and scattering patterns for intensity calibration have worked well with this arrangement.

In an effort to extend characterization of microstructure to longer distance scales, data from the 10-Meter Digital SAXS Camera has been augmented with data obtained on the MSEL double crystal SAXS camera (USAXS) at the National Synchrotron Light Source. These data have shown that degradation of the detector sensitivity in the immediate vicinity of the beam stop of the 10-meter camera is a barrier to interpretation of the data at q-values below approximately 0.2 nm^{-1}. On the other hand, the higher q-range of the 10-meter camera provides an important complement to the data from the USAXS facility, particularly for weak scatterers like polymers.

Small-angle orientation texture has become a dominant theme in characterizing structures of materials produced by industrial processes. Such materials most often exhibit rotational or orthorhombic symmetry. SAXS experiments must be designed so as to account for this factor in order to extract meaningful microstructural information. This has led to the application of a simplified method called "oblique incidence SAXS" with films and thin sheets in an effort to obtain patterns that contain important axes of symmetry. Further work is needed in quantifying these data in order to develop test protocols for more complete microstructural characterization.

Materials Characterizations

1) Investigations on polyisoprene gels attempt to evaluate the differences in scattering behavior between concentrated solutions of the polymer in a solvent and in swollen cross-linked gels. These results are to be compared with earlier rheological studies on the same systems.

2) Studies of network formation in brominated epoxies are undertaken to characterize the structural changes that take place as epoxy networks undergo chemical cross-linking.

3) Limiting power law behavior for anisotropic particulate scatterers is investigated. Models for the scattering from oriented assemblies of particulate scatterers in composite materials and track-etched membranes indicate that the limiting exponent (n in the expression $I \approx Aq^{-n}$) can differ from a value of 4 if the chord length distribution has a strong directional dependence. Data indicating the need for improved models was obtained from earlier collaborations with workers from the Army Materials Laboratory, Renssellaer Polytechnic Institute and Sandia National Laboratories.

4) Scattering from nanophase sintered nickel films, in collaboration with Dr. Jorg Weissmueller, guest worker in the NIST Metallurgy Division, shows considerable

promise with respect to characterizing the residual porosity in these materials.

5) Under a CRADA with Dow Chemical Co. samples of syndiotactic polystyrene (sPS) are characterized by SAXS. Previous work on SAXS from sPS has been extended to include scattering at temperatures up to and slightly above the melting point of the lamellar microstructure by utilizing the modified microscope hot stage. This work demonstrated that the apparent absence of scattering from the lamellar microstructure below the T_g of sPS is a consequence of the virtually identical densities of the "glassy" and "crystalline" phases. The quotes in the previous sentence are meant to indicate that our observations and work published by others have shown that sPS is a very unusual material with regard to its molecular packing.

6) Collaborative research with Dr. Ruizhong Hu and Scott Lambert of W. R. Grace Co. involves preparing materials that are models for those made with processes used to produce oriented polyethylene films. This work has demonstrated that "oblique incidence SAXS" is a vital addition to other SAXS sampling methodologies applied to the characterization of microstructural features that occur in film processing.

Outputs

External Collaborations

The SAXS facility was used by researchers from Mobil Chemical Company Research & Development Laboratories, W. L. Gore Company, and Cryovac Division of W. R. Grace to characterize materials of interest to their companies. In addition, Dow Chemical Company provided funding through a CRADA to have their materials characterized.

Publications

D.L. VanderHart, R. St. John Manley, and J.D. Barnes, *Proton spin diffusion studies of polymer blends having modest monomer size. 2. Blends of cellulose with either poly (acrylonitrile) or poly (4-vinylpyridine)*, Macromolecules **27,** 2826 (1995).

B.J. Bauer, D-W Liu, C.L. Jackson, and J.D. Barnes, *Epoxy/SiO2 Interpenetrating Polymer Networks*, Polymer Adv Tech. (submitted).

B.J. Olivier, R.R. Lagasse, D.W. Schaefer, J.D. Barnes, and G.G. Long, *A Small Angle Scattering Study of the Pore-Orientation Periodicity in Porous Polymer and Carbon Materials*, Macromolecules (Submitted).

C.L. Jackson, B.J. Bauer, A. Nakatani, J.D. Barnes, *Synthesis of Hybrid Organic-Inorganic Materials from Interpenetrating Polymer Network Chemistry*, Chemistry of Materials (submitted).

Tutorials, workshops and short courses

J.D. Barnes, *Microstructure on the Nanometer Scale,* Tutorial Workshop at 1995 American Crystallographic Association Annual Meeting, Montreal, with N.M. Berk, S.F. Trevino, A. Karim, W. J. Orts, S. Krueger.

J.D. Barnes, *SAXS in the Industrial Lab,* 1995 Denver X-Ray Conference - with E. S. Clark, R. Barton.

Presentations

J.D. Barnes, *Porod's Law and Anisotropic Porous Materials*, 1994 Materials Research Society, Boston, MA, December, 1994.

J.D. Barnes, *SAXS in the Industrial Lab*, University of Cincinnati, Department of Materials Science, Cincinnati, OH, March, 1995.

J.D. Barnes, *SAXS in the Industrial Lab*, Procter and Gamble Co., Cincinnati, OH, March, 1995.

J.D. Barnes, *Standard Data Formats for Small-Angle Scattering Using Area Detectors*, American Crystallographic Association Annual Meeting, Montreal, Canada, July, 1995.

Goals

The Dental and Medical Materials Program provides measurement methods, data, and concepts needed by the U.S. health care industry to develop dental composite restorative materials of greater durability and wear resistance. Dental restorative composites are heterogeneous materials having three essential phases: 1) a polymeric matrix which comprises the continuous phase, 2) silicate 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. The polymeric matrix of a dental composite is formed by free radical polymerization, under ambient conditions, 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. While all three phases are important in determining the properties of the composites, this program focuses primarily on the interfacial and polymer matrix phases. Although only a minor component of these composites, the interfacial phase that develops from the interaction of the silane coupling agent with the polymer matrix and the siliceous filler exerts a profound effect on the properties of the composites. Because these composites are used in an aggressive, aqueous environment that constantly challenges the vulnerable silane mediated polymer-glass bond, understanding of this critical interfacial phase is being acquired so that strategies can be developed for its improvement.

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

FY-95 Significant Accomplishments

- In an effort to improve access to spiro orthocarbonate (SOC) monomers capable of double ring-opening polymerization with expansion, a simple one-pot synthesis of multifunctional SOC oligomers was developed from inexpensive starting materials. The process can be easily scaled up.

- Several meetings were held with dental materials manufacturers interested in exploring the use of spiro orthocarbonate (SOC) monomers to minimize the polymerization shrinkage of dental resins and composites. Representatives from L.D. Caulk, Ivoclar-Vivadent and Jeneric/Pentron were involved in separate discussions to examine the potential applications and practical implementation of expanding SOC monomers.

- Prepared and evaluated several fluorinated urethane methacrylate monomers and oligomers for use as hydrophobic matrix materials for dental composite applications. Demonstrated that these fluorinated materials have mechanical strengths equivalent to that of conventional composites with up to 20x less water uptake.

- Demonstrated that fluorinated cyclopolymerizable oligomers offer low polymerization shrinkage and good hydrophobicity.

- A molecular modeling program which can predict molecular volumes of monomers based on Van der Waals radii has been used to estimate monomer densities and the density of reactive groups per unit volume. These values allow proposed monomers to be screened on the basis of shrinkage predicted for simple addition polymerization.

- Demonstrated that both aryliminodiacetic and alkyliminodiacetic acids effectively demineralize the surface of dentin, but only the aryl conditions can initiate the self-polymerization of dental monomers, resulting in significantly improved bond strengths of dentin bonding systems.

- A patent disclosure entitled "Improved Dental Compositions Via Improved Interfaces" has been filed and several dental companies (Caulk, 3M and Degussa) have expressed an interest in the technology.

- Demonstrated that a dental composite with amorphous calcium phosphate as the filler phase can, under oral-simulating conditions *in vitro*, remineralize carious lesions in bovine enamel.

- Produced and characterized Standard Reference Material 2910, Calcium Hydroxyapatite.

- Demonstrated the feasibility of using siloxanes both as binders and preceramic agents for preparing porous ceramics at moderate temperatures. These porous frameworks can be silanized and infiltrated with *in situ* polymerizable monomer systems for the preparation of interpenetrating phase composites.

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

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Objective

The objective of this project is the development of high conversion, low shrinkage polymeric materials for use in dental resin and composite applications. In addition, the program seeks to increase the resistance of dental polymers to the damaging effects of water and various other chemical species which may be encountered in the oral environment.

Accomplishments

Synthesis and Characterization of Dental Resin Systems with Reduced Polymerization Shrinkage.

The polymerization shrinkage of dental resins and composites remains as one of the most commonly cited deficiencies of these materials. The double ring-opening polymerization of spiro orthocarbonate (SOC) monomers offers a viable route to expansion during polymerization. Because of relatively complex monomer synthesis pathways and the low modulus and low molecular weights of ring-opened SOC polymers obtained by a cationic polymerization mechanism, these materials have had limited practical utility. In an effort to address all these problems in a single approach, a simple, high yield synthesis from inexpensive, readily available starting materials was devised to provide oligomeric SOC prepolymers. In this approach, the multifunctional SOC oligomers were expected to undergo ring opening polymerization with crosslink formation to yield strong polymeric matrices with an expansion in volume. Oligomeric SOCs were successfully prepared in virtually quantitative yield in two steps. This involved the conversion of triols to bis(hydroxymethyl)SOC intermediates followed by chain extension via diisocyanates or diacid chlorides. However, cationic polymerization of the SOC oligomers produced completely ring-opened but predominantly noncrosslinked polymers by an interesting new mechanism which appears to involve the urethane or ester functional groups appended to the SOC rings. Model studies are currently underway with functionalized SOC monomers to define the unique polymerization/fragmentation process in an effort to control and exploit this novel pathway.

In an alternate approach, if the number of polymerizable groups per unit volume of a resin is decreased, then the overall shrinkage of the system will also be reduced. This approach can be applied through the use of monomers with larger molecular volumes or by minimizing the amount of low molecular weight diluent monomer needed in a resin formulation. Several studies have demonstrated that the crosslink density in typical dental polymers can be reduced without sacrificing mechanical strength. Toughness of materials can also be improved by a reduction in crosslink density. In an effort to make dimensionally stable, inert polymeric matrix materials for dental composite applications, fluorinated methacrylate resins have been examined. By use of a MOPAC computer modeling program, the solvent excluded molecular volume of various monomers can be determined and compared against conventional dental monomers. Through these modeling studies, fluorinated difunctional monomers, with molecular weights much higher than that of Bis-GMA, had molecular volumes not substantially different than Bis-GMA. The addition of a bulky spacer group between the reactive methacrylate groups increased the monomer molecular volume of the fluorinated monomers to between two and three times that of Bis-GMA with no reduction in mechanical strength properties of the photocured resins. These modeling studies will be verified by evaluation of the polymerization shrinkage of the experimental fluorinated and control resins with our newly rebuilt mercury dilatometer. In addition to the increased molecular volume of the fluorinated monomers, they need significantly less diluent comonomer added to modify resin viscosity. Therefore, even greater reductions in the

reactive group density in these resins is achieved.

