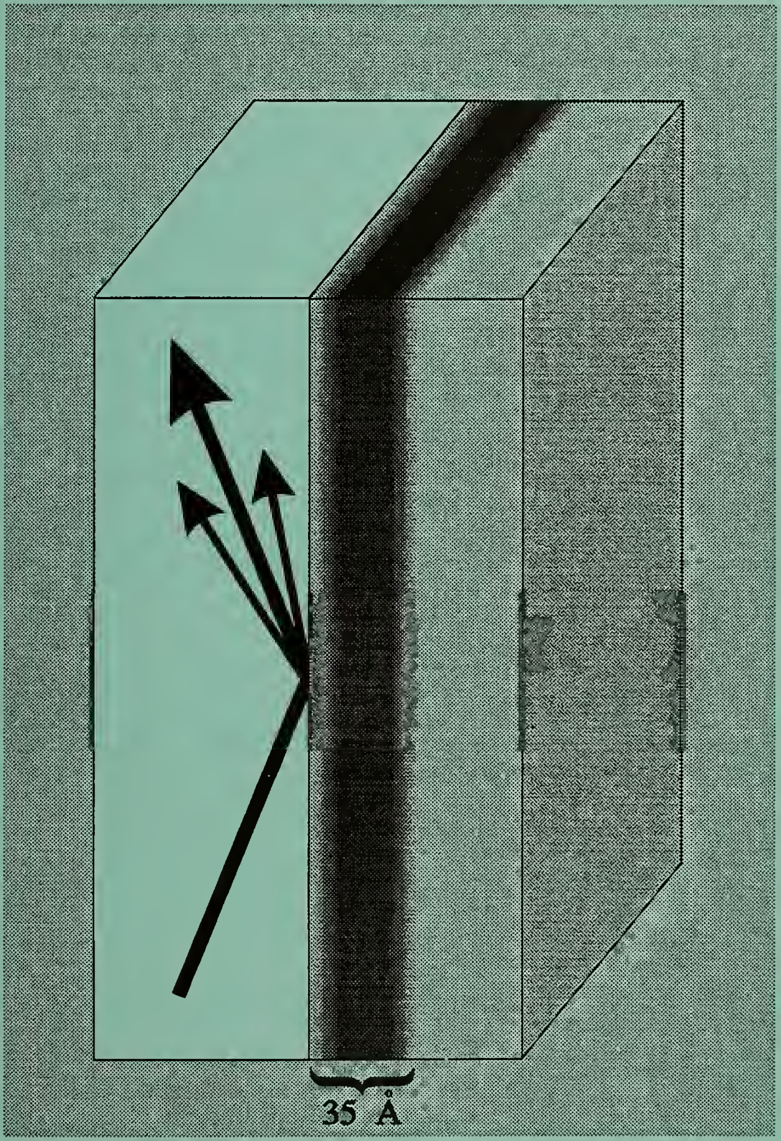
MSEL Amis

Materials Science and Engineering Laboratory

POLYMERS



Technical Activities 1992

NISTIR 4966
U.S. Department of Commerce
Technology Administration
National Institute of Standards
and Technology

Neutron reflectivity is used to determine the distribution of moisture in a polyimide film attached to a silicon substrate. The moisture concentration, indicated by the grey scale, is higher within a few nanometers of the interface than in the bulk.

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POLYMERS

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

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Technical Activities
1992

February 1993

U.S. DEPARTMENT OF COMMERCE, Ronald H. Brown, Secretary
National Institute of Standards and Technology, John W. Lyons, Director

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INTRODUCTION

POLYMERS DIVISION

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

The Polymers Division provides standards, measurement methods, and fundamental concepts of polymer science to assist U. S. industries that produce or use synthetic polymers in essential parts of their business. This broad mission has to be focussed, however, to match the finite resources and technical capabilities of the Division. The primary way in which these priorities are set is by assessing customer needs and evaluating the potential payoff to the industry and the nation. Industrial input into program planning and direction came from four NIST/Industry Workshops held during the past year on sensors for polymer processing, polymer blends, polymer composite processing and performance of high technology polymers.

A useful way to categorize our industrial customers is as resin producers, processors, or users of polymers in end products. These user communities have different types of problems and capabilities and also face different competitive situations. For example, resin producers are primarily large, sophisticated, often multi-national companies that want to produce higher value-added materials that also have significant potential volume markets. They need, and can use, 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 effects of shear and 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. An industrial consortium on polymer blends processing is being formed to transfer results more effectively to industry.

Captive processors of polymers can also be large, sophisticated companies with significant R & D resources. Independent processors frequently do not have such resources and often cannot take advantage of technical opportunities unless the research is very specific to their process and the development risk quite small. The Division's programs on process monitoring and control are therefore aimed at specific sensor needs identified through industrial workshops and a NIST/Industry consortium was established to develop sensor technology needed by industry and transfer the technology to industry.

Industries that use polymers to a significant extent in their products can be found in nearly every manufacturing sector of the economy. Faced with such diversity, the Division has focussed on two industry sectors, transportation and electronics, which have the largest and most pervasive economic effect. A major task in meeting the technical needs of these industries is finding and overcoming the barriers to more effective use of polymers in their products. The Division's program on polymer composites is an example of the process by which barriers were identified and projects begun in response to those needs. Previous NIST/industry workshops identified resin transfer molding (RTM) to have significant potential for rapid and reliable processing of large thick cross-section structures from polymer composite materials. The Division's Polymer Composites Group addresses the need, identified by industry, for computer simulations of resin flow in RTM. The flow simulation software is used in automotive and commercial aviation applications of RTM.

Technology transfer is an integral part of all of the Division's program plans. The most effective method of technology transfer is through direct interaction with individuals from industry who know both their business and technical needs. Many of these interactions come through scientists who collaborate with us on technical projects of mutual interest. Last year the Division cooperated with 54 Research Associates and 86 Guest Scientists who together spent over 50 staff years of effort at our laboratories. In addition, many industrial scientists have spent one or two days at a time using specialized equipment developed by Division scientists to make collaborative measurements or to make proprietary measurements on their developmental materials. Many of these interactions are briefly described in the section on Industrial and Academic Interactions in the Appendix to this report.

Patents are another effective way to transfer technology. Patents package technical developments into discrete units that focus on those elements that are truly novel so that industry can more easily evaluate the potential utility of the work. In addition, the intellectual property is protected in a way that future development costs, which are almost always needed, can be recovered. This year the Division has 6 patents granted or pending on subjects given in the Appendix.

All of the Division's programs are described in this report, organized according to these six Groups:

SPECIALTY POLYMERS
CHEMICAL PERFORMANCE
MECHANICAL PERFORMANCE
POLYMER COMPOSITES
POLYMER BLENDS AND SOLUTIONS
DENTAL AND MEDICAL MATERIALS

These Groups have made a number of significant accomplishments during the last year. Some of these are summarized below. More information about the work may be found in the project summaries.

- Five companies joined NIST in the formation of a consortium whose purpose is to develop real-time measurement technology based on optical and fluorescence methods to monitor important polymer processing parameters.

- A micro-model for flow through porous media successfully predicted the permeability of a unidirectional fiber preform with impenetrable fiber tows. The shape and geometric arrangement of the tows have been modelled, and this provides an important first step towards goal of scientifically designing preform microstructure to optimize processing and performance.

- The third Industry Workshop on Polymer Composite Processing brought together 22 industry experts to review the NIST research program and to provide guidance for future program planning. The attendees strongly supported the current effort in liquid molding of composites and encouraged the development of new activities in process monitoring and control technology, and preform preparation.

- A versatile flow animation program was developed to analyze the results from finite element programs for mold filling in the liquid molding process. The animation makes it easy to observe filling behavior from all angles and stop the flow simulation at any point for detailed examinations. This represents a major advancement in the analysis of flow simulations.

- A NIST/industry workshop was organized and held to review the current scientific understanding and technology of polymer blends processing. A consortium involving industry and NIST is being formed to develop the scientific basis of processing blends/alloys, especially interfacial characterization and control.

- A workshop was organized on "Aging, Dimensional Stability and Durability Issues in High Technology Polymers." Participants from 17 U.S. companies as well as several government agencies, National Labs and private research foundations reviewed the current scientific knowledge base and recommended additional research into the physical aging phenomena common to dimensional stability and performance.

- By application of neutron reflectivity, the concentration of absorbed water in a polyimide near an interface with a solid surface (silicon) was quantitatively determined for the first time. The results show that the water content within the first 25Å of the interface is more than 6 times the value in bulk polymer. This measurement is a critical step in understanding the problem of environmental attack on interfaces.

- In collaboration with Michigan Molecular Institute polyamidoamine dendrimers have been studied by small angle neutron scattering. Single chain scattering is similar to that expected from a uniform sphere. Long range order is strongly affected by the pH of the solution.

- Better routes to low shrinkage resins were developed using cationic polymerization initiators which were shown to yield 100% ring-opening. The cationic initiators can be used in conjunction with free radical initiators to provide dual cures for methacrylate-spiro resin systems.

- Significant advancement in the understanding of the influence of shear flow on the static and dynamics of phase behavior has been achieved. Experimental studies of the molecular weight effect on the Ginzburg criterion of cross-over from mean-field to Ising critical behavior as well as the shear rate dependence of the system behavior cross-over from weak to strong shear dependence were carried out. Results compared favorably with theoretical predictions.

- Time-resolved small angle neutron scattering techniques have been developed to measure the phase diagram of blend systems which are normally inaccessible experimentally due to the interference of glass transition temperatures.

RESEARCH STAFF

Antonucci, Joseph M.	o Synthetic and polymer chemistry o Dental composites, cements and adhesion o Antioxidants
Barnes, John D.	o Gas and vapor transport in polymers o X-ray scattering o Computer applications in polymer measurements
Bauer, Barry J.	o Polymer synthesis o Neutron, x-ray and light scattering o Dendrimers
Bennett, Patricia S.*	o Synthetic and polymer chemistry o Nuclear magnetic resonance
Blair, William R.	o Ultratrace metals speciation o Biotransformation of metals o Polymer analysis by size exclusion chromatography o Environmental durability of coatings
Bowen, Rafael L.*	o Adhesion o Dental composites o Biocompatibility
Briber, Robert J.	o Structure and morphology of polymers o Electron microscopy o X-ray scattering
Brinckman, Frederick E.	o Environmental metal transport o Organometallic chemistry o Biological mediation of surface chemistry o Ultratrace metal speciation and particle biogenesis o Molecular structure-activity relationships
Broadhurst, Martin G.+	o Dielectric measurements o Piezoelectric and pyroelectric modeling and theory o Equation of state of polymers o Ionic conduction

* Research Associate
\+ Guest Scientist

Brown, Walter E.[*]	o Solution chemistry of calcium phosphate (CAPH) compounds o Biological CAPH compounds o Atherosclerotic plaque
Bur, Anthony J.	o Dielectric properties of polymers o Fluorescence and optical monitoring of polymer processing o Piezoelectric, pyroelectric polymers o Polymeric transducers
Campbell, Jr., Gordon C.[+]	o Solid state NMR of polymers o Off-resonance proton irradiation techniques
Carey, Clifton M.[*]	o Dental plaque o Microanalytical analysis techniques
Chai, Herzl[+]	o Experimental mechanics o Mechanics of adhesive bonds o Fracture of composite materials
Chang, Shu Sing	o Thermal properties of polymeric and composite materials o Composite process monitoring o Electronic packaging materials o Polymer phase transitions o Precision electrical and temperature measurements
Chiang, Martin Y.	o Computational mechanics (finite element analysis) o Strength of materials o Engineering mechanics of polymer based materials
Chow, Lawrence C.[*]	o Calcium phosphate compounds o Dental and biomedical cements o Solution chemistry o Topical dental fluorides
Crissman, John M.	o Mechanical behavior o Environmental stress-cracking o Failure and fracture of polymers