As mentioned above, fluorinated monomers are being evaluated in dental resin and composites as a means of increasing hydrophobicity and chemical resistance as well as decreasing polymerization shrinkage in these materials. Since cyclopolymerization of 1,6-diene monomers obtained by formaldehyde addition to simple acrylates has been shown to provide for 30-40% reductions in polymerization shrinkage and improved degrees of conversion compared with conventional dimethacrylate monomers, a study of fluorinated cyclopolymerizable monomers and oligomers was undertaken. Previous work in this field had shown that the electron withdrawing effect of a fluorine group substituted on an acrylate ester group resulted in a significant amount of an undesirable side reaction product during the diene monomer synthesis. In addition, the fluorinated ester groups were subject to facile hydrolysis. Therefore, the current monomers under study incorporate the fluorinated substituents in a position remote from the acrylate ester groups such that there is no electronic interaction. Further, the fluorinated groups are attached via a hydrolytically stable ether linkage. Multifunctional fluorinated oligomers with 1,6-diene repeating groups along the oligomer backbone were prepared and characterized. Photocurable resins based on these cyclopolymerizable oligomers required only small percentages of diluent comonomer addition. Composites derived from these resins have exhibited low water uptake and high contact angles with water. Mechanical strength of the composites has generally been less than that of conventional hydrocarbon control materials due to the relatively low cohesive energy that is characteristic of fluorinated polymers. In preliminary work with a bromine-substituted fluorinated oligomer, which was designed to have a relatively high refractive index, mechanical strength results are significantly improved. This is presumably because of the increased stiffness of the brominated core group built into the oligomer. The polymerization shrinkage of the fluorinated resins remains to be measured with the mercury dilatometer, but relatively low values are expected due to the cyclopolymerization process.

Low Surface Energy Monomers with Varied Fluorine Contents and Distributions.

In a study designed to elucidate structure-property relationships of fluorinated monomers and their polymers as well as devise methods to increase the mechanical strength of these polymers, a series of dimethacrylates was evaluated. Resins and composites were evaluated for monomers which varied in fluorine content from 23 to 60%. The fluorine was incorporated into these monomers as $-CF_3$ groups, $-(C_2F_n)F$ groups or mixtures of the two. It was found that the resin refractive index and density were very highly correlated to the overall fluorine content, regardless of the type of substitution. The degree of conversion of photopolymerized resin films was significantly improved by the introduction of fluorine as the $-(CF_2)_nF$ groups. While the water contact angles measured on the composite surfaces tended to increase with the overall fluorine content in the resin, the water uptake showed no correlation at all to either fluorine content or its manner of incorporation. All of the fluorinated composites had extremely low water uptake (0.4-0.13 wt%) compared with the control material (1.22 wt%). However, composite mechanical strength as measured by diametral

tensile strength was inversely related to the monomer fluorine content. All the fluorinated dimethacrylate based materials produced mechanical strength results which were significantly lower than that of the conventional hydrocarbon dental monomers.

As a means of improving the mechanical strength of fluorinated resins, difunctional monomers and multifunctional oligomers, which include urethane functional groups, were prepared. The extended hydrogen bonding due to the urethane groups serves to increase the cohesive energy of the fluorinated polymeric network. By coupling the fluorine-containing substituents and urethane linkages into one monomer, resins with mechanical strength properties as good as or better than those of traditional dental materials were prepared. If the urethane groups and fluorinated substituents were included on separate monomer molecules, low strength polymers were obtained presumably due to microphase separation. In some cases, the introduction of the urethane groups in the monomers increased the water uptake of the fluorinated polymers. However, with the appropriate isocyanate or diisocyanate used to form the urethane groups, extremely low water uptake and excellent mechanical strength can be combined in a material that has good practical potential.

Outputs

Publications

J. W. Stansbury, S. Dickens, D.-W. Liu, *Preparation and characterization of cyclopolymerizable resin formulations*, J. Dent. Res. 1995, 74, 1110.

J. W. Stansbury, J. M. Antonucci, G. Scott, *Photocured composites based on dimethacrylate monomers of varied fluorine content*, Polym. Prepr. 1995, **36**(1), 831.

J. M. Antonucci, J. W. Stansbury, *Molecularly designed dental polymers* in Functional polymers for emerging technologies, ACS Books.

J. W. Stansbury, D.-W. Liu, S. Sim, *Use of polymer-supported quinuclidinyl catalysts for the synthesis of cyclopolymerizable monomers via the aldehyde-acrylate coupling reaction.* Cleared Div. review (to be submitted to Macromolecules)

J. W. Stansbury, *Polymerization studies of functionalized spiro orthocarbonate monomers.* Cleared Div. review (to be submitted to Macromolecules)

J. W. Stansbury, S. Kim, G. Scott, J. M. Antonucci, *Low surface energy monomers with varied fluorine contents and distributions.* (to be submitted to Macromolecules)

Abstracts accepted for AADR/IADR meetings

J. W Stansbury, S. Kim, G. Scott, J. M. Antonucci, *Low surface energy monomers with varied fluorine contents and distributions,* AADR Meeting San Antonio, TX, March '95.

B. B. Reed, J. M. Antonucci, J. W. Stansbury, *Cationic polymerization of vinyl cyclic acetals by visible light*, AADR Meeting San Antonio, TX, March '95.

C. Gingreau, J. M. Antonucci, J. W. Stansbury, *Visible light polymerization of vinyl ether-acrylic monomer systems*, AADR Meeting San Antonio, TX, March '95.

J. M. Antonucci, J. W. Stansbury, S. Kim, *Effect of long chain silane coupling agent on composite strength,* IADR Meeting Singapore, July '95.

Presentations

Photoinitiated cyclopolymerization of polyfunctional acrylic monomers. Hercules Research Center, Wilmington, DE, 10/94.

Polymers and cyclopolymers from highly fluorinated monomers and oligomers. ACS Div. of Polymer Chemistry, Biennial Symposium, San Juan, PR, 11/94.

Overview of research in the Dental and Medical Materials Group at NIST. AADR Open House for dental students, 3/95.

Ring-opening polymerization and its use in dentistry. Lunch and Learn Seminar at the AADR meeting. 3/95.

Patents

J. W. Stansbury, *Improved monomers for double ring-opening polymerization with expansion.* US patent 5,362,889, issued Nov. 8, 1994.

J. M. Antonucci, J. W. Stansbury, Cheng, *Novel multifunctional acrylates and the synthesis thereof.* US patent 5,380,901, issued Jan. 10, 1995.

J. M. Antonucci, J. W. Stansbury, *Improved dental compositions via improved interfaces,* invention disclosure filed.

J. M. Antonucci, J. W. Stansbury, C. Gingreau, *Improved photoinitiator systems for polymeric dental compositions*, invention disclosure filed.

Dental Composites With Improved Interfaces

J. M. Antonucci, W. G. McDonough, J. W. Stansbury, F. W. Wang

Objective

The objective is to compare the efficacy of 10-methacryloxydecyltrimethoxysilane (MDTMS) and 3-methacryloxypropyltrimethoxysilane (MPTMS) as silane coupling agents by traditional bulk mechanical and by the microbond single fiber tests.

Accomplishments

Methacrylic resin-based dental composites commonly employ MPTMS, a bifunctional silane coupling agent with an intermediary three-carbon connecting segment, to provide the interfacial phase that unites the disparate organic polymer matrix with the reinforcing inorganic phase. In this study, equivalent amounts of MPTMS (0.5 mass%) and the longer hydrocarbon silane agent, MDTMS (0.7 mass%), were used to formulate similar experimental dental composites. A macrosized (average particle size = 44 μm), radiopaque particulate glass filler was silanized with either MPTMS or MDTMS using either a hydrophobic (cyclohexane plus n-propylamine as a catalyst) or a hydrophilic (aqueous methanol plus acetic anhydride as the catalyst) silanization procedure. A dental resin consisting of equivalent mass fractions of BisGMA and TEGDMA (triethylene glycol dimethacrylate) photo-activated with camphorquinone (CQ) and ethyl 4-N,N-dimethylaminobenzoate (4EDMAB) was used to prepare the composites. The results are summarized in Table 1. Both the diametral tensile strength (DTS) and the flexural strength(FS) of the MDTMS-based composites were comparable to a similarly loaded MPTMS-based composite (67 volume %).

A noteworthy property of the MDTMS silanized filler is that it mixes easier with the resin than the MPTMS silanized filler and, therefore, permits the formulation of composites with significantly higher filler loadings. Because of its greater hydrocarbon nature, and its ability to facilitate high filler loadings (Table 1), MDTMS has the potential to aid in the development of dental composites with enhanced strength and durability and with lower polymerization shrinkage.

Traditionally, fracture mechanical techniques, such as the diametral compression and flexural tests, have been used as indirect methods to assess the quality of the interphase in dental composites. Interpretation of failure mechanisms from these bulk property tests can be difficult because of the interaction of many competing failure modes that accompany such composite fracture phenomena. By contrast, the microbond test, a single fiber shear test, has the potential to reduce the complexity of events that confound conventional interfacial failure analysis.

In this study, the feasibility of using the microbond test to probe the interaction of a visible light-activated BisGMA/TEGDMA

Table 1: Effect of Silane Agent on the Properties of an Experimental Composite.

Silane Agent	Vol % Si-Filler	DTS 24h (SD) MPa	FS 24h (SD) MPa	FS 2wk (SD) MPa
MPTMS	67	56.5 (2.9)	99.8 (9.6)	79.8 (4.2)
MDTMS	67	61.8 (3.4)	102.5 (15.8)	94.9 (7.5)
MDTMS	71	61.3 (3.1)	117.5 (13.4)	105.3 (8.8)
MDTMS	74	63.5 (2.7)	136.9 (7.4)	-------

Number of specimens ≥ 5. Specimens stored in distilled water at 37°C for indicated times. Monomers system = BISGMA/TEGDMA 1/1 w/w); photoinitiator system 0.2 wt% CQ, 0.8 wt% EDMAB. Filler system = barium oxide SiO_2 (average particle size 44 μm). SD = standard deviation.

Table 2: Polymer-Fiber Interfacial Shear Strength (t) in MPa

Silane Agent	n	Mean t (SD)	Min t	Max t
none	10	15.40 (4.40)	6.81	20.16
MPTMS	9	35.86 (11.20)	20.50	51.55
MDTMS	6	36.61 (4.53)	29.77	42.35

Monomers system = BISGMA/TEGDMA 1/1 w/w); photoinitiator system 0.2 wt% CQ, 0.8 wt% EDMAB. Fiber = 15 - 17 μm diameter.

(7/3 mass fraction) resin with unsilanized and variously silanized (MPTMS and MDTMS) E-glass fibers was explored. The mean interfacial shear strength, τ, in MPa of the polymerized microdroplets after 24 hours at 23 °C were 15.4 (4.4) for the unsilanized fiber, 35.9 (11.2) for the MPTMS sized fiber and 36.6 (4.5) for the MDTMS sized fiber. (Standard deviations are in parentheses). Analysis of variance ($n \geq 7$) indicated no significant differences existed between the τ values of the two silanized fiber-resin systems, but that significant differences were present in the case of both silanized systems and the unsilanized control ($p \leq 0.05$) These results (Table 2) are in general agreement with our results from both the diametral compression and flexural tests previously conducted on BisGMA composites reinforced with a macrosized glass particulate filler. The microbond test, however, because of the less complex geometry of the interphase/interface, may provide a more direct means of assessing interfacial interactions that occur between dental polymers and silanized glass surfaces.