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Dadmun, Mark D.	o Liquid-crystalline polymers o Polymer Gelation o Light and neutron scattering
Davis, G. Thomas	o Piezoelectricity in polymers o Polymer crystallization o X-ray diffraction of polymers o Polarization distribution
DeReggi, Aime S.	o Polarization-depth profiles in polymers o Space charge in dielectrics o Ferroelectric polymers o Polymeric piezo- & pyroelectric devices
Di Marzio, Edmund A.	o Statistical mechanics of polymers o Phase transitions o Glasses o Polymers at interfaces
Dickens, Brian	o Polymer oxidation o Monomer design and free radical curing o Automation
Dickens, Sabine*	o Clinical dentistry o Dental composites o Dental polymers
Douglas, Jack F.	o Theory on polymer solutions and blends o Polymers at interfaces o Scaling and renormalization group calculation
Eanes, Edward D.*	o Structure of bones and teeth o Calcium phosphate compounds o Effects of biological molecules on precipitation of calcium phosphates o Liposome studies
Eichmiller, Frederick C.*	o Clinical dentistry o Composites o Dentin adhesives

*Research Associate

Eidelman, Naomi N.[*]	o Atherosclerotic plaque
Fanconi, Bruno M.	o Infrared & Raman spectroscopy of polymers o Structure of polymers o Polymer fracture o Process monitoring of polymer composites
Farahani, Mahnaz[*]	o Radiation chemistry/physics o Analytical chemistry
Feng, Yi[+]	o Temperature jump light scattering o Phase separation kinetics of polymer blend
Fowler, Bruce O.[*]	o Infrared and laser Raman structural analysis of calcium phosphates
Giuseppetti, Anthony A.[*]	o Casting of dental alloys o Titanium alloys
Grosfeld, Roselyne C.[+]	o Humidity effects in polymers o Thin films
Guttman, Charles M.	o Solution properties of polymers o Size exclusion chromatography o Diffusion of small molecules into polymeric systems o Semicrystalline polymer chain configurations o Kinetics of polymer crystal growth
Hailer, Arthur W.[*]	o Chemical reactions, chemical analysis
Hair, Dennis W.	o Dynamic light scattering o Polymer blends o Polymer diffusion
Han, Charles C.	o Phase behavior of polymer blends o Phase separation kinetics of polymer blends o Polymer characterization o Polymer diffusion o Small angle neutron scattering o Static and quasi-elastic light scattering

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Hobbie, Eric K.	o Polymer blends o Dynamic light scattering o Thermal analysis
Hoffman, Kathleen M.*	o Synthetic and polymer chemistry o Adhesion
Hunston, Donald L.	o Adhesion science and technology o Fracture behavior of polymers o Processing and failure behaviors of polymer composites o Flow behavior of dilute high polymer solutions o Macromolecular-small molecule binding
Ishikawa, Kunio*	o Calcium phosphate compounds
Jackson, Catheryn L.	o Structure and morphology of polymers and polymer blends o Transmission and scanning electron microscopy o Finite-size effects on crystalline melting and glass transition temperatures o Liquid crystalline polymers o Microcellular foams morphology
Jewett, Kenneth L.	o Redox kinetics of heterogeneous systems o Organometallic speciation o Abiotic transformation of metal species o Analysis of organic mixtures o Diffusion and absorption of gases in polymeric matrices
Johnsonbaugh, David S.	o Atomic absorption spectrophotometry o Microbiology
Johnston, Allen D.*	o Nuclear magnetic resonance o Mossbauer studies o Chemical adhesion
Keeny III, Spurgeon M.	o Gas plasma sterilization o Mechanical testing o Tribiology, dental materials o Fluorescence studies

*Research Associate

Khoury, Freddy A.	o Crystallization, structure and morphology of polymers (including polymer blends) o Analytical electron microscopy of polymers o Wide angle and small angle x-ray diffraction o Structure and mechanical property relationships
Kim, Hongdoo[+]	o Polymer diffusion o Forced Rayleigh scattering o Polyelectrolyte o Polymer blends
Kryder, Samuel J.	o Electronic circuit design and construction o Electronic troubleshooting and repair
Kurakawa, Hidenobu[+]	o Polymer solution thermodynamics o Small angle neutron scattering
Leterrier, Yves[+]	o Physics of polymer glasses o Dilatometry
Levy, Dara[+]	o Permeability o Composite process monitoring
Liu, D.-W.	o Monomer synthesis o Polymer and polymer composites
Lowry, Robert E.	o Applications of fluorescence spectroscopy to polymeric systems o Synthesis of chromophore-labeled polymers
Ly, Agnes M.[*]	o Clinical dental assistant o Adhesion measurements
Mao, Yu[+]	o Dental plaque o Microanalytical techniques
Mathew, Mathai[*]	o Crystallography o Calcium phosphate compounds

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Maurey, John M.	o Ultracentrifugation o Rayleigh light scattering o Osmometry o Densimetry o Refractometry o Intrinsic viscosity
McDonough, Walter G.	o Processing and cure monitoring polymer composites o Failure and fracture of polymers o Microstructure characterization of polymer composites
McKenna, Gregory B.	o Failure, yield and fracture of polymers o Nonlinear viscoelasticity o Molecular rheology o Physics of polymer glasses o Rubber thermodynamics and mechanics o Mechanics of composites
McKinney, John E.[+]	o Tribiology of dental composites, cements and alloys
Misra, Dwarika N.[*]	o Surface chemistry o Adhesion o Chemisorption
Mopsik, Frederick L.	o Dielectric measurements and behavior o Automated measurement design o Computerized data analysis and programming o Electrical properties of polymers
Nakatani, Alan I.	o Polymer blends and solution properties under shear o Small angle neutron scattering o Phase behavior of polymer blends
O'Farrell, Thomas J.[*]	o Mineralization and remineralization
Orts, William J.	o Neutron and x-ray scattering o Polymer morphology and crystallization o Mechanical properties of polymers

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Parnas, Richard S.	o Flow through porous media with heterogeneous structure o Surface rheology o Polymer dynamics
Perez, Ernesto+	o Synthesis and characterization of liquid crystalline polymers
Phelan, Jr., Frederick R.	o Resin transfer molding: modeling and processing studies o Viscoelastic flow modeling o Engineering rheology
Ratzker, Menahem S.*	o Electrodeposition
Reed, Benjamin B.*	o Synthetic and polymer chemistry o Polymerization expanding monomers
Roth, Steven C.	o Piezoelectric polymer transducers-fabrication and applications o Vacuum deposition of metals o Calibration of polymer transducers o Microcomputer interfacing o Fluorescence measurements
Rupp, Nelson W.*	o Clinical dentistry o Amalgams o Direct golds o Composites o Microleakage o Dentin adhesives
Sakurai, Shinichi+	o Polymer blends o Equilibrium and kinetics of phase separation o Light scattering
Sanin, Norman D.*	o Topical dental fluorides
Santore, Maria M.+	o Dilatometry of polymer glasses o Polymer blends

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Schen, Michael A.	o Living polymer synthesis o Polymers for non-linear optics o Molecular electronics o Optical spectroscopy
Schutte, Carol L.	o Surface chemistry o Polymer composite interfaces
Schultheisz, Carl R.	o Failure of composites o Experimental mechanics
Shioya, Masatosi[+]	o Fiber surface science o Fiber-matrix interface
Sieck, Barbara A.[*]	o Calcium phosphate compounds o Chemical analysis
Smith, Leslie E.	o Adsorption of polymers o Polymer degradation reactions
Stansbury, Jeffrey W.	o Synthetic chemistry o Polymers and polymer composites o Polymerization expanding monomers
Takagi, Shozo[*]	o Crystallography o X-ray diffraction o Calcium phosphate compounds
Terech, Pierre[+]	o Small angle X-ray and neutron scattering o Physical gelation
Tesk, John A.	o Bond strength characterization o Casting of alloys o Strength of dental systems o Thermal expansion and properties of dental materials o Finite element studies o Porcelain-metal system o Weibull analysis o Gas plasma sterilization

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Tomazic, Branko*	o Atherosclerotic plaque o Biological calcium phosphate compounds
Tung, Ming A.*	o Biological solution chemistry of calcium phosphate compounds o Equilibrium studies
VanderHart, David L.	o Measurement of orientation in polymer fibers and films o Solid state NMR of polymers o Measurement of polymer morphology at the 2-50 nm scale o Structure of asphalt cements and concretes
Verdier, Peter H.	o Polymer solution properties o Polymer chain dynamics in solution o Statistical analysis of data o Error estimation o Computer simulation of polymer chain dynamics
Vogel, Gerald L.*	o Dental plaque, biological solution chemistry of calcium phosphates o Microanalytical techniques
Waldron, William K.	o Nonlinear viscoelasticity o Mechanics and thermodynamics of rubber
Wang, Francis W.	o Photophysics and photochemistry of polymers o Fluorescence spectroscopy o Thermodynamic and frictional properties of macromolecules
Waterstrat, Richard M.*	o Dental metallurgy o Metallurgical phase diagrams o Structure of alloy phases
Winnert, Laurie A.*	o Glass-ceramics
Wu, Wen-li	o Neutron and x-ray scattering o Electron microscopy o Mechanical behavior of polymers and composites

*Research Associate

Zapas, Louis J.[+]	o Continuum mechanics and rheology o Non-linear mechanical behavior of polymers o Static fatigue of plastics o Finite elasticity (rubbers)

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SPECIALTY POLYMERS

The task of the Specialty Polymers Group is to characterize and evaluate the properties of polymers to be used in special applications. This often requires developing new measurement techniques or adapting existing techniques to specific problems. Examples of special applications of polymers include microelectronic packaging, high energy density capacitors, cable insulation, piezoelectricity, pyroelectricity, and photonics. Measurement techniques include time domain dielectric spectroscopy, thermal pulse measurement of charge and polarization distribution, and photoacoustic spectroscopy for depth profiling.

A new focus for the Group is research on polymeric materials used in microelectronic packaging. Advances in the operating frequency and circuit density of integrated circuits has resulted in transmission velocities limited by the dielectric properties of insulation in interconnects and the protective packaging. Thermosetting resins such as epoxies and polyimides have many properties which make them attractive as interlayer dielectrics for multichip module applications and they are being widely used in the electronics industry, but not without problems. An industrial Workshop on Materials in Microelectronic Packaging held at NIST in 1990, identified the need to develop techniques and data on the properties of thin films in recognition that bulk property values may no longer be appropriate in thin structures. The mechanical, electrical, and thermal properties of thermosets are greatly affected by the curing conditions employed during manufacture of microelectronic components. Techniques for monitoring cure and following physical properties during cure will be studied. The initial attempt is to measure the variation in properties of a cured polyimide film as a function of depth using photoacoustic spectroscopy (PAS). Ideally, PAS produces the infrared spectrum from successively deeper layers of the thin film. Recent advances in both the photoacoustic cell and in step-scanning FTIR have made the technique promising. Properties can be expected to vary with depth because the precursor polyamic acid can interact with metal conductors on the substrate and with oxygen near the free surface. In addition, the concentration of solvent varies with depth as solvent evaporates from the free surface.

Thermal diffusivity of polyimides in a packaging configuration is being measured in a cooperative project with the Process Measurements Division of NIST. Layers of polyamic acid are spin-coated on an alumina substrate and thermally cured in the Polymers Division's work. A chromel/constantan thermocouple is sputtered onto each cured polyimide film in the Process Measurements Division before spin-coating the next layer of polyamic acid. A total of four thermocouples and three layers of polymer comprise the completed structure.

Equipment has been assembled to evaluate candidate films for high energy density capacitors. Film thickness and dielectric constant are measured using a two-fluid capacitor cell. Energy recovery for programmable charge and discharge cycles can be evaluated. Electric breakdown strength can be measured which is free of artifacts from contacting the film and from electrode edge effects.

Polymers to be used for piezoelectricity, pyroelectricity, or second order non-linear optics (NLO) require the introduction of a preferred alignment of the active moiety. Frequently, the alignment is achieved by applying a high electric field at temperatures above the glass transition temperature to align dipoles and then cooling below T_g with the field applied to freeze in the alignment. This procedure employs amorphous polymers with dissolved NLO-active molecules or copolymers with built-in NLO activity. No heating is necessary to effect the reorientation of dipoles in a high electric field in the case of ferroelectric polymers like polyvinylidenefluoride and its copolymers and Nylon 7 and Nylon 11. However, the coercive field and remanent polarization are a function of temperature. Hysteresis experiments have been interfaced with a PC which allows the collection of data as a function of parameters such as maximum applied field, cycle frequency, and temperature.

The degree of dipole alignment or polarization across the thickness of a film can be evaluated using a thermal pulse facility developed at NIST. Distribution and quantity of space charge within a polymer film can also be measured. Unfortunately, a gradient of polarization cannot be distinguished unequivocally from space charge. Experiments are under way which may guide the assignment of measured response to charge and polarization gradients. The role of injected charge and its subsequent decay on the orientation of dissolved molecules or polymer dipoles is being investigated. The study of charge injection and its role in electrical breakdown and electrical tree formation have been the subject of industry-sponsored research.

Dendrimers represent another specialty polymer whose properties are being examined. These are polymer molecules formed by a stepwise synthesis starting from a multifunctional core molecule in which each additional layer doubles the terminal functionality. This causes a highly branched, densely packed structure somewhat like that of a uniform sphere. The single chain properties and long range interactions are being studied by small angle neutron scattering. Polymer samples are supplied through a cooperative research and development agreement with Michigan Molecular Institute.

FY 92 Significant Accomplishments

- The time domain dielectric spectrometer developed at NIST has been converted to be fully operational from a PC.

- Photoacoustic spectra from spin-coated polymer films have been obtained from FTIR scans of only a few minutes. Depth profiling analysis is in progress.

- In collaboration with Michigan Molecular Institute polyamidoamine dendrimers have been studied by small angle neutron scattering. Single chain scattering is similar to that expected from a uniform sphere. Long range order is strongly affected by the pH of the solution.

- Candidate polymer films for high energy density capacitors have been evaluated for dielectric constant, thickness, energy recovery, and electrical breakdown strength.

CHEMICAL AND PHYSICAL CHANGES IN POLYIMIDES DURING CURE

Brian Dickens

Enormous progress in miniaturization and speeding up of electronic devices has been achieved in the electronics industry by integrating more components on a single chip. This allows higher transmission speeds of the signals because the origins and destinations are closer together. Reliability is greatly improved because the signal lines are protected from the environment. The clock rates of consumer items such as personal computers are currently in the range of 50MHz. The trend toward higher speeds and ever smaller devices has focussed attention on the dielectric materials used in packaging because the packaging material now limits the performance of the device with respect to signal propagation time and distortion of the pulse. Furthermore, the current methods of reducing size often connect chips in 2-dimensional or 3-dimensional arrays which place further demands on the chemical and physical properties of packaging materials. Polymers have been used for these applications, but increasing demands are being made on their performance.

The relatively low dielectric constant of some organic polymers makes them attractive for the fast signal propagation required in modern electronic devices. Among the additional requirements for such a film are that they: 1) initially be tractable so that the film can be deposited on the substrate, 2) cure to become inert to the solvents and conditions used in the depositing of successive films, 3) adhere to the substrate, to previously-deposited inert films, and to the metal conductors, 4) have a coefficient of thermal expansion close to that of the substrate, 5) be amenable to photolithographic processes, and 6) planarize rough structures.

Aromatic polyimides have been generally used to produce insulating films in electronic packaging. Because the polyimides themselves are insoluble, the films are deposited from solvent as precursors containing acid or labile ester groups. On being heated, the precursor forms chemical bonds of the imide type. If the precursor is transformed under conditions where the reactive groups are free to rotate, for example in solution, the imide bonds are formed intramolecularly. Where the reaction is carried out in the solid phase, as in the case of the films used in electronic packaging, the imide bonds may also form intermolecularly, depending on the amount of rotation available to the reactive groups. Formation of intermolecular groups links previously separate molecules together into much larger and ultimately insoluble molecules.

The useful polyimides contain rigid structures, originally because this confers thermal stability. Rigid structures have the potential for preferred orientation, for example lying parallel to one another, and provide in polyimides the important property of anisotropic thermal expansion, which is low in directions containing a high percentage of covalent bonds and high in planes containing a high percentage of van der Waals bonds.

The cure of a polyimide thus entails chemical changes which render a soluble material insoluble and heat resistant, and physical changes in which no new chemical bonds are formed but the order in the solid increases. The chemical cure continues until, as a result of the formation of large rigid structures, the remaining reactive groups are not mobile enough to meet one another. Physical ordering also takes place to the extent permitted by the mobility of the polyimide moieties. However, the system does not attain equilibrium. The state achieved depends on the precursor itself, its concentration in the solvent, the rate of loss of solvent and any reaction products (of which water is typically one), and the time spent at each temperature of the cure cycle.

The state of the polyimide governs its dielectric and mechanical properties, the anisotropy of its thermal expansion coefficients, and its inertness. To relate cure realistically to these operational properties, measurements of cure must monitor the chemical and physical transformation in film specimens about 10 μm thick. Films of 5 to 25 μm typically are applied in micro-electronic packaging. The degrees of chemical cure and physical ordering must be separated, preferably as a function of film thickness, in these measurements.

If the extent of chemical cure and the degree of physical ordering in a film specimen are to be separated, the first consideration is to use techniques which are as specific as possible - i.e., techniques that measure the amount of reactant and product groups and the degree of order, rather than techniques which measure properties affected by the cure and order parameters. For chemical changes, infrared spectroscopy has traditionally been invaluable in following which groups appear and disappear and in estimating the rates of these transformations.

Order in the solid state can be studied by diffraction techniques such as X-ray diffraction. To some extent, IR can also be used to infer the existence of orientation from differences in intensities of absorption in chemically identical systems. Although probably no one technique will suffice to characterize cure in polyimides satisfactorily, IR spectroscopy is an ideal technique with which to begin. IR spectroscopy also allows a form of depth-profiling for investigating cure in polyimide films.

Depth profiling is difficult to carry out non-destructively. Depth profiling using IR is possible with attenuated total reflectance (ATR), but only to depths of 1 to 5 μm depending on the wavelength of the incident radiation. Depth profiling with ATR therefore varies across the IR spectrum. Much greater depths, up to 25 μm or so in favorable cases, can be attained with FTIR-photoacoustic spectroscopy. Recent advances in PAS allow the depth profiling to be uniform across the spectrum.

Techniques which are secondary in terms of monitoring cure and ordering can be used. Examples include dielectric measurements and fluorescence. Dielectric measurements are expected to be more precise than IR measurements when ionic groups are absent or present only in very low concentration but are crippled by the presence of significant concentrations of ions and some impurities. Fluorescence measurements are difficult to interpret and may be quenched by atmospheric oxygen. Many materials, some of which may be present as impurities, fluoresce. Because all the information in a typical IR spectrum has only one dimension (the wavelength of the incident radiation), overlaps frequently obscure small details. The technique is rarely precise enough to allow discrimination between 99% and 100% reaction or 0% and 1% presence of components, but on balance is worth examining.

PAS is applied to the study of polyimide films. The technique is simple to describe. Wide-band IR radiation is pulsed onto the film. The radiation enters the film. Wherever radiation is absorbed in the film, heat is generated. The heat diffuses in the film and some of the heat arrives at the film surface, where it heats the ambient gas. A small shock wave is produced and the resultant pressure is registered by a microphone. Pulsing the incident radiation rapidly leaves less time for heat to diffuse to the film surface before the effect of the previous pulse is effaced by the arrival of a subsequent pulse. When compared with the results of a series of slower pulses, this allows a form of depth profiling. A second way to depth-profile is to measure the heat arriving in a small time-slice after changing the mix of wavelengths incident on the specimen. It is the slow diffusion of heat that makes measurement of its arrival time at the specimen surface feasible and thus allows depth profiling.

Preliminary PAS spectra have been collected from polyimide films and interpretation of the results is underway. PAS is a technique which is undoubtedly not suited to all cases and some investigation will be necessary to determine the extent to which it will help in determining the degrees of chemical and physical cure in polyimide films. At the very least, it provides a direct measure of changes in chemical groups over depths comparable with film thicknesses used in electronic packaging. It is rapid, potentially non-destructive, and requires minimal sample preparation.

AUTOMATED DIELECTRIC MEASUREMENTS

F. I. Mopsik

The project to convert the Time Domain Dielectric Spectrometer has reached its first target. The instrument can now be run in its first version on the PC. This target includes both acquisition and data analysis so that the Spectrometer is now fully operational on the PC.

The interface box has been completed and tested under full software control. This includes all the connections to the existing instrumentation and allows a complete measurement sequence with all the clock shifts and filter shifts to take place under the control of the box. Problems with data being clocked onto the acquisition board have been resolved as well as all compatibility issues. All noise concerns, both digital and analog have been resolved.

The program to run the instrument has also been completed and tested in its first version. This includes conversion from archaic Fortran 66 to more modern code. This was a major task wherever any I/O was involved. The setup code was rewritten to be menu driven so that new users will find it much easier to operate. All measurement parameters are cross-checked for compatibility. The plotting routines were redone to take advantage of a laser printer with HPGL capabilities for enhanced hard-copy graphics. Provision was made for allowing several measurements to take place at fixed intervals for simple time evolution studies. The exception and error handling was greatly enhanced as a result of enhanced computer capabilities. The code was also reorganized so that any future updates can be more easily made.

HIGH ENERGY DENSITY DIELECTRICS

F. I. Mopsik, B. Dickens, A. S. DeReggi, and S. C. Roth

Measurements were made on the high field dielectric constant of some polymer films intended for use at high energy densities using the instrumentation developed last year. Time and field dependencies were clearly resolved. The expectations of reproducibility were fully realized. The effect of dielectric relaxation on the efficiency of the dielectric was found and reported.

The original program to measure high field dielectric constant was also expanded. New instrumentation was obtained, involving a programmable arbitrary function generator and more powerful high voltage amplifier to enhance measurement capabilities. Also, breakdown strength measurements were started since energy density is proportional to the square of the applied field. Measurements were made on PVF_2 samples with evaporated aluminum electrodes with fuzzy edges to minimize edge effects. Breakdown was found to occur away from the edges indicating good success. Issues were raised, however, as to just what measure of breakdown strength is meaningful in test specimens since clearing events can take place allowing a higher field to be imposed on the original sample. These issues will have to be resolved in any comparison studies with other measurement facilities since the ASTM standard is quite loose and not fully compatible with high energy density materials applications.

THIN FILM MEASUREMENTS

F. I. Mopsik and S. C. Roth

Two-fluid dielectric constant measurements were extended to measure the thickness of 10-25 μm polyimide layers on a 0.7 mm alumina substrate. For these measurements, a high precision two-fluid cell that featured very high mechanical stability and narrow guard gap was used. These measurements have been a severe test for the technique. Limitations from the variations in the thickness of the alumina substrate and moisture uptake of the polyimide film have limited the reproducibility of the results.

SMALL ANGLE NEUTRON SCATTERING STUDIES OF DENDRIMER SOLUTIONS

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Dendrimer molecules are polymers formed by a stepwise synthesis in which each additional layer doubles the terminal functionality causing a highly branched and densely packed structure. In FY92, work was done in collaboration with Donald Tomalia of Michigan Molecular Institute, who supplied polyamidoamine dendrimers of various sizes. Small angle neutron scattering was carried out to measure the single chain properties and the long range interchain interactions.

The single chain scattering was calculated by extrapolation of the scattering intensity to zero concentration in D_2O. The angular dependence of the scattering intensity is more like that of uniform spheres than like that of gaussian chains, giving radii of gyration that are quite small for molecules of their molecular weights.

When acid is added to the dendrimer/D_2O solution, peaks in the scattering intensity show that long range order develops due to repulsive interactions. The maximum order comes when there is a stoichiometric amount of acid added to the terminal amines of the dendrimers. Excess acid, salt, and base screen the long range interactions, causing the scattering peaks to disappear.

FLAMMABILITY STUDIES OF CROSSLINKED POLYMERS

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Work has begun on the study of the effects of crosslinks on the thermal stability and char formation of polymers. Previous molecular dynamical studies of polymethylene chains have suggested that crosslinks may inhibit the formation of volatile products and hence reduce flammability and increase char formation. Three NIST SRM polystyrenes have been exposed to electron beam irradiation at dose levels low enough to cause branching, but not high enough to cause gel formation. Size exclusion chromatography was used to monitor the disappearance of unbranched material. From this information, the probability of joining two molecules can be calculated for any dose. Samples have been prepared from three polystyrenes of greatly different molecular weights and given doses from 0.05 to 6 MGy to introduce a wide variety of crosslink densities. These samples are being studied by thermogravimetric analysis to measure weight loss as a function of temperature in air and in nitrogen.