Outputs

Publications

J. M. Antonucci, W. G. McDonough, C. L. Schutte, C. K. Moon, *Interfacial Shear Strength Measurements By The Microbond Bead Test,* Journal of Dental Research (special issue) **74** 231 Abst 1754 (1995).

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W. G. McDonough, J. M. Antonucci, C. K. Moon, C. L. Schutte, *Single Fiber Tests for Measuring the Interfacial Shear Strengths of Dental Composites,* Invited Talk and Abstract, The American Chemical Society 29th Middle Atlantic Regional Meeting, 5/95.

Invention Disclosure

J. M. Antonucci, J. W. Stansbury, *Improved Dental Compositions Via Improved Interfaces.*

Improved Adhesive Systems for Bonding to Dentin

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Objective

The objective is an enhanced understanding of the mechanism(s) involved in adhesion to dentin and to develop improved, less technique sensitive bonding systems.

Iminodiacetic acids are a special class of amino acids that are noted for their moderate acidities (pK_as 2-3) and their ability to chelate multivalent metal ions such as the biologically important calcium ion. Previously it was shown that the application of aqueous solutions of N-phenyliminodiacetic acid (PIDAA) to dentin both conditions (demineralizes) and activates the surface for polymerization so that the subsequent application of carboxylic acid monomers results in interfacial polymerization and strong dentin bonding. In this study, two aliphatic imino acids, *N*-methyliminodiacetic acid (MIDAA) and 2-

hydroxyethyliminodiacetic acid (HEIDAA) were compared with PIDAA and 2-carboxyphenyliminodiacetic acid (CPIDAA) for their efficacy as conditioners with polymerization-activating properties in bonding dental composites to dentin. Scanning electron microscopy of dentin surfaces treated by aqueous solutions of the various iminodiacteic acids revealed that they were all effective at a relatively low equivalent concentration of 0.1 mol/L in removing surface debris. However, there were significant differences in the *in vitro* shear bond strengths that developed between the composite and the variously treated dentin surfaces. Mean shear bond strengths (standard deviation) in MPa were: HEIDAA, 6.6(4.7); MIDAA, 8.8(5.2); CPIDAA, 21.0(5.4); PIDAA, 24.2(6.7) when 0.1 mol/L solutions of the iminodiacetic acids were used as conditioners for prepared dentin. Analysis of variances (n=8) showed that dentin treated with the aryliminodiacetic acids gave significantly higher bond strengths than dentin treated with the aliphatic imino acids ($p \leq 0.0001$). These results lend support to the hypothesis that aryliminodiacetic acids, in contrast to their aliphatic analogs, act both as surface conditioning and polymerization-activating agents in dentin bonding systems.

In a related study it was shown that salts of PIDAA at near neutral pH also can condition and activate dentin for interfacial polymerization to give significant composite-dentin bond strengths in a simple, two-step bonding protocol. These types of bonding system may be desirable for use with extremely sensitive teeth. The ability to combine both conditioning and surface-activating functions in one chemical agent greatly simplifies dentin bonding protocols, making them less technique-sensitive.

Outputs

Publications

G. E. Schumacher, J. E. Code, J. M. Antonucci, *N-Phenyliminodiacetic acid (PIDAA) and salts thereof as conditioning primers for dentin bonding*, Journal of Dental Research (Special Issue) 74 151 Abstract No. 1113 (1995).

J. M. Antonucci, *Simple, effective methods for adhesion to tooth structure through the use of N-phenyliminodiacetic acid*, Invited talk and abstract at the Middle Atlantic Regional Meeting of the American Chemical Society, Washington DC, May, 1995.

M. Farahani, J. M. Antonucci, *Mass spectrometric analysis of polymers derived from N-aryl-α-amino acids initiators*, Invited talk and abstract at the Middle Atlantic Regional Meeting of the American Chemical Society, Washington DC, May, 1995.

Patents

J. M. Antonucci, P.S. Bennett, U.S. Patent (U.S. Patent Application Serial No. 08/189,709) A method and composition for promoting improved adhesion to substrates. Patent has been granted and ADA has licenced this invention for commercialization.

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

J.M. Antonucci and J.R. Kelly[1]
[1]Naval Dental School, Bethesda, MD

Objective

The objective is to explore processing feasibilities and the processing-property relationships for interpenetrating phase

composites (IPCs) formed by low temperature pyrolysis of ceramic powders coated with pre-ceramic, polymers, such as polysiloxanes, creating particle networks for subsequent resin infiltration and polymerization.

Accomplishments

There is a need to develop improved aesthetic materials for both machinable (CAD/CAM) and direct (single visit) bonded dental restorations. Conceptually, IPCs can have significantly enhanced properties compared to either traditional composites or dental ceramics. This initial study was designed to prepare a polymer-reinforced, ceramic skeleton type of IPC.

Various cyclohexane solutions of a liquid trimethylsiloxy terminated poly(dimethylsiloxane), 1000 centistokes, were used as binders for the fabrication of pressed discs of either feldspathic porcelain or aluminum oxide powders. Discs were fired for ten minutes at temperatures ranging from 550-745 °C. The resulting porous discs were then silanized with 3-methacryloxypropyltrimethoxysilane, infiltrated with chemically activated methyl methacrylate (2 mass% benzoyl peroxide and 0.5 mass% N,N-dihydroxyethyl-p-toluidine) which was allowed to undergo ambient polymerization. After 24 hours at 22 °C, the excess polymer was removed by mechanical polishing and the easily machined discs were tensile tested in biaxial flexure. Initially a 2x3 factorial design (with the n = 3-8 per group) was used to assess the effects of temperature for ten minutes at two levels; low (655 °C) and high (715 °C): and binder concentration at three levels; 0%, 5% and 20% by mass. Temperatures and binder concentration were both significant ($p \leq 0.001$). The interaction between temperature and binder concentration was not significant ($p \geq 0.76$). Duncan's multiple comparison test (alpha = 0.1) was then used to determine specific differences among the three concentrations. Significant differences were found between 0 and 5 mass% and between 0 and 20 mass%. Based on these preliminary results, the 5 mass% binder was studied at 550, 600, 655, 715, and 745 °C. The optimum temperature for the 5 mass% binder appears to be about 655 °C which yielded an IPC having a mean tensile stress of 140 MPa, similar to that of currently available micaceous phase dental glass-ceramics and higher than traditional feldspathic dental porcelains. Mean tensile strengths for aluminum oxide discs were 180 MPa, prepared with 5 mass% binder at a pyrolysis temperature of 600 °C .

The use of glass-forming pre-ceramic polymers as binders allows neck-formation sintering to occur at significantly lower temperatures than those employed for un-aided sintering, and removes constraints dictating traditional sintering temperatures based upon ceramic type and particle size. It should be quite feasible to formulate mixed powder compacts (*e.g.*, crystalline oxide and glass powders) or compacts of widely varied particle sizes, and sinter these under conditions dictated by the pyrolysis behavior of the pre-ceramic polymer as opposed to the ceramic powder. The described technology should allow for the fabrication of IPCs from virtually any ceramic or glass under similar low temperature processing conditions. Because of their well infiltrated polymer content, these IPCs combine strength and toughness and have potential to be bonded to dental resin cements. This type of composite also provides many opportunities for control over translucency and color, both of which are critical for materials used in restorative dentistry. IPCs represent a significant improvement over either current CAD/CAM

ceramics or traditional (resin matrix) dental composite restoratives. The further development of polymer infiltrated ceramics formed to "net shape" dimensions that are flaw tolerant, wear and water resistant, machinable and aesthetically pleasing can be easily envisioned. It is foreseen that this type of material could be suitable as an amalgam replacement, machinable blocks, veneer materials for metal substructures, denture teeth and denture bases. Negative clinical influences of polymerization shrinkage, associated with conventional use of resins, may be eliminated.

Publication

J. R. Kelly , S. M. Smith, J. M. Antonucci, *Fabrication of porous ceramic networks for interpenetrating phase composite,* Proceedings of the American Association for Dental Research Annual Session, San Antonio, TX, 8-12 March, 1995. J Dent Res 74(AADR Abstracts):166, Abstract #1237.

Patent

J. R. Kelly, J. M. Antonucci, Patent application filed: NIST docket #95-006

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

J.M.Antonucci, D.Skrtic[1,2], E.D.Eanes[2] and S.Takagi[3]

[1] Ruder Boskovic Institute, Croatia

[2] National Institute of Dental Research (NIDR), NIST

[3] Paffenbarger Research Center, American Dental Association Health Foundation (PRC/ADAHF), NIST

Objective

The objective is to develop polymer based composites with amorphous calcium phosphate as a bioactive filler with remineralization potential.

Accomplishments

Amorphous calcium phosphate (ACP), a highly soluble, non-crystalline calcium phosphate with propensity for facile conversion to hydroxyapatite (HA), has potential as a remineralizing agent for defective mineralized tissues. Recent studies have shown that polymeric composites derived from dental acrylic polymers and stabilized ACP powders showed sustained release of calcium and phosphate ions over extended periods of time.

In this study we assessed the *in vitro* efficacy of a visible light activated ACP composite to remineralize caries-like lesions in extracted bovine incisors. Levels of calcium and phosphate ions released from a specimen disks of the ACP-composite greatly exceeded those from specimen disks of a similar HA-composite (Fig.1).

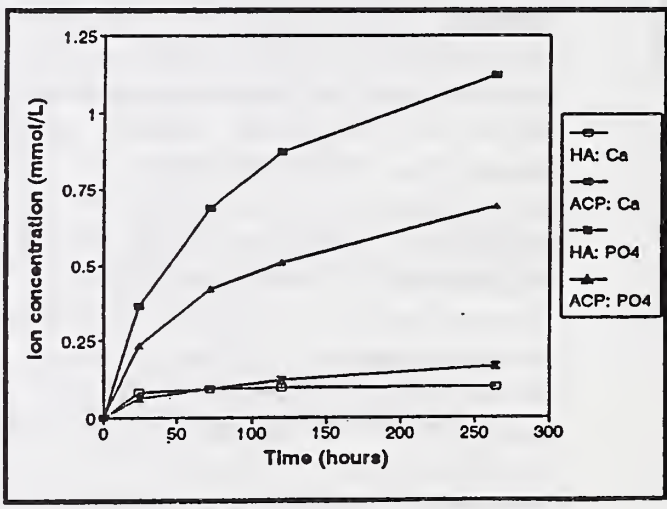
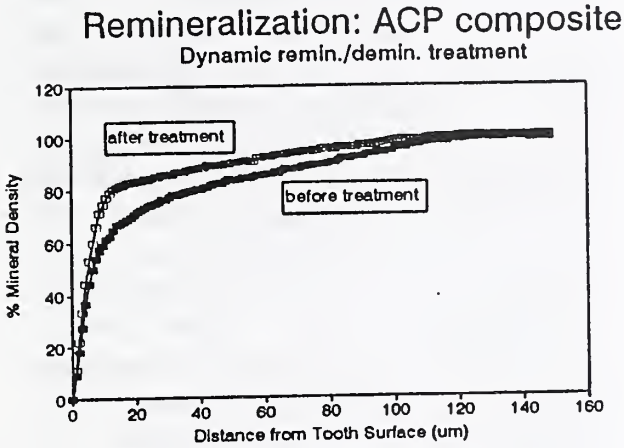


Fig.1. Ion release from ACP- or HA-filled BisGMA/TEGDMA based composite disks.