THERMAL PULSE THEORY

A. S. DeReggi

The thermal pulse method of measuring charge distributions in dielectrics continues to be useful in a variety of dielectric characterization problems. Incremental development of the method driven by changing needs for nonlinear optics (NLO) applications is occurring mainly in the area of calibration of the measurements as well as on ways of distinguishing space charge from polarization effects. The NLO properties come from polarization induced by poling but the poling process may inject space charge that makes the poling field and NLO properties spatially nonuniform. Although the two types of charge are electrically similar, physical differences in the way they interact with the dielectric provide response signatures specific to each type of charge. Because these signatures change with a change in material properties, information can be obtained about the types of charges present by varying external parameters such as temperature, or applied voltage. When the material has an accessible glass transition temperature, varying the temperature across this transition produces large changes in material properties with possibly significant changes in response signatures.

Space charge is monopolar while polarization charge is dipolar. Monopolar charges as a rule are weakly bound to the dielectric matrix and interact weakly with one another through the spherically symmetric Coulomb force. They have, usually but not always, weakly restricted translational freedom of motion and may be driven in and out of the dielectric with an applied field or diffuse within the dielectric. Dipolar charges occur in positive and negative pairs, have a very strong pairwise interaction (covalent bond) that is highly directional and, as a rule, are strongly bound translationally to the matrix. Their most important motional freedom is rotational. As a result of their physical differences, the response-determining coefficient for space charge and polarization charge are different. In the thermal pulse measurement, the response-determining coefficient is the logarithmic derivative of the sample capacitance with respect to temperature.

Calibration of thermal pulse data is accomplished by comparing measurements made on the same sample with and without an applied calibration voltage. Analysis of the response for an ideal sample with planar capacitor geometry, predicts an incremental response produced by the applied voltage consisting of a unit step with a height proportional to the voltage and the sample capacitance. For many dielectric samples, a rounded step is found and the step height is found to have history dependence. Finding suitable models that account for the behavior of such dielectric samples is a goal of the work.

Analysis of the response of a voltage-biased sample using a model that includes two types of charge predicts a voltage dependence for the response that involves the ratio of the polarizations associated with two types of charge. This analysis suggests that measurements as a function of voltage may help differentiate space charge and polarization charge contributions to the response. Experimental tests of this hypothesis using the well known ferroelectric polyvinylidene fluoride (PVDF) have so far been hampered by the nonideal behavior of this material.

SPACE CHARGE MEASUREMENTS IN NONLINEAR OPTICAL MATERIALS

A. S. DeReggi and G. T. Davis

Polarization and space charge distribution measurements have been made using the thermal pulse method on candidate host materials for optically nonlinear guest-host systems in which the host is a polymer and the guest a dye molecule with strongly nonlinear optical properties.

A major problem with such guest-host systems has been the instability against ageing time of the dye polarization induced by a poling process. The trend of research has been to use amorphous polymers or copolymers with high glass transition temperatures as hosts, such as polymethylmethacrylate (PMMA) and the vinylidene cyanide--vinyl acetate copolymer (P(VDCN-VAc)). After poling above the glass transition temperature and cooling below it, a limited amount of orientational stabilization of the dye polarization is provided by the glassy state. Thermal pulse measurements on these host materials has shown that the polarization distribution induced by poling is highly inhomogeneous. This is attributed to a significant conductivity acquired by the materials at the high poling temperatures that must be used.

In recent years, the benefits of using semicrystalline ferroelectric polymers as host materials have been investigated in our laboratory. After poling, such materials have stable polarization in the ferroelectric crystallites which produces a large internal field in the amorphous part where dye molecules reside. Orientational stabilization of the dye polarization is thus provided by the internal field of the poled ferroelectric host.

Because space charge may enter the system or be internally generated during the poling process, it may reduce the internal field but, it may also play a role in stabilizing the orientation of the crystallites that produce the internal field. Thus, the amount of space charge in our guest-host systems may be an important controllable factor affecting the stability of the NLO properties. Thermal pulse measurements are underway for samples poled at different temperatures and aged at different temperatures to help sort out the variety of processes involving charge motions.

PVDF-PMMA BLEND AS HOST MATERIAL FOR NLO GUEST-HOST SYSTEMS

A. S. DeReggi, G. T. Davis and N. Tsutsumi[1]

[1] NIST Guest Scientist, Kyoto Institute of Technology, Kyoto, Japan

Ferroelectric polymers being semicrystalline, generally have the undesirable property of scattering light and thus have not been materials of choice for optical applications. The PVDF-PMMA blend is investigated as a possible host material for NLO guest-host systems. Within a restricted range of composition, this blend may be quenched and thermally annealed in such a way that the crystallites are in the desired ferroelectric β phase and the size of the crystallites are small compared to the wavelength of light. The blend thus may combine two desirable properties for a host material, namely optical clarity and ferroelectric stabilization of guest orientation.

The behavior of the internal field and the charge distribution in this blend containing a small amount of the NLO dye dimethylaminonitrostilbene (DANS) is studied for a variety of poling conditions. In addition, the thermal ageing characteristics of this blend-dye system has been investigated. The internal field in the amorphous part of the blend was determined by using the dye itself as a field probe. The optical absorbance of DANS in the near ultraviolet shows electrochromic effects which are measured and are used to calculate the internal field. The thermal pulse method was used to determine the charge distribution and the mean polarization confirming separate pyroelectric coefficient measurements. This blend shows unusual behavior in that the internal field remains stable beyond the temperature when a substantial loss of mean polarization is observed based on the pyroelectric response. This behavior suggests that space charge, which cannot contribute to the pyroelectric properties, contributes substantially to the internal field. This behavior is not fully understood but suggests that the PVDF-PMMA blend is a promising host material.

SPACE CHARGE AND BREAKDOWN

A. S. DeReggi

The notion that space charge accumulation in dielectrics is related to breakdown is gaining strength and has recently been strongly promoted by French researchers Dr. Claude LeGressus of Saclay and Prof. Blaise of Orsay. Both have taken considerable interest in the thermal pulse research done in the Division in the area of the charging behavior of dielectrics exposed to high voltages and an informal collaboration has been established. A manifestation of this collaboration has been the organization of the Interdisciplinary Conference on Dielectrics: Properties, Characterization, Applications which took place in Antibes, France in March 1992, in which the NIST Polymers Division played a prominent part. The collaboration is continuing with measurements of the charging behavior of polymers and inorganic materials before and after exposure to electron irradiation. These measurements are aimed at testing the hypothesis that irradiation alters the charging behavior and the charge storage properties of insulators.

In another collaboration, this one with Prof. Jacques Lewiner and colleagues at the Ecole Superieure de Physique et de Chimie, the charge injection from a sharp needle point embedded in polyethylene (PE) has been investigated using a pressure pulse method analogous to the thermal pulse method. The pressure method is advantageous because the probing acoustic pulse can be focused and directed towards the point in such a way as to give the spatial distribution of the charge injected by the point. Although the measurement is difficult, preliminary results show that the injected charge is sharply confined to the region of the point. This is as expected since the space charge field of the injected charge reduces the injection field at the point below the threshold for injection and no further injection can take place until the charge migrates away from the point. These results lend support to the idea that sharp asperities at the interface between metallic conductors and polymeric insulation in high voltage cable can be a source of space charge. This work is a precursor of planned work in collaboration with the Union Carbide Corporation on the effects of divergent fields on the charging behavior.

CHEMICAL PERFORMANCE

The goal of the Chemical Performance Group is to develop measurement methods, data, and models for the control of polymer processing and to develop highly functionalized polymers for use in sensors, fiber optic smart structures and photonics.

The need for improved monitoring of polymer processing has escalated in recent years because of the large demand and market for advanced polymeric products whose manufacture requires tight controls in processing conditions over a broad range of variables. To satisfy these new requirements, in-line measurement technology based on optical and fluorescence methods is under development to monitor important polymer properties during processing. The objective of the polymer processing program is to utilize this new in-line measurement technology in conjunction with process models to predict and control the materials properties and performance of final products. The measurement goals of this program were established after extensive exchange of information with industry to determine measurement needs which cannot be filled with existing technology. Interactions with the polymer processing industry have been formalized with the establishment of an NIST/industry consortium, New Measurement Technology for Polymer Processing. In addition, a collaborative project with the University of Massachusetts, Lowell has been initiated to develop an in-line method for monitoring the uniformity of mixing in a blend of recycled plastics.

In the applications of fluorescence spectroscopy to cure monitoring, a fluorescence method, based on the change of the emission wavelength of a probe, has been developed to monitor the cure of an epoxy resin and to detect the onset of its gelation, in collaboration with Professor K. F. Lin, a guest scientist from the National Taiwan University. In collaboration with scientists from AT&T Bell Lab, a fluorescence method has also been developed to monitor the formation of polyimides from their precursors. The Group also collaborated with the Dental and Medical Materials Group to develop a fluorescence method for cure monitoring of dental composites, and with Enimont America to develop a fluorescence method for in-line monitoring of a microwave cure process.

The revolutions in the optoelectronic industries and advances in composite materials technology have opened up the new field of fiber optic smart structures that offers engineers the opportunity to incorporate fiber optic nervous systems into their designs. Among the possible smart structures are aircrafts that communicate if it is safe to take off and monitor and correct for structural changes, and artificial limbs that can feel, react and touch. These smart structures require intelligent materials, which according to the Science and Technology Agency (STA) of Japan, are "materials with the ability to respond to environmental conditions intelligently and manifest their functions." As a result of the promotion by the Army Research Office and the Society of Non-Traditional Technology (a subsidiary of STA), the concept of intelligent materials has been widely accepted as a guiding principle of future materials science development. The development of smart structures requires the participation of many disciplines including experts in the fields of materials, structures, actuators, signal processing, sensors and systems. The Group has initiated a program to evaluate pigment-containing polymers as active materials for smart structures and has entered into discussions of a joint project with a fiber optics research center.

Externally funded work in metal-polymer interactions focuses on determination of the reaction mechanisms involving toxic species and biopolymer systems with which they interact. With support from EPA and NIH, and in collaboration with University of Maryland at Baltimore, work is conducted on the stability of well-characterized lead solutions in polycarbonate containers and watering bottles. Liver and kidney tissue samples from animal toxicity studies have been examined for total arsenic and/or indium.

FY 92 Significant Accomplishments

- Five companies joined NIST in the formation of a consortium whose purpose is to develop real-time measurement technology based on optical and fluorescence methods to monitor important polymer processing parameters.

- The fluorescence anisotropy of rod-like probes doped into a polymer melt matrix was measured as a function of shear and extensional stress. The anisotropy was observed to be insensitive to applied shear stress, but displayed significant change with the application of extensional stress. Thus, these probes can be used to monitor the presence of extensional flow fields in the presence of overlapping shear flow.

- In collaboration with Drexel University, an injection molding machine was instrumented with both ultrasonic and optical probes. The addition of these sensors permits investigation of important events during injection molding such as mold filling, crystallization and polymer solidification.

- A fluorescence method, based on the emission-wavelength shift of a fluorescent probe dissolved in an epoxy resin, was developed to monitor the cure of the epoxy resin and the onset of its gelation.

- Liver and kidney tissue samples from animal toxicity studies were examined for total arsenic and/or indium. Since the animals were dosed at several concentrations and sacrificed at different times, an assessment was made as to the most suitable experimental conditions under which a speciation study will be performed.

- Freshly prepared lead dosing solutions and lead solutions after use were monitored on a monthly basis to ensure that animals were receiving correct lead exposure during the duration of a long term experiment. A problem in loss of lead concentration during the feeding procedure was detected and, together with UMAB personnel, a solution that protected the integrity of the experiment was reached.

POLYMER PROCESSING

A. J. Bur, F. W. Wang, R. E. Lowry, S. C. Roth, C. L. Thomas[1] and J. L. Rose[1]

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The objective of this program is to develop in-line measurement technology based on optical measurement methods to monitor important polymer processing parameters. The major optical method employed involves the detection of fluorescence spectra from fluorescent dyes which have been doped into the polymer material to be processed. The character of the fluorescence, i.e. its intensity, polarization, and wavelength distribution, yields information about the state of the polymer matrix. The research has concentrated on developing concepts and methods to measure shear and extension stress, shear and extension strain rate, non-Newtonian viscosity, temperature, morphology and the onset of thermodynamic transitions.

The measurement goals of this program were established after extensive exchange of information with industry to determine measurement needs which cannot be fulfilled using today's technology. Interaction with the polymer processing industry has been formalized with the establishment of an NIST/industry consortium, New Measurement Technology for Polymer Processing. This consortium, which is centered at NIST, was initiated on June 1, 1992. Membership in the consortium remains open until November 30, 1992.