The caries-like lesions in the bovine teeth that were covered with a sealant layer of the photocured ACP-composite regained considerably more of their lost mineral than did lesions coated with HA-filled composite. (Fig.2).



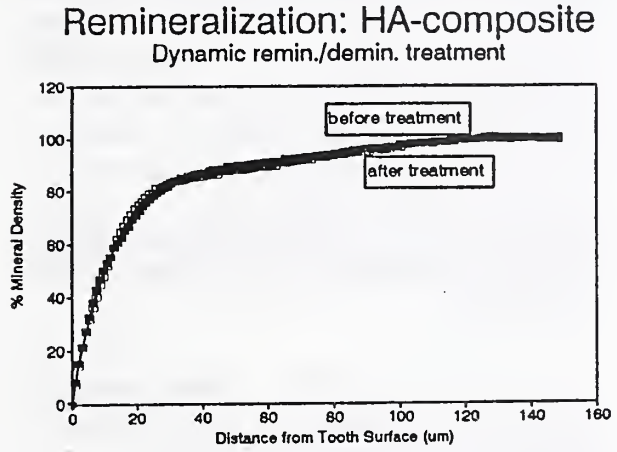


Fig.2. Relative change in mineral content of bovine enamel lesions sealed with ACP- or HA-filled composites.

The changes in mineral content were quantitatively assessed by digital image assisted microradiographic analysis. These results suggest that ACP-composite sealants and adhesives have the potential to facilitate the repair of defective enamel and other mineralized tissues.

Outputs

Publications

D. Skrtic, E. D. Eanes, S. Takagi, J. M. Antonucci, *In vitro remineralization of amorphous calcium phosphate/methacrylate coated enamel lesions*, Journal of Dental Research (Special Issue) 74 185 Abstract No. 1388 (1995).

J. M. Antonucci, D. Skrtic, E. D. Eanes, *Remineralizing dental composites based on amorphous calcium phosphate*, Polymer Preprints 36(1) 779 (1995).

D. Skrtic, E. D. Eanes, J. M. Antonucci, *Bioactive methacrylate composites based on amorphous calcium phosphate. In vitro assessment of remineralization efficacy.* Poster presentation and abstract at the Middle Atlantic Regional Meeting of the American Chemical Society, Washington DC, May, 1995.

D. Skrtic, E. D. Eanes, J. M. Antonucci, *Polymeric calcium phosphate composites with remineralization potential.* Chapter 25 in: Industrial Biotechnological Polymers (Gebelein,C.G. and Characher,C.E., eds.), Technomics Publ. Co. Inc., Lancaster, PA, 1995, in press.

J. M. Antonucci, D. Skrtic, E. D. Eanes, *Bioactive polymeric materials based on amorphous calcium phosphate - effect of coupling agents.* In: Hydrogels and Biodegradable Polymers for Bioapplications (Ottenbrite,R.; Huang,S. and Park,K., eds.), ACS Books, Washington DC, 1995, accepted for publication.

Patents
J. M. Antonucci, E. D. Eanes U.S. Patent (U.S. Patent Application Serial No. 08/189,708) entitled Polymeric amorphous calcium phosphate compositions.

Support for the Biomaterials Integrated Products Industries

J.A. Tesk, Steve Hsu[1]
[1] Ceramics Division

Objective
The objective is to support U.S. industries that manufacture biomaterial integrated products.

Accomplishments
Efforts have involved planning for future initiatives, workshops to identify industrial needs and participation on standards related boards and committees.

A March 30-31 workshop, with 51 participants from orthopaedic companies, universities, hospitals, the Food And Drug Administration (FDA) and NIST, reviewed current orthopaedic material wear screening test methods. The workshop summary report (issued) defined the need for accelerated test methods for evaluation of the wear properties of orthopaedic joint implant materials. A steering committee, comprised of a representative from each of seven orthopaedic companies, devised a research plan for Cooperative Research and Development Agreements (CRADAs) on work toward identification of the needed tests. Draft CRADAs are currently being reviewed by orthopaedic companies and NIST. It is anticipated that CRADAs with industry will be signed by the end of calendar year 1995. Announcement (Federal Register and Commerce Business Daily) of the intended research elicited interest from the Academy of Orthopaedic Surgeons and several orthopaedic allied businesses.

The results of the proposed research are expected to find use in: national and international standards for orthopaedic devices, foreshortening the time for acceptance of device submissions to the FDA (Industry representatives have estimated that shortening acceptance time for only one device by *ca.* two weeks would recoup the research expenditures), product quality assurance, and uniform test methods for archival research investigations.

Outputs
Publications
J. A. Tesk, *Summary of Total Joint Replacements Workshop*, April, 1995. Distributed to workshop participants.

W. E. May, C. D. Erlich, M. Herman, L. A. Johnson, S. Katz, S. M. Seltzer, J. A. Tesk, *Committee Report on NIST Strategic Workshop: Health Care Technologies for the 21st Century.*

Durability and Processing of Dental Ceramic, Metallic and Ceramic-Metal Materials

J.A. Tesk, J.R Kelly[1] (guest scientist), K.Asaoka[2], J. Lechner[3], S.C. Saunders[4], R. Sorensen[5], H. Morris[6], & R. Mais[6].
[1] United States Navy Dental Corps
[2] Tokushima University
[3] Statistical Engineering Division
[4] Washington State University
[5] University of California, Los Angeles
[6] Department of Veterans Affairs

Objective
The objective is to explore potential analytical and test methods which may be useful for high confidence level prediction of the durability and survivability of medical/dental synthetic biomaterials and implants respectively.

Accomplishments
A collaborative effort with the Department of Veterans Affairs, Washington State University and the NIST Statistical Engineering Division has employed a two-parameter Weibull model to analyze clinical data that included left-, right-, and interval censoring. The analysis developed Weibull parameters that produce a survival curve that is consistent with experience up to the right-hand censoring time (ca. 10 years) and predicts a 10% survival of 30 ± 10 years (± values are for one standard deviation). Work is currently in progress to explore whether some particular physical significance may be attached to the Weibull shape parameter.

Recent success was achieved with what is believed to be the first mathematical modeling to simulate survivability data from *in vitro* and *in vivo* testing of dental all-ceramic fixed partial dentures. This work will be extended to include the effects of cyclic fatigue.

Outputs
Publications
J. A. Tesk, M. Y. Chiang, S. M. Keeny, J. Tang, Y. Sato, *Identification of failure origin through testing and the Weibull risk-of-rupture*. J. Res. Natl. Inst. Stand.Technol. **99**, 505-510, (1994).

J. R. Kelly, J. A. Tesk, J. A. Sorensen, *Failure of all-ceramic fixed partial dentures in vitro* and *in vivo*: *analysis and modeling*. J. Dent. Res. **74**(6) 1253-1258, (1995).

Volumetric Contraction Measured by a Computer Controlled Mercury Dilatometer.

B. Reed[1], S. Dickens[1], B. Dickens, E. Parry[1] ([1]ADA Health Foundation).

Objectives
To provide a routine, robust measurement of polymerization shrinkage as a function of time.

Accomplishments
Polymeric dental composites are widely used as restorative materials because of their excellent esthetics and durability. Typically, excessive polymerization shrinkage produces internal stresses and induces formation of micro-cracks. To follow polymerization shrinkage as a function of time, a mercury dilatometer (R.W. Penn, Dent. Matls., **2**, 78 1989) thermally insulated to ±0.01C was modified to eliminate the insulation by redesigning to reduce the amount of mercury and by providing computerized corrections for temperature fluctuations, including those from the visible light source used to initiate polymerization. The sample, placed on a glass plate, is covered by a 4 mm diameter vertical tube subsequently filled with mercury. The mercury level is monitored by a linear variable displacement transducer. Temperature is followed using a thermistor in the mercury. The sample is photo-polymerized under computer control. After shrinkage is deemed to be complete, the correspondence between mercury level and thermistor reading is established without knowing the amount of mercury present or its thermal expansion coefficient by subjecting the apparatus to a second short heating from

the lamp. Multiple regression between the mercury level and the temperature movement resulting from the second illumination provides a general correspondence between mercury level and temperature. This is then used to remove the effect of temperature variations from all measurements of the mercury level. Because expansion of the mercury due to the initiation lamp can be removed in this way, it is possible to obtain a good approximation of the degree of shrinkage with time even during initiation, i.e., the first 30 to 60 seconds of polymerization.

A formulation of 89 wt% 2,2-bis[p(2'-hydroxy-3'-methacryloxy propoxy) phenyl]propane and 10 wt% triethyleneglycol dimethacrylate was activated with 0.2 wt% camphorquinone and 0.8 wt% ethyl p-dimethylaminobenzoate. Resin samples were irradiated in the mercury dilatometer with a commercial visible light source for 60 s. Polymerization shrinkage was followed for up to 72 hours. At 90 min, the average polymerization shrinkage was 5.2±0.2% (n = 4). This contraction correlates to an estimated conversion of 48.1% of double bonds using the equation of S. Loshaek and T.G. Fox (J. Am. Chem. Soc., 75, 3544 1953). Three thin films of the same resin formulation photopolymerized under similar conditions as the shrinkage specimens had average conversion of 49.7±2.0% as estimated using FTIR. This work was supported by the ADA Health Foundation, NIST, and NIDR Grant No. DE09322-06.

THEORY AND MODELING PROGRAM

Goals

In the past few years major advances in computation and communication have led to a revolution in the theory and modeling of materials. Huge gains in computing power and corresponding reductions in cost have led to the widespread use of computational techniques to solve materials research problems. The interdisciplinary nature of materials science has led to collaborative development of theories and software that increase our ability to predict materials properties and behavior. At NIST, researchers from different laboratories and divisions share techniques and algorithms from fields such as fluid dynamics, chemistry, and fire research in developing new tools for materials modeling.

MSEL Theory and Modeling efforts in FY95 continued their focus on the behavior and properties of materials over the range of length scales from atoms to bulk materials. On the atomistic scale, researchers have used molecular dynamics simulations to study fracture in brittle materials, and a new program to model dislocations in metals is underway. On mesoscopic length scales, simulations of phase behavior, stability, separation kinetics, and morphological evolution in alloys, polymer blends, liquid-crystalline polymers, and homopolymer/copolymer blends complement ongoing experimental efforts in the polymers, metallurgy, and reactor divisions. Simulations of such materials processing problems as, e.g., dendritic growth during solidification and spinodal decomposition of chemically reacting polymers ranged from minute-long calculations on single-processor workstations to week-long calculations on massively parallel super computers. On macroscopic length scales, finite element computer codes have been developed to model a variety of materials processes, such as injection molding for automotive parts, solder geometry in microelectronic interconnects, physical aging in composite materials, and mechanical properties of ceramic microstuctures.

The Center for Theoretical and Computational Materials Science (CTCMS) is a new initiative begun this year to develop and apply state-of-the-art theoretical and computational materials science techniques and to help industry integrate them into technology development. The center is a "distributed" or "virtual" center using electronic linkages to bring together researchers in government, academia, and industry to define and attack key materials and materials processing problems. NIST provides an infrastructure and support for the distributed members, including a World Wide Web information server. The center also established and maintains a computing facility for the use of center members at NIST and elsewhere.

The CTCMS uses workshops as the first step in defining research programs and building collaborative teams. Over the past year, CTCMS workshops have spawned ongoing programs in solder interconnects, Green's functions and boundary element methods, glass formation, micromagnetics, and pattern formation in polymer/liquid crystal mixtures. Other recent workshops covered fracture, rational design of advanced materials, large scale computation of realistic microstructure, theory and modeling of collective dislocations, the development of residual stresses during thermoset composites curing,

the prediction of hygrothermal effects on the performance of polymers and polymeric composites, molecular beam epitaxial growth, and optimal design for materials and structures.

Theory and Modeling in Polymer Physics: Off-Lattice Computer Simulations of Glass Forming Systems

P.H. Verdier and D.E. Kranbuehl[1]
[1] College of William and Mary

Objective

The objective is to develop and apply off-lattice computer simulations of polymer dynamics in the condensed phase to predict the phenomena of structural recovery in polymeric glass forming systems.

Accomplishments

The processibility of plastics and the final characteristics of their fabricated end-products depend in large part upon the relaxation behavior of the high-polymer chains of which these materials are primarily composed. Better theoretical treatments of polymeric systems will lead to more efficient processing and to better fabricated end products. Present work addresses the inability of current theories to treat excluded volume and chain entanglement effects in a realistic way. Although most of our previous effort has been on dilute solutions the present activity is on the following properties of solids: volume (i.e., density) as a function of temperature above and below the glass transition, the time dependence of the rate of approach to final volume after quenching, and the estimation of glass transition temperature as a function of quench rate. The systems studied consist of dense collections of chains of beads with hard-sphere repulsions and finite short-range attractive interbead energies. The "temperature" of the system is taken to be inversely proportional to the attractive interbead potential. Starting at a potential where the system exhibits liquid like behavior, the system is "quenched" to a glassy state by increasing the attractive energy at various rates. As the quench progresses, the density increases until a point is reached at which the system "freezes". The density at freezing depends upon the quench rate; the slower the quench, the higher the density at which freezing occurs.

Of current interest is the effect upon glass transition temperature of polymers confined to small pores. Systems confined to small tubular regions closed at one end were simulated and the obtained transition temperatures obtained were compared to those resulting from quenches of "bulk" systems. In our model systems, the transition to a glassy state occurs at a lower temperature in systems confined to pores than in the same systems in bulk.

Study of the effects upon chain dynamics of excluded volume and chain connectivity yielded the chain-length dependence of long internal relaxation times τ_1 as a function of bead size in isolated chains. This models dilute-solution behavior. For relatively large beads, the bead size forces a chain connectivity constraint, but chains with small beads can be studied with or without chain connectivity. The chain-length dependence of the τ_1 can be represented as the sum of two parts, one determined by bead size and due to chain expansion by excluded volume, and one independent of bead size and determined by the presence or absence of chain connectivity constraints. These results help to explain the long-standing differences between simulation

results and the predictions of scaling theory, which includes chain expansion but no chain connectivity.

Outputs

Publications

P.H. Verdier, and D.E. Kranbuehl, *Separating connectivity and expansion effects in polymer single chain dynamics,* Macromolecules (submitted).

Theory and Modeling in Polymer Physics: Entropy Approaches to Polymer Viscosity

E.A. DiMarzio, S. Glotzer and Arthur Yang[1]
[1] Armstrong World Industries

Objective

The objective is to establish a rigorous theoretical basis for the Adam-Gibbs entropy model of the temperature dependence of polymer viscosities above the glass transition temperature by developing a statistical mechanical basis for the relationship between molecular mobility and the configurational entropy of polymer chains. This involves the following steps: refine the configurational entropy, Sc = 0 criterion of glass formation and show that the concepts of percolation and frustration are implicit in the entropy formulation; then generalize the entropy theory of glasses in order to predict the frequency and temperature dependence of the viscosity of polymer glasses.

Accomplishments

The Adam-Gibbs model has been highly successful as an empirical tool for describing the temperature dependence of polymer melt viscosities, but has no firm basis in statistical mechanics.

Because the Adam-Gibbs model and other entropy models have been very useful in describing the structural recovery of glasses and nonlinear viscoelastic behavior of polymers, putting these on a firm physical ground, rather than a semi-empirical one, provides a strong underlying support for efforts in the Viscoelastic Behavior of Polymers Program.

Prior work established the background for the use of the equilibrium configurational entropy theory of glass formation to calculate kinetic properties. This consisted of 4 parts:

[1] Showed that it predicts the equilibrium properties correctly for 9 different classes of polymer systems. However, agreement with experiment is a necessary but not sufficient condition for a theory to be correct.

[2] Showed that the same lattice model that makes correct predictions for glasses also correctly predicts, with no added parameters, the isotropic to nematic phase transition for rigid-rod molecules. Plate-like molecules are also shown to undergo an isotropic to lamellar phase transition. In all cases, the reason for the transition is a configurational packing entropy problem.

[3] It was shown that the crystal phase is not ubiquitous. For some materials the low temperature phase is necessarily amorphous, rather than always a metastable phase compared to the crystal.

[4] Kauzmann's paradox was resolved. Kauzmann's paradox begins by assuming that the reason for the leveling off of the Sc versus T curve or of the V versus T curve is due to the enormously large viscosity near the glass temperature. This suggests that the equilibrium values of S and V below Tg

could be obtained by extrapolating the high temperature (low viscosity region) entropies and volumes through the glass temperature. However, when this is done, negative entropies and volumes lower than crystal volumes are obtained. The entropy theory of glasses resolves Kauzmann's paradox by predicting an underlying second order phase transition. at the point where Sc=0.

However, the universal applicability of Kauzmann's paradox to all glassy materials shows that there is a universal link between configurational entropy and the viscosity. As the configurational entropy approaches zero the viscosity becomes indefinitely large. This is explained qualitatively as follows. Entropy is a measure of the number of allowed points in configuration space. At high temperatures the number of allowed points is large and the energy barrier between these allowed points is small-it is easy for the configuration point to move from one allowed point to another.

As the temperature decreases the allowed configuration points are fewer in number and therefore farther apart in configuration space. It is therefore more difficult to move from one point to another; consequently the viscosity increases and the diffusion coefficient decreases. As the entropy approaches zero the viscosity becomes indefinitely large. Thus the resolution of the paradox provides an entry into the problem of predicting the viscosity.

Quantification of the above picture requires a more precise description of configuration space. Most of the large number of allowed points in configuration space consist of high energy wells and only a small fraction of very deep wells. At high temperatures the few deep wells are of no consequence and the flow dynamics can be obtained by considering the configuration point to be wandering among the configurational sea of high energy wells. At very low temperatures the configuration point spends most of its time in the very deep wells and only rarely jumps up to the configurational sea where it wanders until locating another deep well where it resides for a very long time. Because these wells are so deep the model adopted is a version of the trapping model, except that instead of a particle being trapped as in the ordinary trapping models, in our model the configuration point is trapped.

The solution to the problem then is to construct a minimal model of the essential topology of the potential energy surface in configuration space and then to describe mathematically the motion of the configuration point on the potential energy surface. There are 3 facts about the problem that allow us to proceed.

[1] Escape from the deep wells is exponential in time. This is true no matter what the shape profile of the well is, as long as the well is deep.

[2] The average time to escape from the well is exponential in the well depth.

[3] The number of wells of depth E is quadratic in E. This is a result of computer calculations.

These 3 facts allow us to determine the motion of the configuration point in configuration space and therefore also the diffusion coefficient $D(T,t)$ and viscosity $\eta(T,t)$ or equivalently $\eta(T,\omega)$ where t is the time, ω, the frequency, and T is the temperature. Preliminary results show Vogel-like temperature dependence and stretched exponential-like time dependence. The dielectric response is straightforwardly obtained.

Outputs

Publications

E.A. Di Marzio, C. Castellano and A.J-M.Yang, *Glass Temperature Depression by Use of Mixed Plasticizers*, J. Poly. Sci. Part B, (in press).

E.A. DiMarzio, *The Entropy Theory of Glass Formation After 40 Years*, J. Computational Material Science, (in press).

Theory and Modeling of the Transport Properties of Polymer Solutions

J.F. Douglas

Objective

The objective is to develop theory relating to the transport properties of polymer solutions. Understanding of the transport properties of such materials is important for the control of fabrication processes and the ultimate properties of composite products.

Accomplishments

First, a novel probabilistic method for calculating flow velocity fields for pipe flows having arbitrary cross-sectional shape is developed and implemented. The method is based on an exact formal solution of Poiseuille flow velocity fields in terms of the average first-passage time for a random walk within the cross-section to hit the boundary of the tube. Implementation of the solution requires the Monte Carlo sampling of random walk paths. The calculational procedure is especially advantageous for complex-shaped boundaries where other methods have difficulties. The calculations also apply to open channel flows which are important for modeling flow in extruders. Calculations are first made for analytically tractable and experimentally studied flow geometries to check the accuracy of the numerical method. Calculations show agreement towithin about 1% error in our preliminary calculations, which is about the same agreement as obtained in recent laser Doppler measurements of velocity fields in ducts having idealized cross-sections. The probabilistic method was also applied to tubes having rough (i.e., "fractal") boundaries which revealed unusual characteristics of flow near rough boundaries. The new method of calculating velocity fields is shown to have promise for modeling the average velocity field of turbulent pipe flows and the permeability of porous media.

Recently, the apparent hydrodynamic radius of tracer particles in supercooled liquids (e.g. glass-forming polymer fluids, etc.) has been observed to decrease strongly upon lowering temperature. In the second part of the project this important phenomenon is modeled using a probabilistic method which relates the average volume swept out by a Brownian particle per unit time to the effective hydrodynamic particle radius. Molecular dynamics simulation suggests that a dynamic particle clustering occurs in supercooled liquids and this effect on particle transport is modeled by assuming the relatively immobile particles can be idealized as rigid impenetrable obstructions which inhibit particle motion and whose concentration increases upon lowering temperature. The model shows a decrease of the apparent hydrodynamic radius as the increasing obstruction concentration gives rise to an inhibited tracer particle motion and the apparent hydrodynamic radius vanishes at a percolation threshold where the tracer particles become localized. The extension of the modeling to describe rotational relaxation in supercooled liquids shows that the obstructions have a small influence on the

apparent hydrodynamic volume measured from an orientation relaxation measurement, as observed experimentally.

Typically, the properties of multiphase materials vary rapidly when the concentration of one of the components nears the geometric percolation threshold where that component becomes physically connected. For complex shaped particles, such as polymers, this threshold is strongly dependent on particle shape. To obtain insight into the dependence of the percolation threshold on particle shape, the percolation threshold p_c of overlapping ellipsoids of revolution is calculated numerically for a large aspect ratio range and the p_c estimates are compared with a variety of functionals of object shape (capacity, radius of gyration, integral of mean curvature, surface area, intrinsic conductivity, excluded volume) to determine whether these other functionals could generally describe the shape dependence of the percolation threshold. It is found that p_c is a rather unique functional of object shape and only approximate bounds in terms of other object shapes were possible. The numerical evidence indicates that $1/p_c$ is minimal for all objects of finite volume and this isoperimetric relation is conjectured to be exact.