Over the past year our specific objectives have been: (1) to initiate the consortium research program; (2) to measure fluorescence anisotropy of rod-like probes under both shear and extensional stresses; (3) to design an extensional flow apparatus; (4) to develop a model for in-situ measurement of extensional strain rate; and (5) to collaborate with Drexel University employing optical and ultrasonics measurements to monitor polymer injection molding. Three significant achievements are summarized:

New Measurement Technology for Polymer Processing Consortium

This consortium is an outgrowth of an NIST/industry workshop which was held at NIST in December, 1990 [1]. The objectives of the workshop were: (1) to seek industry responses to the question: what on-line, real-time measurements do you need to make during polymer processing but are unable to do so because the measurement technology does not exist? and (2) to put together a collaborative NIST/Industry research program for the development of new measurement technology. Processors identified their measurement problems by describing various processing operations. Workshop discussions yielded a consensus of the following measurement needs: (1) in-line rheological measurements; (2) improved in-line temperature measurements; and, (3) in-line and on-line measurements of polymer morphology. The direct interaction with industry at this workshop provided the framework for defining the consortium research program which is dedicated to the development of new in-line measurement technology for polymer processing based on optical and fluorescence methods. The consortium research program will extend over a period of four years during which rheology and temperature measurement systems and concepts will be developed.

Fluorescence Anisotropy Measurements

This measurement involves the use of polarized light to determine the fluorescence anisotropy of a dye molecule which has been doped into a polymer matrix at low concentrations. Previous work used anthracene-tagged polybutadiene as a fluorescent probe doped into a polybutadiene matrix. For this probe, anisotropy was found to decrease with increasing shear stress; a model to describe this behavior was developed [2,3]. The difference between the effects of shear stress and extensional stress was examined by developing a model for the relationship between anisotropy, molecular orientation factors, shear stress and extensional stress. An essential requirement for anisotropy to be affected by shear stress is that the probe molecule engage in the entanglement network of the matrix polymer, i.e. it must be macromolecular in size. Thus, under shear stress, the anthracene tagged polybutadiene probe showed significant change with shear stress, but small fluorescent probe molecules, which are unable to engage in the molecular entanglement network of the matrix, are insensitive to shear stress.

For extension, however, the entanglement requirement does not apply. This is probably because large orientations are possible under extension stress whereas only limited weak orientation occurs under shear stress [2,3]. Small rod-like fluorescent molecules, such as anthracene and diphenyl hexatriene, which associate their long axis with the polymer main chain extension, display fluorescence anisotropy change with applied extension stress, but show no significant change with shear stress. These observations were carried out using cross-linked polybutadiene. They demonstrate that the rod-like probes can be used to detect the presence of extensional stress in a mixture of extension and shear stress fields. Future extension experiments will be done using polymer melt (uncross-linked) in flow. To do this, we have designed an extension flow apparatus with which the flow can be controlled with a constant strain rate.

Optical and Ultrasonics Monitoring of Injection Molding

This program aims to develop new measurement methods for monitoring polymer injection molding processing. Ultrasonics and optical measurements are being employed to measure, in real-time, resin flow front velocity, mold filling time, resin temperature at the injection nozzle, onset of resin solidification in the mold, part shrinkage upon solidification and cooling, and resin modulus. Considerable progress has been made with several of these measurements, e.g. mold filling time and solidification time. The data present a view of resin state changes in the mold cavity during the most critical phase of the mold cycle.

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FLUORESCENCE MONITORING OF CURING REACTIONS

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The goal of this program is to apply the fluorescence monitoring method to a variety of curing systems in the polymer processing industry, and to evaluate the stability of fluorescent probes in the presence of a variety of polymerization initiators. Currently, we are addressing the industrial needs brought to our attention by such companies as Enimont America, Raychem and Ford Motor Company.

Fluorescence Monitoring of Polarity Change and Gelation During Epoxy Cure

The Stokes' shift of 1-(4,dimethylaminophenyl)-6-phenyl-1,3,5-hexatriene, which was dissolved in a stoichiometric mixture of diglycidyl ether of bisphenol A and diethylene triamine, decreased during the curing reactions because of the change in the polarity of the epoxy resin. In an isothermal cure, the Stokes' shift decreased linearly with the cure time until the gelation occurred. The total change in the Stokes' shift that occurred from the beginning of the isothermal cure to the gelation time was 1,000 cm^{-1} and was independent of the cure temperature, implying that the chemical structure of the infinite network at the gelation time was independent of the cure temperature. The rate constant K_T for the polarity change during an isothermal cure of the epoxy resin was defined as the rate constant for the linear decrease of the Stokes' shift before the gelation time. The activation energy of K_T was estimated to be 60 KJ/mol and represented the energy barrier to the curing reactions which led to the polarity change of the epoxy resin.

Cure Monitoring of Polyimides by Fluorescence Spectroscopy and FTIR

Aromatic polyimides have been widely used as an interlayer insulator for microelectronic devices because they have many desirable properties, such as planarization, thermal and chemical stability, and mechanical toughness. For solution application of condensation polyimides, films of their soluble precursors, poly(amic acids) are prepared by casting onto a substrate. During subsequent thermal treatment often referred to as cure, poly(amic acids) are converted to polyimides. While the imidization reaction takes place during a thermal cure cycle, the elimination of the solvent and the by-product water, and the rearrangement of polymer segments also occur. Monitoring of changes during thermal treatment is important because the desired end properties often depend on the cure schedules. A fluorescence method was used to monitor the changes during thermal cure of two polyimides, one made from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and p-phenylenediamine and the other made from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and p-phenylenediamine. The data from the fluorescence method, together with the FTIR data indicated that, for these polyimides, the changes in fluorescence spectra upon thermal treatments were partly due to imidization, and not solely due to the change in molecular aggregation.

METAL-POLYMER INTERACTIONS

K. L. Jewett, W. R. Blair, and F. W. Wang

When metals species react in biosystems at specific chemical sites the intended function of the biopolymer is altered. The bioactivity of these materials is dependent not only on their chemical compositions but also their three dimensional structural features. At important positions along molecules, metals may exert toxic effects by impeding a benevolent metal species from assuming its functional position or by rendering a specific molecular site unavailable to perform its designated task. Research activities are currently underway that are designed to develop a better understanding of biopolymer-metal binding processes in mammalian systems.

Intracellular Chemical Speciation of Lead: Relation to Nephrotoxicity

When ingested, lead acts as a neurotoxic agent. Small children are especially vulnerable to the effects of lead poisoning and are generally at significant risk from lead exposure in urban, suburban and rural geographical locales of this nation. Lead-biopolymer binding at the molecular level is under investigation in a collaborative study with University of Maryland at Baltimore (UMAB) to map out a lead distribution in various tissue samples primarily including mammalian kidney, liver and blood samples after exposure to lead in various doses. Aqueous size exclusion chromatography (SEC) coupled to atomic absorption (GFAA) and multiple wavelength uv-vis (UV)detectors have been assembled and standard protein solutions have been used to calibrate the apparatus. With this accomplished, work is now proceeding to determine a set of elution parameters where charged metal ions will only demonstrate size exclusion separation properties. The ultimate aims of these experiments are: 1) to identify the molecular weight fractions that contain lead and 2) to perform metal binding studies with model compound and real samples in order to determine the binding coefficients of these metal-polymer interactions.

NIST periodically supplies UMAB with well-characterized lead solutions (50, 250, and 1000 ppm) as feed water to experimental animals. The solution concentrations are continuously monitored in order to ensure that they meet experimental requirements. During the last year our joint 2 to 3 year animal study was threatened when the concentrations of solutions routinely fell below an acceptable level. Working with UMAB personnel the source of the problem was determined and appropriate corrections made.

At 6 month interval tissue samples are received from rats who are part of a long term lead toxicity study from UMAB. These samples and others that follow will be analyzed upon completion of the SEC-UV-GFAA system.

Toxicity from III-V Semiconductors

The chemical form of an element and the environment in which the element is contained are important factors in determining the toxic influences that a material may exert. For example, indium arsenide (InAs), an important semiconductor, is a fairly nontoxic material. However, when ingested into the body InAs decomposes. The consequence of this degradation process results in the formation of indium or arsenic containing species which may be very toxic to the host.

In collaboration with UMAB, a survey was performed of several hamster kidney and liver specimens in which the host animal had been treated with InAs, $NaAsO_2$, or $InCl_3$. Graphite furnace atomic absorption spectroscopy was used to analyze tissue samples for their arsenic and/or indium content. Samples for SEC-UV-GFAA analysis have been selected based on the total concentration of either indium or arsenic in the sample. The concentration profile of the two elements in several tissue samples has been determined and studies initiated that involve the identification of the molecular weight fractions containing these elements and the examination of the binding strengths between indium or arsenic and selected proteins, polypeptides and peptides.

MECHANICAL PERFORMANCE GROUP

Goals

Understanding the mechanical performance of polymeric and composite materials is essential to their efficient use and successful implementation in the industrial and consumer marketplaces. The goals of the Mechanical Performance Group are to perform research into the factors affecting the lifetime and durability of polymers and polymer based composites and to relate the information obtained from the research to the needs of the U.S. Polymer industry and its efforts to remain competitive in the Global market.

Changes

During the past year the Mechanical Performance Group saw many changes beginning with the change in leadership with the Group now coming under the direction of Gregory B. McKenna. The Group's capabilities were greatly augmented by the transfer of the mechanical performance component of the Composites Program to the Mechanical Performance Group. This transfer of responsibility was accompanied by placement of two staff (Martin Y. Chiang and Carol L. Schutte) from the Composites Group into the Mechanical Performance Group as well as a new hire (Carl R. Schultheisz) into the Mechanical Performance Group to work in this area. The Group capabilities were reduced by the retirement of our expert in polymer morphology (Freddy A. Khoury). Also, the Group saw the addition of an ASEE post-doctoral research fellow (Peter H. Mott), a guest scientist from France (Yves Leterrier), and two guest scientists from Israel (Hanan Dayan and Roselyne Grosfeld) to carry out research in the mechanics, non-equilibrium thermodynamics and dimensional stability of polymers for composite and electronic packaging applications. The Group also made a term hire (William K. Waldron) to work in the area of elastomeric seal compatibility for Halon substitutes on a contract with the U.S. Air Force.

Research Areas

The Mechanical Performance Group has a diverse range of activities that impact on the understanding of the mechanical performance of polymers and polymer based composites. This work is focussed in four areas: 1) Glassy Polymers--volume recovery, physical aging and dimensional stability, 2) Polymer Networks--mechanics and thermodynamics of swelling, 3) Microstructural Characterization--small angle and wide angle X-ray scattering, nuclear magnetic resonance, optical and electron microscopy and positron annihilation lifetime spectroscopy, 4) Composite Materials--durability and finite element analyses. These areas overlap and the group plans for the future include increasing cooperativity in these activities. Details are presented subsequently.

Industrial Interactions

The Mechanical Performance Group interacts with U.S. industry in a variety of ways. The NIST 10-meter Small Angle X-ray Scattering (SAXS) Facility is a user facility and responds directly to problems of industry by performing measurements of both research and proprietary nature. The Facility made a major effort this year to increase its outside use and industrial use increased by 50%. Clients came from a range of U.S. industries, National Laboratories and U.S. universities.

Past contacts with U.S. industries aimed at establishing collaborative relationships continued to bear fruit during the year as collaborative efforts to study aging in polymers were continued with Kodak and Xerox. A new, informal collaboration was established with MTI Instruments and IBM to develop measurement methods for the z-direction coefficient of thermal expansion of thin films used in electronic packaging applications. Additional contacts were made by holding a NIST/Industry workshop on "Aging, Dimensional Stability and Durability Issues in High Technology Polymers." This workshop helped establish a collaboration with the technical staff of Owens-Corning in the area of interface durability. It also identified areas of research in which the Mechanical Performance Group could contribute that would impact a spectrum of industries including automotive, electronic packaging, civil aeronautics, imaging and structural resin suppliers. The Group has also worked to establish relations and contacts with the Automobile Composites Consortium (ACC) and provided them with a highly useful survey of the literature on the interface and coupling agents used in glass reinforced composites. Invited technical presentations on physical aging were made to two workshops concerning durability of materials for the High Speed Civil Transport (HSCT)--one was sponsored by NASA for the aerospace industry and one by Boeing to bring together expertise concerning the scientific base available for long term durability testing methodologies. Expansion of these activities and developments of others are expected.