The fourth task, which extends work of previous years, considers the concentration dependence of transport properties. Virial expansions are given for the viscosity, electrical, and thermal conductivity, dielectric constant and other properties for suspensions of particles and droplets of fluids (e.g. one polymer dispersed in another) having general shape. Such calculations are important for understanding the effective material properties of polymer mixtures and the stabilization of polymer blends by surfactant additives.

Outputs

Publications

F.Y. Hunt J.F. Douglas, and J. Bernal, *Probabilistic Computation of Poiseuille Flow Velocity Fields*, J. Math. Phys., 36, 2386(1995).

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

E.J. Garboczi, K.A. Snyder, J.F. Douglas, and M.F.Thorpe, *Geometrical Percolation Threshold of Overlapping Ellipsoids*, Phys. Rev. E, 52, 819(1995).

J.F. Douglas, and E.J. Garboczi, *Intrinsic Viscosity and Polarizability of Particles Having a Wide Range of Shapes*, Adv. Chem. Phys., 91, 85(1995).

Presentations

J.F. Douglas, *Defect Model of Glass Relaxation*, Workshop on Glasses and the Glass Transition: Challenges in Materials Theory and Simulation, Stephensville, MD, Feb., 1995.

J.F. Douglas, *Friction Coefficient and Intrinsic Viscosity of Polymers and Other Complex Shape Particles*, American Physical Society, March Meeting, San Jose, March, 1995.

J.F.Douglas, *Intrinsic Viscosity of Polymers and Other Complex Shaped Particles*, Texas A & M University, Chemistry Department, May, 1995.

Goals

In response to requests from other federal agencies the Division conducts research on a reimbursable basis to solve specific needs of the requesting agency. The nature of these activities changes from year to year depending on national priorities. Specific projects include an ONR effort to develop neutron and x-ray reflectometry for characterization of thin polymer films and interfaces (included under the Electronic Packaging and Interconnects Program), part of the *Halon Fire Suppressant Replacement Program* at NIST supported by the US Armed Services and the Federal Aviation Administration, an effort sponsored by the National Archives and Records Administration to improve the storage environment for archival records, assistance to the Bureau of Consular Affairs, Department of State to evaluate candidate security laminates and a long term activity with the National Institute of Dental Research to develop improved dental restorative materials. The last mentioned project is included in the report on the Dental and Medical Materials Program.

FY-95 Significant Accomplishment

- NIST's work with the State Department on the evaluation of laminating materials has enabled the implementation of significant improvements in the security measures for US passports.

Protection of Archival Records

C. M. Guttman and W. R. Blair

Objective

Assist the National Records and Archives Administration improve the storage of archival records by determining the absorption and diffusion of pollutant gases through various boxes used in the storage of archival records.

Accomplisments

The National Archives and Records Administration (NARA) seeks to improve the storage of records by reducing exposure to atmospheric pollutants. This project assists the NARA objective by studying the shielding mechanisms of boxboard containers commonly used in protecting archival materials from atmospheric pollutants as sulfur dioxide (SO_2) and nitrogen oxides.

The absorption of NO, SO_2 and NO_2 by box-board and specially prepared handsheets with varying amounts of α-cellulose, kraft, and $CaCO_3$ was studied. Studies of NO_2 in humid air at 45% relative humidity were made in the concentration range from 0.1 μL/L to 5 μL/L over periods as long as a week. Most samples were studied for at least 80 hours.

Handsheets made from α-cellulose alone picked up the smallest amount of either NO_2 or SO_2. The addition of $CaCO_3$ and the mixing of Kraft with the cellulose increased the amount of the two pollutant gases absorbed.

For the same materials, the absorption of NO_2 was found to be considerably less than that of SO_2. After about 80 hours of exposure at about 5 μL/L the SO_2 pickup was almost twice that of the NO_2 pickup for the two NARA boxboards studied. The amount of

NO absorbed was too small to be detected by this apparatus.

Halon Fire Suppressant Replacement: Elastomer Seal Compatibility

W.K. Waldron, G.B. McKenna, P.H. Verdier, F. Horkay, and W.H. Han

Objective

The objective is to establish the compatibility between candidate Halon substitutes and the types of elastomers and greases used in storage and extinguishing systems through the use of classical solvent/polymer/network thermodynamics approaches and by measuring compression set and tensile properties as a function of time and temperature during long term exposure.

Accomplishments

By international agreement, commercial production of Halon has ceased. The result is that there is a need in commercial and military aircraft systems to find an alternative to the Halon. The research described here is part of a larger program through the Building and Fire Research Laboratory of NIST to evaluate potential Halon substitutes for suitability in aircraft systems.

Two types of experiments were conducted to characterize the compatibilities of 4 agents with 7 commercial elastomers and 3 lubricants:
(i) swelling measurements due to sorption of the agent into the elastomers (or lubricants) at four different temperatures between 35 °C and 150 °C, and
(ii) durability measurements, which produced data on residual mechanical properties of the elastomers after exposure from 1 to 74 weeks at 75 °C and 5.86 MPa.

In (i) the solvent uptake of elastomers (both cross linked and uncross linked samples) and lubricants was determined as a function of the vapor pressure. Using the Flory-Huggins theory, the polymer/solvent interaction parameter (χ) was obtained for each polymer/diluent system. In (ii) the physical and chemical damage of the samples (cross linked elastomeric o-rings) were determined by compression set and tensile test measurements.

The results of the vapor sorption measurements in conjunction with those of the durability tests were used to define the compatibility of elastomeric seals and greases with fire suppressant fluids. A rating system was proposed to characterize the compatibility of elastomers (and lubricants) with the different agents based on the results of swelling measurements. Good compatibility (i.e. an elastomer or lubricant is acceptable for use in the fire suppressant system) was defined as the value of χ determined at 35 °C being larger than 1.2. Bad compatibility ($\chi <$ 0.9) corresponds to excessive swelling. For values of $0.9 < \chi < 1.2$, the agent was considered to have fair compatibility with the elastomer or lubricant and represents a marginally acceptable system.

The compression set measurements indicated significant differentiation between the results obtained for the elastomers in each agent. The experimental compression set vs time data were fitted to a Kohlrausch-Williams-Watt type stretched exponential function. This approach allows extrapolating to longer exposure times to predict the long term resistance of elastomers in-service condition. An activation energy analysis (activated

process model) was used to determine the temperature dependence of the compression set data. By contrast, the tensile test results (ultimate elongation data) did not show systematic variation with the exposure-time.

This study also provided new insight into the thermodynamics of swelling of polymer networks. The ability to vary the molar volume of the swelling agent in a controlled way (by varying the pressure and the temperature over a wide range) allowed experiments with 'solvents' of different chemical quality, but equal molar volume (isomolar volume condition). The experimental results clearly indicated the important role of the solvent molar volume in the thermodynamics of swelling.

Outputs

Publications

McKenna G.B., Horkay F.: Effect of Crosslinks on the Thermodynamics of Poly(vinyl alcohol) Hydrogels, Polymer 35, 5737-5741 (1994).

Horkay F., McKenna G.B., Waldron W.K.: The Effect of Molar Volume on the Swelling of Poly(dimethylsiloxane) in Fluorocarbon Fluids, Polymer Communications (in press).

McKenna G.B., Horkay F.: Gels, in AIP Handbook of Polymer Properties, Ed. J.E. Mark, AIP Press (in press).

McKenna G.B., Horkay F., Verdier H.P., Waldron W.K., "Interactions of Agents with Elastomers and Lubricants," NIST SP 890 (Nov. 1995) Vol. I, pp 201-247.

McKenna G.B., Waldron W.K., Horkay F.: Swelling of Elastomers in Sub- and Super Critical Fluorocarbons, Deformation, Yield and Fracture of Polymers, Cambridge, UK., April 11-14, 1994.

Horkay F., Waldron W.K., Jr., McKenna G.B.: Elastomer Compatibility with Fluorocarbons by Vapor Sorption Measurements," 1994, Polymeric Materials: Science and Engineering, 1994, 71, 735-736.

Presentations

G.B. McKenna, *The Effect of Molar Volume on the Swelling of PDMS in Fluorocarbon Fluids*,
American Physical Society March Meeting, San Jose, CA, March, 1995.

W.K. Waldron, Jr., *Swelling Measurements of Polymer Solutions and Gels in HCFC Agents*, Meeting of the Rubber Division, American Chemical Society, Philadelphia, PA, May, 1995.

Development and Utilization of Test Methods for Qualification of Passport Laminates

W.G. McDonough, and D.L. Hunston

Objective

The objective is to perform testing and provide consultation to assist the Bureau of Consular Affairs at the U.S. Department of State in selecting and purchasing the plastic laminate that is used to protect the photograph and descriptive information on the U.S. Passport.

Accomplishments

The area of the passport that contains the photograph and descriptive information is called the data page. A plastic laminate is used to protect this page from dirt, spills, and abrasions that may occur during normal use. In addition, the laminate must resist attempts

to tamper with the photograph or data page. When new laminating material is needed, the Department of State issues a solicitation inviting manufacturers to submit products for evaluation. NIST has a continuing cooperative program with the State Department to assist in this activity. NIST's responsibilities include: (1) consulting on the plan for evaluation tests included in the solicitation, (2) performing these tests as part of the solicitation process, (3) examining new materials and security concepts that become available, and (4) developing new test methods as required by progress in the field. Finally, where appropriate, NIST and the State Department provide feedback to the manufacturers on the performance of their technology in the evaluation. This assists them in making better materials for the future and thereby helps the Government improve the security of the passport.

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

During the past year, NIST completed the testing associated with one full solicitation. In addition, a number of new concepts in lamination technology were evaluated and compared as a guide to future directions for this field. The results were reported to the State Department and in many cases discussed with the companies involved so they can develop improved materials in the future.

Outputs

Reports on the work are provided to the State Department on a periodic basis. In addition, a series of meetings were held with the State Department and individual manufacturers to provide feedback on the performance of their materials.

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

OUTPUTS/INTERACTIONS

Publications

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NIST is a member of the **IPC, Institute for Interconnecting and Packaging Electronic Circuits**, Roadmap Steering Committee which develops the research agenda for the U.S. printed wiring board and assemblies industry. NIST contributed substantially to the final roadmap report, *The National Technology Roadmap for Electronic Interconnects.*

NIST is a participating member of the **Semiconductor Research Corporation** Packaging Science's Technical Advisory Board.

NIST is working with **3M** to use neutron reflectivity, electron microscopy and atomic force microscopy to characterize changes occurring at interfaces between phase separated domains in blends of reactive components. The correlation between two dimensional surface properties and three dimensional bulk properties is critical to understanding interfacial behavior in polymer blends.

In collaboration with NIST Polymers Division researchers, **Exxon, Raychem** and **Goodyear** are using small angle neutron scattering at the Cold Neutron Research Facility to investigate phase separation kinetics in polymer blends.

NIST developed technology for temperature measurement by fluorescence methods have been implemented by consortium member **Dynesco** in a prototype fiber optic bolt suitable for use in a standard extruder line sensor port.