The NIST 10m Small Angle X-ray Scattering (SAXS) Facility has continued to be a resource for U.S. Industry. The level of use increased approximately 50% during the past year and projects on various aspects of effects of processing on the SAXS measured structure of polymers were performed with Amoco, Gillette Research Lab, Hercules, Inc., Hoechst-Celanese, Mobil Chemical Company, Raychem Corporation, Shell Oil Company and Sonoco Corporation. Efforts are continuing to expand these interactions and form new ones.

Other Agency Interactions

Other government agency support includes funding by the Cold Regions Research Laboratory of the Army Corps of Engineers for a study of the "Elasticity of Pavement Joint Seals" and a multiyear contract with the U.S. Air Force to study the compatibility of elastomeric seals with Halon fire suppressant replacements. Sandia National Laboratories also contracted with NIST to perform studies on the Small Angle X-ray Facility. A contract with the U.S.

Department of Transportation to develop test methods to determine the compatibility of liquid hazardous materials with polyethylene packagings was brought to a successful conclusion.

FY 92 Significant Accomplishments

- A workshop was organized on "Aging, Dimensional Stability and Durability Issues in High Technology Polymers." Participants from 17 U.S. companies as well as several government agencies, National Labs and private research foundations reviewed the current scientific knowledge base and recommended additional research into the physical aging phenomena common to dimensional stability and performance.

- A survey of the literature on the environmental durability of the glass fiber/matrix interface in composites was prepared and distributed to the Automotive Composites Consortium.

- A Positron Annihilation Lifetime Spectroscopy test facility was designed and built for studies of microstructure of polymer glasses.

- An isopiestic test facility for studying the thermodynamics of elastomer swelling was designed and built. The swelling activity parameter (S) in crosslinked networks was found to be a sensitive function of temperature. The peak in S as a function of degree of swelling was found to disappear over a narrow range of temperatures--a phenomenon not consistent with current theory.

- Experiments using the torsional dilatometry facility showed that the "heirarchical" nature of time scales found in down-jump temperature experiments is not reproduced in up-jump experiments. Where the down-jump experiments show the viscoelastic response to cease evolving towards an apparent equilibrium more rapidly than does the volume response, in the up-jump experiment the volume attains its equilibrium value well before the mechanical response ceases to evolve.

- A Finite Element Elastic Plastic Analysis of Mode II crack propagation in adhesive joints showed that the behavior observed experimentally can be described through a pressure dependent yield criterion for the adhesive.

- A methodology for inducing transcrystallization of polycarbonate thermoplastic polymer onto graphite fiber surfaces was established.

- Model calculations of proton spin diffusion profiles in two phase systems were completed which show that the spin diffusion estimates of domain size are relatively insensitive to the geometry modeled, e.g. lamellar vs rod/matrix domains.

- NMR spin diffusion studies of high temperature blends demonstrated that phase separation occurs 50-60°C below the glass transition.

- The NIST 10 meter SAXS Facility increased its usage by industrial clients by approximately 50%.

GLASSY POLYMERS--Volume Recovery, Physical Aging and Dimensional Stability

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Investigation of the Hierarchy of Time Scales in Polymer Glasses

Previous work in this laboratory established that, after a quench from above the glass transition temperature to below it, the time scales involved in property evolution towards an apparent equilibrium state was "hierarchical" in nature. In these[1] down-jump temperature experiments, performed using the NIST torsional dilatometer, it was observed that the physical aging time scales for the evolution of the viscoelastic properties of a model epoxy glass, as measured by the aging time shift factor, were up to two decades faster than the volume recovery time scale in the same experiment. Similarly[2], the yield stress evolved into equilibrium at a time intermediate between the viscoelastic and volumetric scales.

During the past year investigations began into the evolution of the volumetric and viscoelastic responses during de-aging after up-jumps in temperature. In these experiments it is found[3] that the volume recovers to its equilibrium value one to two decades in time sooner than the aging time shift factor for the viscoelastic response attains equilibrium. These results suggest strongly, that contrary to current volume or free volume based models of glassy materials, the mechanical response does not depend on the volume as the thermodynamic "state" value for these non-equilibrium materials. The possibility that enthalpy is the appropriate state variable, or that an internal ordering parameter approach is required for full description of the glasses' behaviors remain for future investigations.

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Effects of Moisture on the Behavior of Polymeric Glasses

Moisture is known to have dramatic effects on the mechanical response of polymeric glasses. In collaboration with Eastman Kodak Corporation a project was initiated to study the effects of moisture on the viscoelastic response of poly(ethylene terephthalate)(PET) films. In addition, the effects of moisture on the response of model epoxies used in a range of studies in the Group are under investigation. The underlying premise of the experimental program is that moisture acts primarily as a plasticizer for the polymer and consequently changes the glass transition. The goal is to establish equilibrium moisture content-temperature diagrams for the chosen epoxies and PET film. Once these are established, relative humidity-jump experiments can be performed and "aging" effects observed in a manner to those normally observed after temperature jump experiments.

Two approaches have been undertaken in order to perform these experiments. First, a system of relative humidity chambers are constructed that can be used to "condition" samples at a known RH prior to jumping to a new RH in a chamber attached to the test machine used for viscoelastic testing. Such experiments will demonstrate the validity or lack of validity of a simple plasticization model for the effects of moisture on the material viscoelastic response. The work required to create the moisture content-temperature surfaces at constant partial pressure of water have just commenced. In the second approach, dilatometers have been modified so that volume recovery experiments at constant moisture content can be performed. These experiments will allow the determination of the relative volume recovery kinetics of model epoxy glasses as a function of moisture content, without the superimposed problem of moisture diffusion into or out of the sample during the experiment. (We note here that most dilatometric experiments are performed in the dry state for this reason.)

Measurement of the Through Thickness Coefficient of Thermal Expansion in Thin Films

The coefficient of thermal expansion in polyimide films used by the electronics industry for multi-chip modules is anisotropic. Therefore, measurements of the CTE in the x-y plane do not tell the chip engineers the z-direction (thickness direction) CTE that can be important in determining the durability of the film. In collaboration with IBM Corporation and MTI Industries a non-contact method has been developed for measuring the CTE in the film thickness direction and for measuring the film thickness. IBM has provided polyimide films that have been spin cast onto quartz substrates and subjected to different thermal histories to determine the effects of the processing history on the CTE. The films have thicknesses of 8-20 μm. MTI industries has provided the probes and NIST is building the apparatus that has the required dimensional stability to assure measurement reliability. Initial calibration measurements have been carried out and the apparatus is going through a further design modification.

Effects of Physical Aging on the Yield Response of a Polystyrene-Poly(n-butyl methacrylate) Copolymer

In this on-going study, NIST and Xerox Corporation are collaborating in a study of the evolution of the yield response of a copolymer glass after a quench from above to below the glass transition. The polystyrene-poly(n-butyl methacrylate) copolymer is used in toner applications and the yield stress is related to the processing of the polymer into a fine powder for toner applications. The choice of this copolymer is based on its current use in toner applications. Future work will expand to examine newer materials being evaluated by Xerox for future applications.

The results of our studies have shown that the compressive yield stress of the copolymer increases with time after the quench when the aging temperature is fewer than 50 K below the glass transition temperature measured by conventional means. At 55 K below the glass transition temperature the yield stress does not change appreciably after up to 1000 h of aging. As was found previously (see above), the yield stress is found to cease to age after some characteristic time when the aging takes place near to the glass transition. Measurements of the compression modulus from the constant rate of deformation experiments show that the time for the modulus to cease to evolve is shorter than that for the yield stress to cease to evolve. This is similar to what was observed for the thermosetting epoxies studied previously and suggests that the hierarchical nature of the timescales for the copolymer glass is similar to that of the network glass. Dilatometric experiments need to be performed to ascertain the total similarity of the two systems.

POLYMER NETWORKS--Mechanics and Thermodynamics of Swelling

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The Anomalous Peak in the Swelling Activity Parameter

A major unresolved problem in the behavior of crosslinked rubber relates to the Frenkel[1]-Flory-Rehner[2] (FFR) hypothesis that the elastic free energy of a swollen network can be represented by a separable function of the mixing contribution and the elastic contribution. Thus, in recent work from this laboratory, McKenna, et al.[3,4] concluded from studies of the mechanical response of swollen and unswollen natural rubber networks that the FFR hypothesis appears to be valid. In that work, however, it was pointed out that there is an anomaly in that the peak[5-7] in the swelling activity parameter $S=\lambda_s \ln(a_c/a_u)$ vs λ_{2s} plot, i.e., calculations of S from the equations describing the network elasticity and the mixing contributions to the activities a_c and a_u for the crosslinked and uncrosslinked systems, respectively, do not result in a peak in S. Furthermore, Neuberger and Eichinger[7] have obtained results that seem to vary significantly with temperature and that have not been systematically explored. This has lead to our pursuit of the current work which will ultimately lead to measurements of S and the elasticity of the same materials over a wide range of vapor pressures and temperatures, network crosslink density and polymeric chemical species. In the work accomplished to date, we have examined a synthetic isoprene network crosslinked with dicumyl peroxide at a range of pressures (from near zero to the saturation pressure) and temperatures (10-50°C).

In isopiestic measurements one can obtain the activity of the solvent in the solvent solute system by measuring the weight uptake, and if solvent/solute additivity of volumes holds true, as it does in the benzene/isoprene system, the following equations can be used:

$$\ln(a_u) = [\ln(1-v_2) + v_2 + \chi_u v_2^2] \tag{1}$$

$$\ln(a_c) = [\ln(1-v_2) + v_2 + \chi_c v_{22}] + V_1 w'(\lambda_s)/RT\lambda_s \tag{2}$$

$$S = \lambda_s \ln(a_c/a_u) \tag{3}$$

where a is the activity and χ is the Flory-Huggins activity parameter. The subscripts u and c refer to the uncrosslinked and crosslinked polymers respectively. v_2 is the volume fraction of rubber, V_1 is the molar volume of the solvent, R is the gas constant, and w is the elastic contribution to the Helmholtz free energy. w' is the derivative of w with respect to the stretch λ and in the case of swelling $\lambda_s = v_2^{-1/3}$. S is a dimensionless quantity that we refer to as the swelling activity parameter that has been referred to erroneously[4] in the literature as a dilational modulus. Equations 1-3 are used to analyze the data obtained at different vapor pressures.

A major accomplishment during FY 92 was the design and construction of an apparatus for performing isopiestic measurements on crosslinked and uncrosslinked networks at different vapor pressures.

Experimental measurements were made of the mass uptake of benzene in samples of uncrosslinked and peroxide crosslinked synthetic isoprene at constant vapor pressure in benzene. The swelling activity parameter S was determined for the systems at 10, 30, 40, 42.5, 45 and 50°C. From 10 to 45°C the behavior is consistent with the ideas of the FFR hypothesis allowing that the Flory-Huggins interaction parameter in the crosslinked and uncrosslinked rubbers be different. However, upon performing measurements at 50°C there is a significant change in behavior. First there appears the "anomalous" peak in the S vs λ_s^2 curve that has been the subject of much discussion in the literature. It is our feeling at this time that the peak's appearance, in addition to presenting a problem for the so-called FFR hypothesis of separability of the elastic and mixing contributions to the free energy of swollen networks, creates problems for the theories that purport to explain this peak and is a subject which merits further exploration. This is because, to our knowledge, there is no ready explanation for the dramatic change in behavior over such a narrow temperature range (10°C). These are ongoing studies.

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The Strain Energy Density Function of a Sealant: Measurements and Use in a Finite Element Analysis of a Seal

In a collaborative contract with the Cold Regions Research and Engineering Laboratory, measurements are conducted of the elastic free energy of two silicone rubber joint sealants of the "self-leveling" type. By carrying out torque and normal force measurements on the cylindrical samples of the sealants subjected to torsional deformations, the Valanis-Landel[1(VL)] form of the strain energy density function derivatives are obtained using procedures developed by Penn and Kearsley[2] and Kearsley and Zapas[3]. The sealants are typical of those used to form seals in concrete pavement joints and have linear modulus differences of a factor of three. Here, the VL function is determined experimentally for each rubber and calculations are made of the material property parameters necessary to enter into a commercial nonlinear elasticity finite element analysis computer code. The code is then used to calculate the stresses in a rectangular cross section butt joint seal in extension and compression loading.