A NIST/industry consortium, "New Measurement Technology for Polymer Processing" develops real-time measurement technology based on optical and fluorescence methods to monitor important processing parameters. Member companies includes **Dow Chemical, DuPont, 3M, Rohm & Haas and Dynesco (Flow Vision).**

A NIST/Industry polymer blends consortium investigates the effects on polymer blend properties of mixing/demixing under shear flow as well as methods of understanding and characterizing the interface. Members of the consortium include **Rohm and Haas, Raychem Corp., 3M Company, Goodyear Tire & Rubber Co., Armstrong World Industries, Aristech Chemical Corp. and Sandia National Laboratories.** In addition, **Exxon** participates under a separate CRADA.

A Cooperative Research Agreement with **Armstrong World Industries** studies the viscoelastic properties of plasticized PVC coatings. The work will use NIST's specialized characterization facilities to study the relationship between processing conditions and

properties for model material systems provided by Armstrong. There is also a program to use the entropy model of the glass transition to describe the behavior of mixed solvent systems used in the production of insulating foams.

NIST is working with the **Automotive Composites Consortium (ACC)** formed by **Ford, Chrysler,** and **General Motors** to develop the technology which will make liquid composite molding the most attractive fabrication method for light-weight structural automotive parts. The technology permits the use of computer simulation rather than expensive, time consuming experiments to optimize tool design and processing conditions. NIST uses its process simulation models to predict mold filling for parts of interest to the ACC and to measure the preform permeabilities required by the analysis. A recent example is the simulation of injection/compression molding process of interest to the ACC in manufacture of a truck box. The ACC provides details on the part design and feedback on the validity or the predictions from the simulation so the models can be refined and improved.

A cure sensor and process control system developed in cooperation with industry has been transferred to **Northrop-Grumman Corporation** where it will be implemented on prototype production equipment as part of an ARPA program.

A CRADA between NIST and the **Composite Civil Structures Consortium** was signed to effect the use of the NIST flow simulation models by the consortium in the design of various components.

NIST is working with **Structural Dynamics Research Corp.** to develop a graphical user interface enabling interfacing of the NIST flow modeling software with mechanical design software.

A number of companies continue to use the pure-injection liquid composite modeling program developed at NIST. They include **Automotive Composites Consortium, Northrop-Grumman Aerospace, Boeing Aerospace,** and a consortium involving **AlliedSignal, Northrop-Grumman** and **Allison Engine Co.** Negotiations are currently underway with **Lockheed.**

In a collaboration with **Owens Corning and Osi** the effects of coupling agents on the susceptibility of glass fiber-matrix interface to attack by moisture is investigated. The industrial collaborators provide materials and advice on glass fibers and surface treatments.

A collaboration with the **Automotive Composites Consortium** and **Dow Chemical Co.** investigates the effects of water and other fluids (notably windshield washer and brake fluids) on candidate E-glass/urethane materials of interest to the automotive industry.

NIST works with the **Textile Research Institute** to develop an automated single fiber fragmentation instrument for efficient measurement of interface strength in polymer

composites. An image analysis system has been interfaced with imaging optics and sample loading hardware to automate the experiment.

NIST collaborates with the **Textile Research Institute** to develop measurement methods and models to describe fluid flow in deformed porous media. Fiber reinforcements used in composite manufacturing are often deformed during the preforming process, altering their permeability in the deformed region. Since such changes can alter mold filling behavior, measuring the magnitude of the permeability change, and understanding the relationship between the fabric deformation and the permeability is highly desirable.

The utilization of composites in off-shore oil applications brings together **Exxon, Hercules** and NIST through sponsorship of the Advanced Technology Program to investigate durability aspects of composites in marine environments.

Rheometrics Instrument Co. participates in studies at NIST to develop modifications of their instruments that incorporate measurement advances made at NIST.

The Thermoplastic Engineering Design Program, carried out by **GM** and **GE** with NIST ATP support, uses NIST developed thermoviscoelasticity data in finite element calculations to predict shrinkage and warpage of injected molded parts.

Dow Chemical Co. and NIST perform cooperative research into the behavior of new semicrystalline polymers made by metallocene type chemistry.

A collaboration with Dr. Paul Danis of **Rohm & Haas** investigates the molecular characteristics of a NIST poly(methylmethacrylate) SRM by MALDI mass spectrometry, size exclusion chromatography and infrared and NMR spectroscopies.

The NIST SAXS facility was used by researchers from **Mobil Chemical Company Research & Development Laboratories, W. L. Gore Company,** and **Cryovac Division of W. R. Grace** to characterize materials of interest to their companies. In addition, **Dow Chemical Company** provided funding through a CRADA to study the morphology of syndiotactic polystyrene.

L.D. Caulk, 3M and Degussa have expressed interest in a NIST patent disclosure entitled "Improved Dental Compositions Via Improved Interfaces".

The R&D group at **Ivoclar-Vivadent** has prepared and evaluated ring-opening spiro orthocarbonates monomers described in our patent for use as dental polymers.

A Cooperative Research and Development Agreement between **E. I. duPont de Nemours Co.**, Circleville, OH and NIST investigates moisture effects in films used as electrical insulators. This resulted in a post-doctoral level researcher, I. Spinu, working in the Polymers Division.

An agreement has been signed by the **American Dental Association Health Foundation** to license a U. S. patent to be issued to NIST on March 12, 1996. The invention, which deals with a new adhesive technology, has generated interest from a number of dental companies that may want to sublicense the patent.

Creative Biopolymers, Dentsply/Caulk and **3M** have shown interest in a US patent to be issued to NIST which deals with the development of bioactive composites with remineralization potential.

Ceramco/Dentsply, Ivoclar Ag, Vident and **ZAHNFABRIK** expressed interest in a U.S. patent to be issued to NIST which deals with preceramic polymers for the fabrication of interpenetrating phase composites.

Industrial/Academic
In conjunction with the **Semiconductor Research Corporation, IBM, Digital Equipment Corp., Dow Chemical Co., the National Center for Manufacturing Sciences Printed Wiring Board Consortium, the University of Maryland CALCE Center, University of Texas, Cornell University, NASA Jet Propulsion Laboratory and the Naval Surface Warfare Center** NIST has been evaluating the limitations and errors associated with measurement of out-of-plane coefficient of thermal expansion of polymer thin films by thermomechanical analyzers.

In collaboration with **Ford Scientific Research Laboratory, the University of Nottingham, and Ecole Polytechnique du Montreal** NIST has conducted round robin permeability measurements on candidate glass fiber preforms for distribution as SRMs and generation of a permeability data base including data on preform materials of interest to the ACC.

Under ARPA funding NIST collaborates with **Northrop-Grumman, AlliedSignal, Allison Gas Turbine, Atlantic Research Corporation, Rensselaer, Drexel and Rutgers** in the development of process sensors and control software to manufacture ceramic engine components by resin transfer molding polymer precursors.

Under the auspices of the NIST Center for Theoretical and Computational Materials Science, Polymers Division staff organized a NIST/Industry/University workshop on "Hygrothermal Effects in Polymers and Composites".

A collaborative study of the use of composites in infrastructure applications (such as bridges) involves **Northwestern University's Basic Industrial Research Laboratory, University of Kentucky, Morrison Molded Fiber Glass** and a number of State Departments of Transportation.

NIST is collaborating with **Gelest, Inc.** and the **University of Pennsylvania** to develop a spin-on polymer-based dielectric for VLSI circuits.

Academic
A collaboration with Professor Ben Wong and Julie Spoerre of the Industrial Engineering Department of **Florida State University** resulted in direct comparisons of controlled variations in processing with void content and interlaminar shear strength of fiber reinforced composites.

The development of a fluorescence sensor to provide information from the 100 Å region adjacent to the reinforcement fiber in a composite is the goal of a joint project with Professor Steven Pollack of **Howard University**.

A thermo-viscoelastic constitutive model developed by Professor J. M. Caruthers and co-workers at **Purdue University** is being evaluated by conducting experiments at NIST.

A collaborative effort with the Department of Veterans Affairs, **Washington State University** and the NIST Statistical Engineering Division explores analytical and test methods for high confidence level prediction of the durability and survivability of medical/dental synthetic biomaterials and implants.

A joint program is underway between NIST and Prof. John Hoffman at **Johns Hopkins University** to study on-line process monitoring in liquid composite molding. As part of this effort a PhD student, Dara Woerdeman, is working at NIST to develop an evanescent-wave, optical-fiber, fluorescence measurement. This work will permit detailed measurements of the local resin behavior deep within a composite part during processing.

A collaborative program with the **University of Delaware** investigates the polymer/solid interface in composites. Pearl Chin, a PhD student of Prof. Roy L. McCullough, uses the NIST modified JKR technique for measuring work of adhesion between solid surfaces. The results will be correlated with other experiments conducted at both NIST and Delaware to assess interface properties. The goal is to provide the understanding needed to optimize the interface structure for the best composite performance.

A collaborative program with Professor Frank Karasz at the **University of Massachusetts** was initiated to examine the mechanisms responsible for loss of intensity from electroluminescent polymers during application of voltage.

Two Ph.D. students from the **University of Southern California**, Brett Ermi and Diane Valachovic, are collaborating with NIST staff in the investigation of polyelectrolytes in aqueous and non-aqueous solutions. Static and dynamic light scattering and small angle neutron scattering are used to study interactions of charged polymers of controlled geometry in media of varying dielectric constant.

Experimental studies of the phase diagrams and dynamics of polymer blends are conducted with collaborators from **Kyoto University, Massachusetts Institute of Technology, University of Michigan, University of California, Santa Barbara, University of Connecticut, University of Wisconsin-Madison, Michigan Tech, Colorado School of**

Mines, Polytechnic University, Pennsylvania State University, University of Maryland, Cornell University, Princeton University, Tokyo Science University, and East China University of Chemical Technology.

Theoretical studies of phase dynamics in polymer blends is conducted with Professor M. Muthukumar of the **University of Massachusetts**.

In collaboration with Professor Charles Thomas, **University of Utah**, ultrasonic sensors are developed to monitor polymer processing. The program involves the development of sensors for use at high temperature and the modeling of the rheological and thermodynamic behavior of polymer melts under processing conditions.

The Dental and Medical Materials Group participated in collaborative research efforts with scientists from the following academic institutions: **McGill University** (Canada), the **University of Western Ontario** (Canada), the **University of Washington**, **Howard University**, the **University of Maryland**, **Indiana University**, **Tokushima University** (Japan), **Nihon University** (Japan), and the **U.S. Naval Dental School** (Bethesda). Research projects included studies of the organic matrix of dentin by immunolabeling and chromatography; the synthesis and evaluation of dentin bonding system components; effects of particle size on the properties of an amalgam alternative; tooth remineralization; dentin desensitization; properties and mechanisms of calcium phosphate cements; and surface roughness of glass-ceramic inserts for composite restorations.

A joint project with Prof. A. Lee of **Michigan State University** is investigating the physical aging behavior of rubber toughened epoxy resins in creep and stress relaxation.

A joint program with Prof. Suresh Advani at the **University of Delaware** investigates liquid molding. The interaction involves the development of micro-flow models in an effort to predict permeability and an experimental study to visualize and model 3-dimensional flow effects in multi-layer preforms. A Postdoctoral Fellow from the University, Sridhar Ranganathan, is working at NIST on the modeling effort.