Although finite elasticity codes are widely available, few studies have been made using realistic elastomer parameters. Since the lifetime of pavement joints is dependent on the stresses in the joints, calculations using realistic material parameters is an important contribution to the selection criteria and design criteria used in sealant applications for runways, highways, buildings, and other infrastructure related areas.

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Elastomer Seal Compatibility with Halon Fire Suppressant Replacements

Halon is a brominated fluorocarbon that is used as a fire suppressant in civilian and military aircraft. Owing to concern about its destructive impact on the ozone layer of the atmosphere, its use will be banned in coming years. In response to the problem, the U.S. Air Force is sponsoring efforts at NIST to evaluate replacements that are less harmful to the atmosphere and that still serve the purpose of being effective fire extinguishing agents. As part of this NIST effort the Mechanical Performance Group is evaluating elastomer seal and lubricant compatibility with 11 gaseous or liquid (at ambient conditions) materials that the Air Force has selected as potential Halon replacements.

The approach adopted is based upon the classical swelling thermodynamics of rubber and polymers based on Flory-Huggins[1] theory and the Flory-Rehner[2] hypothesis. We will study under isopiestic conditions the Halon replacement uptake by the candidate seals and lubricants over a range of temperatures (ambient to 150°C) and pressures (near zero to 125 MPA). The project began only at the end of FY 92 and test apparatus design for isopiestic measurements under high pressure have just begun.

MICROSTRUCTURAL CHARACTERIZATION--Small and Wide Angle X-ray Scattering, Nuclear Magnetic Resonance, Optical and Electron Microscopy, Positron Annihilation Lifetime Spectroscopy

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Small Angle X-ray Scattering and Pole Figure Facilities

Introduction: The NIST Small Angle X-ray and X-ray Pole Figure Facilities are being increasingly used by Industrial, National Laboratory, Other Agency and University clients. At the same time these facilities are contributing directly to research projects within the Mechanical Performance Group. Significant efforts are also involved in the upgrading of the facilities.

The currently active roster of outside users includes eight industrial organizations, one government laboratory and two universities. The range of materials studied includes commercial fibers, specialty electronic materials, copolymers, polyurethanes, microporous filter media, energetic materials, and films.

Facility Upgrades: Data acquisition and analysis hardware is being updated to take advantage of recent technological progress. New computer hardware has been acquired to replace the VAX system previously used for data reduction and archiving. Newly acquired commercial visualization tools greatly enhance our ability to manipulate SAXS images and prepare them for publication. The data reduction software is now being "ported" to the UNIX and Macintosh hardware. The data acquisition system is expected to be completed during FY 93.

Commercial apparatus for using area detectors to measure pole figures is now coming on line from Siemens USA. Contacts with personnel from this company are expected to lead to a collaborative effort in evaluating the software for this method and in studying ways to extend its use to polymeric materials.

Calculations of SAXS scattering from isolated particles as a function of orientation have been made for several cases where closed-form calculations are possible. The calculations will next be extended to more realistic electron density distributions representative of typical practical materials.

Efforts to simulate x-ray diffraction pole figures on the basis of idealized models of crystalline orientation have centered on investigating the forms of suitable functions to represent crystalline orientation distributions (ODFs). Defining the "orientation distance" is a basic problem in this area. It has proven to be difficult to find a measure of the difference between two orientations that is appropriate for assigning relative probabilities. An alternative to the usual Euler angle representation of orientations has emerged, in the form of a vector representation pioneered by Rodriguez and rediscovered by F.C. Frank that shows great promise because it resolves the orientation into an axial portion and rotation about that axis.

Probability density functions based on this description look very promising, especially for representing ODFs with strong fiber axis components, which appear to be fairly common in polymers. In order to produce model pole figures the probability density functions must be incorporated into path integrals over the orientation space. This project is currently seeking methods for carrying out these complex path integrals.

Damage in Composite Materials: A preliminary study to evaluate the feasibility of SAXS methods as a tool for assessing damage in composites was undertaken. This study used carbon-fiber/epoxy composites. The scattering signal from the internal microstructure of the carbon fibers swamped any contribution that may have been present from damage wrought by compressive loading of the specimens. Efforts are underway to procure composite specimens that do not exhibit such intense scattering.

Three Phase Materials (Intensity Standards): A collaborative effort to assess microstructure in propellant materials consisting of a filler in a solid matrix, undertaken with personnel from the Reactor Radiation Division, revealed the difficulties in correlating x-ray and neutron scattering results. This material is representative of three-phase materials containing voids in addition to the two major phases. Under suitable conditions the combination of x-ray and neutron scattering data should yield information regarding the interface area and the interface roughness between the void-matrix, void-filler, and matrix-filler phases. However, in the absence of materials that are suitable for direct intercomparison of neutron and x-ray scattering data it becomes very difficult to obtain the appropriate factors for scaling the data.

This study has led to NIST involvement in the American Crystallographic Association Small Angle Scattering Special Interest Group as a focal point for a study aimed at obtaining materials and methods that are suitable for performing calibration of intensity and momentum transfer over a broad range of experimental conditions. Some clients of the SAXS facility have revealed that some of the literature methods for obtaining "absolute" scattering intensities have not worked well for them.

Outside Users: As a result of a public information campaign new industrial users were attracted to the SAXS facility during FY 92. Billings for proprietary work have increased approximately 50 percent. These new users have brought more demanding problems. Current users have also begun to emphasize cross-correlation with scattering measurements carried out on other facilities. This is necessitating a reevaluation of the resolution and dynamic range of the NIST 10-meter SAXS camera. These studies are expected to involve ray-tracing calculations and measurements to better validate the modelling that was done previously on the three-pinhole camera configuration and the evaluation of detectors and interfaces with higher data throughput. Detector designs that are thought to be less easily damaged by high photon fluxes are also being examined.

Crystallization and Morphology of Poly(vinylidene fluoride)

The formation of banded spherulites of the α-form of poly(vinylidene fluoride) (PVF2) crystallized from miscible blends of PVF2 and poly(hydroxy butyrate) (PHB) has been investigated (in collaboration with H. Marand and D. Reinhard, Virginia Polytechnic Inst.). The purpose of this study was to compare the morphology of the α-PVF2 spherulites grown from this blend system with those grown from blends of PVF2 and poly(ethyl acrylate) (PEA) with particular regard to the morphological underpinnings of the periodic banding in each case.

Banding in polymer spherulites has been commonly attributed to a periodic twisting of the radiating lamellae in the spherulites about the radial direction. In a previous study of banded PVF2 spherulites grown from PVF2/PEA blends (R. M. Briber and F. Khoury), light optical and electron microscopical evidence was presented which revealed that the banding in the spherulites was governed by a radially periodic repetition of a complex growth motif involving lamellar twisting coupled with a fan-like splaying of lamellae about the radial direction. A main objective of the present study was to determine whether a similar motif, which differs in its fan-like lamellar splaying component from banding due to just a helicoidal twisting of lamellae, is also manifested in spherulites grown from PVF2/PHB blends. Light microscopical observations obtained to date indicate that this is indeed the case. Confirmation at the electron microscopical level of resolution has so far been frustrated by the difficulty of finding a suitably selective solvent for extracting the PHB from the crystallized samples for examining the PVF2 spherulites in detail. This problem is being pursued. Among the possibilities being considered is the biodegradation of the PBH.

NMR Characterization of Polymer Structure Using Spin Diffusion: There is a class of solid-state NMR experiments referred to as "spin diffusion" (SD) experiments which, under favorable circumstances, allow one to extract information about spatial relationships between various morphological regions in polymers. Thus, for example, SD experiments have been used to obtain the minimum distances across crystalline domains in semicrystalline polymers or across phase separated domains in polymer blends or block copolymers. While the concept of spin diffusion can also be used to determine the partitioning of a minor species in a complex polymer morphology, our focus in the following discussion is to use these experiments to extract minimum domain dimensions (MDD's) in phase separated blend morphologies. Two features about this method attract us to pursue these experiments; the first is that the lower limit of MDD's which can be determined is about 2.5 nm (below the usual resolution limit of imaging techniques). Second, these experiments can provide some information about stoichiometries of the phases in blends--information unobtainable from scattering techniques.

SD experiments involve the controlled production of non-equilibrium polarization gradients based on compositional or dynamical differences between regions. These gradients are analogous to imposed temperature gradients in the sense that the response to the imposition of such gradients is a diffusional transport (of polarization per spin in our case) such that a condition of polarization equilibrium is approached. If one knows the diffusion constant for the process, then information about characteristic distances can be inferred from the time taken for this equilibration process.

1. **Mathematical modelling of spin diffusion profiles**: In collaboration with Dr. Geoffrey McFadden of the Mathematical Modelling Group in the Applied and Computational Mathematics Division calculations modelling spin diffusion for various idealized morphologies were performed. In general, from the NMR data, the time dependence of the integrals of total polarization in various morphological regions are obtainable. The calculations are designed to generate a perspective on the task of identifying a morphological model which is consistent with the spin diffusion profiles. To this end we calculated and compared spin diffusion profiles for different idealized geometries, such as lamellar and rod/matrix (with both square and hexagonal arrays of rods).

These calculations have provided useful perspectives: 1) One cannot easily distinguish lamellar from rod/matrix models; differences are quite subtle and appear only at longer spin diffusion times. 2) The most sensitive parameter to match is the initial slope of the spin diffusion curve. 3) This initial slope can be related to the total interfacial surface area and this correspondence is model-independent when the overall composition and the diffusion constant are known. 4) In a given experiment for a given initial slope, the characteristic distances corresponding to the idealized morphologies just enumerated can be calculated. From the initial slope one can estimate, within a factor of 1.4, the average repeat distance in the direction of minimum domain dimension.

2. **Search for a better magic-angle-spinning/multiple-pulse sequence during which molecular-motion-determined relaxation occurs**: The most successful SD experiments performed in our laboratory to date on blends have been based on polarization gradients generated from differences in chemical shifts of the component protons. It is also highly desirable to generate these gradients on the basis of differences in the molecular mobilities of the molecules in each domain. Multiple pulse (MP) methods have the advantage of producing sharp gradients because SD is quenched during the preparation of gradients. If there were sufficient contrast in molecular motion between two regions, then, if further relaxation were allowed to occur in the presence of a MP sequence, sharp polarization gradients could be generated based on these motional differences. Thereby, the applicability of the spin diffusion experiments for probing morphology could be greatly extended.

From earlier work it appeared that the so-called MREV-8 MP sequence was the most promising even though magic-angle-spinning (MAS) caused periodic anomalous relaxations, unrelated to molecular motion, at resonance offsets which were half-multiples of the MAS frequency. In recent work several other MP sequences were investigated, most of which have very serious interferences with the MAS frequency. The most promising sequence identified to date is the HW-8 (Haeberlen-Waugh 8-pulse) sequence. It too has certain offset frequencies (also related to the MAS frequency) where anomalous relaxation takes place. However, these intervals are more widely separated than for the MREV-8 sequence; thus, they look more promising for performing SD experiments in which the gradient is generated based on a difference in molecular motion between regions.

3. **Characterization of Spin Diffusion behavior in a thermodynamically miscible blend (PS/PXE)**: Poly(styrene) (PS) and poly(xylylene ether) (PXE) form a thermodynamically miscible blend over a wide range of composition. The SD behavior of a 50/50 blend of PS/PXE has been examined in order to measure experimentally the time required for polarization equilibration within modestly small monomers and to measure the equilibration time between dissimilar polymers when such polymers are mixed on a molecular scale. These two characteristic times are important in the interpretation of SD experiments on phase-separated blends having similar monomer sizes. The reason is that the primary interest is in interphase SD, i.e. that which occurs between domains; however, the initial movement of polarization is often dominated by equilibration processes occurring within the homopolymers and between dissimilar polymers within a given phase (when each phase is a different mixture of the two homopolymers). On the basis of the greater physical proximity of the protons involved in these latter two equilibration processes, relative to the interphase equilibration process, the interphase equilibration is expected to be the slowest process. To capture the time dependence of interphase diffusion requires precise knowledge of the SD time past which the interphase equilibration is dominant.