A collaboration with Professor H. Chai of **Technion University** investigates failure mechanisms in adhesive joints by comparison and analysis of experimental results using elasto-plastic finite element methods.

The measurement of domain size and stoichiometry in blends of cellulose and hydrogen-bonded polymers by solid state nuclear magnetic resonance spectroscopy is conducted jointly with **McGill University**.

A NATO sponsored collaborative effort with the **Instifuto de Ciencia y Tecnologia de Polimeros**, Madrid, Spain investigates smectic liquid crystalline polymers.

NIST staff co-organized a workshop with Professor Knauss of **California Institute of Technology** on "The Time Dependent Constituent Behavior of Engineering Plastics" under the auspices of the Institute of Mechanics and Materials in La Jolla, CA, June, 1995.

NIST staff organized a tutorial workshop on "Small Angle Scattering" at the 1995 American Crystallographic Association Annual Meeting in Montreal, Canada.

NIST staff organized a workshop on "SAXS in the Industrial Laboratory" at the 1995 Denver X-Ray Conference.

Associated Activities

Invited Talks

Division personnel presented a total of 150 invited talks on research activities at the following types of organizations and symposia: industrial laboratories, 32; international symposia, 17; universities, 30; topical symposia, 16; national and government laboratories, 12; professional society meetings, 41; and Gordon Conferences, 2.

Patents

J.M. Antonucci, J.W. Stansbury, *Improved dental compositions via improved interfaces,* NIST Docket #95-012.

J.M. Antonucci, J.W. Stansbury, C. Gingreau, *Improved photoinitiator systems for polymeric dental compositions,* NIST Docket #95-015.

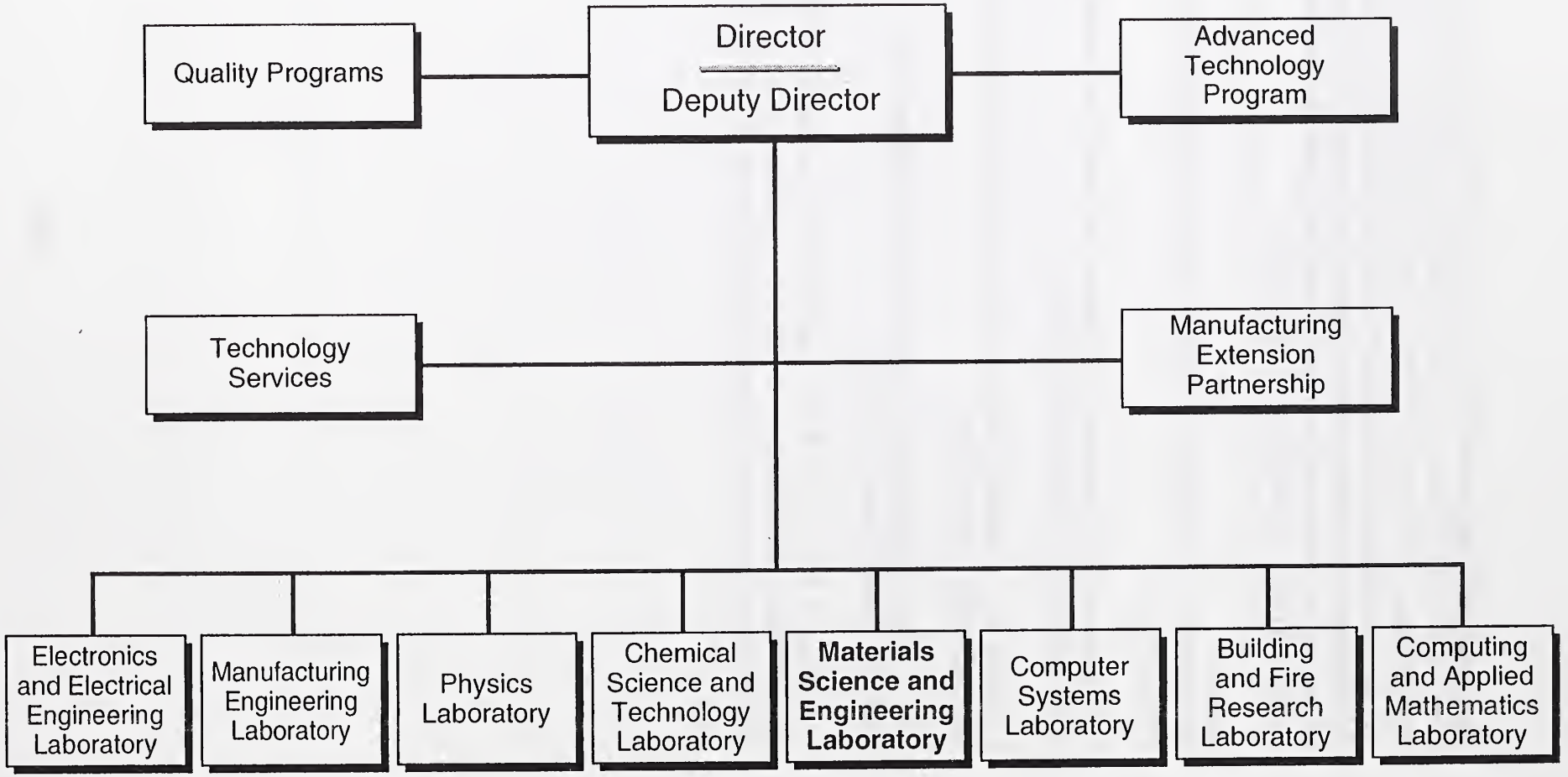
J.R. Kelly, J.M. Antonucci, *Use of preceramic polymers in fabrication of ceramic composites*, Application Filed, June 7, 1995.

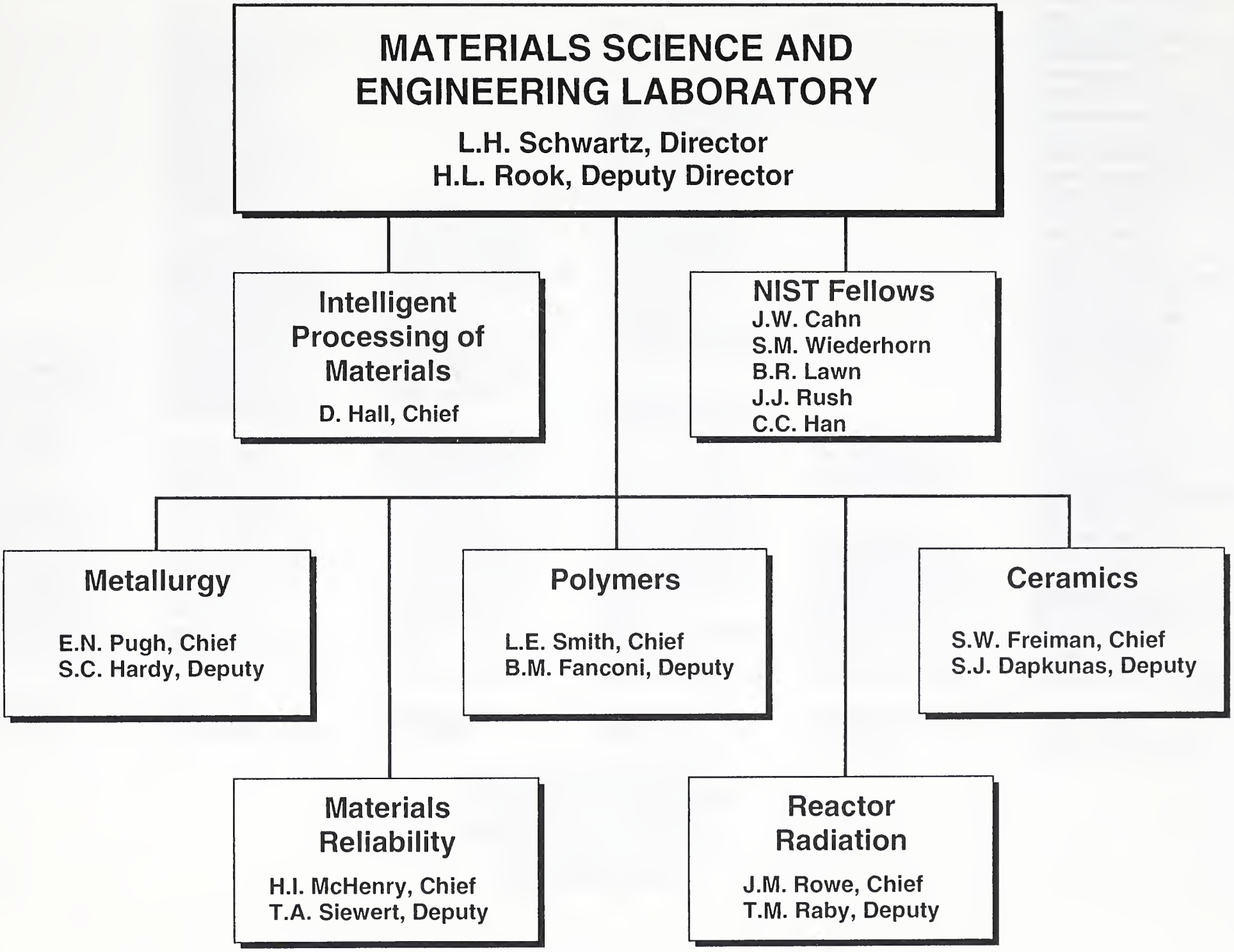
J. W. Stansbury, *Monomers for double ring-opening polymerization with expansion.* US patent 5,463,008, issued October 31, 1995.

F.W. Wang, R.E. Lowry, K.F. Lin, *Non-destructive method for determining the extent of cure of a polymerizing material and the solidification of a thermoplastic polymer based on wavelength shift of fluorescence*, invention disclosure filed, February 15, 1995, NIST Docket #95-011.

National Institute of Standards and Technology

Organizational Chart

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S.J. Dapkunas, Deputy
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Green, Janice M., Mrs., Secretary

ELECTRONICS APPLICATIONS

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Mopsik, Frederick I., Dr.
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Wallace, William E., Dr.
Wu, Wen-li, Dr.

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Spoerre, Julie K., Mrs.
Woerdeman, Dara L., Mrs.

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Waldron, William K., Dr.

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Tesk, John A., Dr.

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Rupp, Nelson W., Dr.
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Lin, Chency, Mr.
Liu, Xiaodu, Mr.
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Morrison, Faith A., Dr.
Mullins, Carol A., Mrs.
Pitcher, Matthew B., Mr.
Register, Richard A., Dr.
Reichart, Glenn C., Mr.
Sung, Li-Piin, Dr.
Valachovic, Diane, Miss
Yu, Jae-Woong, Dr.
Zhou, Chunlin

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Tomazic, Branko B., Dr.
Tung, Ming S., Dr.
Vogel, Gerald L., Dr.
Zhang, Zhen, Mrs.

Natl Inst of Dental Research

Eanes, Edward A., Dr.
Fowler, Bruce O., Mr.
Hailer, Arthur W., Mr.

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Kelly, John R., Cmdr.

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Nikaido, Toru
Schumacher, Gary E.
Skrtic, Drago
Tateosian, Louis H.