It was found that the intramonomer equilibration was finished in about 1 ms while the intraphase equilibration was 70% complete in 0.25 ms, 80% complete by 1 ms, and 95% complete by 4 ms. The rapid initial movement of polarization between dissimilar polymer chains indicates that a substantial number of monomers have nearest neighbors of the other species, i.e. these chains are truly mixed on a molecular scale. However, this equilibration goes to completion over a longer time frame compared with intramonomer equilibration owing to the statistics of mixing between dissimilar monomers.

The conclusion is that for phase separated blends whose monomers have a size comparable to PS and PXE, the measurement of initial slopes that can be attributed to heteropolymer equilibration (between dissimilar chains) can be determined from the slope at 1 ms extrapolated to zero time. However, to ensure that interphase heteropolymer equilibration is dominating the slope, the slope should be determined at about 4 ms and extrapolated to zero time. If the domains are small (<5 nm), this extrapolation becomes less precise because the interphase equilibration process has passed the linear region at 4 ms; hence the slope determined at 4 ms will be smaller than the true initial slope of the interphase equilibration process. The inaccurate slope determination will have two effects: first, the minimum domain dimensions (MDD) will be overestimated and second, the stoichiometry of the phases will appear to be more mixed than is actually true, since a lowering of the intercept at zero time is that which is expected from a mixed phase when faster intraphase heteropolymer equilibration takes place. When ambiguities like this exist, it is desirable to have auxiliary information available, such as small-angle X-ray scattering, which may offer further comment on the MDD's. Narrowing of the uncertainties related to MDD's reduces the uncertainties in the determination of stoichiometries from the NMR data.

4. **Characterization of domain size and stoichiometry in blends of cellulose and hydrogen bonding polymers (P4VPy and PAN):** In a collaboration with McGill University in Canada, samples of cellulose (CELL) blends with either poly(4-vinylpyridine) (P4VPy) or poly(acrylonitrile) (PAN) were examined. These blends are interesting from at least two perspectives: first, CELL is the most ubiquitous natural polymer and to find additional uses for it could be quite valuable; second, CELL is a very strongly associating chain (with itself) and provides a good test of the hypothesis that polymers which strongly hydrogen bonding would blend with CELL and be stabilized by the hydrogen bonding. P4VPy and PAN have nitrogen sites which should form strong hydrogen bonds with the hydroxyl groups of CELL.

Previous work, which included DSC, dynamic mechanical and NMR measurements, by Manley and his collaborators at McGill University indicated that the CELL/P4VPy blends were mixed on a rather intimate scale (<2.5 nm). On the other hand, in the CELL/PAN blends, dynamic mechanical measurements indicated a rather strong coupling of the CELL and PAN responses at stoichiometries which were CELL-rich, while certain NMR measurements showed little evidence of mixing below the 30 nm level. The MP SD measurements that could performed in our laboratory offer more precision in defining MDD's. Of equal interest, however, was the possibility that the NMR experiments could provide stoichometric information, which is a qualitative indicator of compatibility in these blends. A complicated preparation procedure makes possible the formation of blends which are mixed on a very fine scale but whose domains are comprised of nearly pure homopolymers.

NMR SD measurements were performed on CELL/P4VPy blends of stoichiometries 30/70, 50/50, and 70/30. Also, CELL/PAN having stoichiometries of 32/68, 35/65, 56/44, 61/39, 75/25, 82/18 and 88/12 were examined. Both proton SD measurements and ^{13}C CPMAS experiments were conducted on the latter samples. Moreover, as a modest attempt to couple the results to other techniques, SAXS patterns were taken and analyzed for the 50/50 CELL/P4VPy and the 56/44 CELL/PAN blends.

The results of these studies are summarized as follows: For the CELL/PAN blends, overall repeat distances (the sum of the shortest average distance across both the CELL and the adjacent PAN domains ranged from 17 - 25 nm for all blend stoichiometries using either the lamellar or the rod/matrix assumptions to interpret the initial slopes. The tailing of the data to longer times occurred more gradually for the data than for the corresponding model calculations for a matched initial slope. Thus, distributions of MDD's were indicated. A SAXS experiment on the 56/44 CELL/PAN blend showed this blend to be a strong scatterer and the Lorentz-corrected data (a q^2 weighting of the intensity) gave a scattering peak at 17.9 nm compared to a 17.6 nm repeat distance inferred from the lamellar model of the SD NMR data. The excellent agreement for the repeat distances derived from the NMR and SAXS data indicated that our modelling of the SD data was quite good. For all the CELL/PAN blends studied, the phases were nearly pure homopolymer. Depending on whether just one or both phases are expected to be of mixed character a maximum of 5% or 10%, respectively, of the minor homopolymer would occur in the phase whose dominant constituent was the other homopolymer.

5. **Aging study of a 50/50 PEI/PBI blend below T_g**: Previously, spin diffusion measurements were conducted on a 50/50 blend of poly(etherimide) (PEI) and poly(benzimidazole) (PBI). These are considered high performance polymers owing to their high T_g's (220 and 420°C, respectively.) These blends, when cast from DMSO solvent, are very intimately mixed (on at least a 2.5 nm scale) and show a composition-dependent T_g, which for the 50/50 blend is about 347°C. Nevertheless, phase separation is also observed when the sample is heated up to its T_g. In fact, spin diffusion experiments revealed domain size and stoichiometric information of samples which had been annealed in a nitrogen atmosphere for 1 h at various temperatures from 250 to 400°C. In that study, phase separation on the 6 nm scale was evident already at annealing temperatures of 310°C. Therefore, a sample was selected which had already been annealed at 280°C for 1 h and it was annealed at 310°C for successively longer periods of 15 m, 1.25 h, and 16 h. The earlier study raised other issues besides the surprising observation of phase separation 40°C below T_g. One issue was the role of a small amount of residual solvent in the originally annealed samples which might provide for phase separation at a lower temperature. The second issue was the importance of crosslinking in phase separation. Crosslinking was inferred from a decreased solubility of the annealed specimens compared to the unannealed samples.

The aging results were as follows: the sample aged at 310°C had most of the solvent removed by its initial annealing at 280 °C; yet the spin diffusion curves after 1.25 h of annealing at 310 °C looked very similar to those seen before and after 1 h of similar annealing. Thus, the presence of residual solvent seemed insignificant. Second, while very little phase separation occurred in 15 m, there was a substantial growth in the phases between 1.25 and 16 h, with the MDD's at 16 h averaging about 10 nm. As to solubility, samples were still soluble in DMSO at 100 °C for annealing times of 15 m and 1.25 h but an insoluble, PBI-containing (by amber color) insoluble residue remained following an attempt at dissolution of the 16 h-annealed sample.

Probably the most significant deduction, aside from the recognition that this SD technique can detect very early stages of phase separation, is that the maximum service temperature that one can expect for this material whose DSC-determined T_g is very high (347°C) is probably 50 - 60°C below this T_g when the thermodynamics favor phase separation. Secondarily, crosslinking, although capable of arresting phase separation after long annealing times, still allowed growth up to 16 h.

A Positron Annihilation Lifetime Spectrometer for Microstructural Measurements on Amorphous Polymer Glasses

Positron annihilation lifetime spectroscopy (PALS) is becoming a readily available and powerful tool for probing "microstructure" as "free space" in amorphous polymers both above and below their glass transitions[1]. When positrons interact with matter, one reaction is the formation of ortho-positronium, which decays with a lifetime characteristeric of the "hole" size and intensity characteristic of the total number of holes in the sample. The hole size measurable from the ortho-positronium diameter is between approximately 0.1 nm and 2.5 nm. The power of this type of probe to look at the "microstructure" of amorphous materials lead to the construction of a PALS spectrometer to examine problems associated with the aging and mechanical response of model epoxy glasses. The NIST PALS spectrometer has been designed and constructed with two things in mind. First, by selecting a model system with a low glass transition temperature, the fast plastic scintillators may be placed in the oven with the sample and temperature jump experiments conducted with the spectrometer. Second, the mechanical deformation stage is set up to operate in simple shear, a (to first order) isochoric deformation. Therefore, simultaneous positron annihilation lifetime measurements and mechanical probes of physical aging measurements may be performed.

At this stage, the apparatus is nearly completed and preliminary measurements should soon be underway. It is anticipated that information concerning microstructural changes accompanying physical aging will be obtained from the measurements. Of particular interest will be to observe whether or not the technique provides the sensitivity to detect changes occurring on differing length scales that might correlate with the "hierarchy" of time scales observed in the combined dilatometric and mechanical experiments described above.

[1] Y. C. Jean, Microchemical J., 1990, 42, 72.

COMPOSITE MATERIALS--Durability and Finite Element Analyses

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Interfacial Degradation in Glass Fiber Reinforced Polymer Composites

As part of the new Composites Task of studying the durability and mechanical performance of polymer based composites, a literature survey on environmental degradation in glass fiber based composites was undertaken for two purposes. The first purpose was to develop the in-house background necessary to decide on an experimental program to address the important scientific and technological issues in this area. In addition, the survey was ultimately distributed to the Automotive Composites Consortium as part of our ongoing interactions with this group. The results of the survey are summarized, briefly, below.

The survey contains approximately 100 references. Although our long range goal is to address fundamental and universal issues in durability of composites, the immediate and specific interests focused on the composites of interest to the US Automotive Composites Consortium. Therefore, the review contained only papers that address studies of composites that contain glass fibers - typically, requirements for mechanical performance and cost dictate the use of glass fibers in the majority of composites used for applications in the automotive industry. Where studies using carbon fibers were relevant, however, as in single fiber tests, this review included these results.

The loss of properties of the components of the composite - fiber, matrix, and interface - involved issues including stress corrosion of the glass fibers, hydrolysis of the matrix, chemistry and morphology of the coupling agent on the surface of glass, and mechanochemical degradation at the interface. The use of single-fiber tests allowed for the characterization of mechanical properties of the fiber/matrix interface. For studies of the effect of exposure of these interfaces to the environment, these systems yielded useful information both qualitatively and quantitatively.

Many studies in this area were observations of loss of macroscopic properties upon exposure to the environment, and several papers illustrated, for example, changes in weight, tensile modulus, and tensile strength. One paper illustrated the effect of the processing method on the degree of degradation as a function of exposure to the environment.

Theoretically, many environmental elements can degrade polymer composites; however, the majority of papers found in the survey addressed the problems of exposure to moisture.

Subsequent to completion of the survey and its distribution to the ACC, an experimental research program to address the problems of interfacial durability in moisture environments commenced. The goals of the program are to establish the relative importance of chemisorbed and physisorbed layers on the interfacial durability of glass fiber/polymer matrix composites exposed to differing moisture and temperature environments for extended periods. The test method for assessing the durability is the fragmentation test technique that is available in this laboratory.

In preliminary tests an E-glass/epoxy model system was evaluated by the fragmentation test to characterize the relative interfacial shear strength of samples immersed in a 100% RH environment at 65 °C for up to 53 days. The experimental protocol will be extended to different coupling agent morphologies and to resins used in structural reaction injection molding (SRIM) polyurethanes and polyisocyanurates. These are systems of interest to the ACC with whom we are interacting in order to define the types of resin, fiber and environment that are relevant to the automotive industry. Other industrial interactions include Owens Corning Fiberglass, Dow Chemical and Dow Corning as suppliers of model and industrial grade glass fiber, resin and coupling agent systems, respectively.

The Effect of Transcrystallization on the Carbon Fiber/Polycarbonate Interfacial Shear Strength

Determination of whether the effect of polymer transcrystallization at the surface of carbon fibers is beneficial or detrimental to the mechanical performance of fiber reinforced crystallizable polymer composites has been and remains an issue of considerable industrial interest. Among the tests used to characterize the fiber/matrix interfacial interactions (adhesion, stress transfer) in composites, is the fiber fragmentation test carried out on single fiber reinforced polymer specimens. Given certain assumptions, this test provides an indirect method of deriving the interfacial shear strength between the rigid fiber and the more ductile polymer matrix. In the present study, this test has been used to probe and compare the interfacial mechanical characteristics of polycarbonate/ carbon fiber specimens devoid of any transcrystallization in relation to specimens exhibiting uniform transcrystallization along the fiber length.

The continuous filament type of carbon fiber used in this study is a poly(acrylonitrile) based, surface treated, but unsized, high modulus fiber denoted HMS4 (tens. modulus=338 Gpa, str.=2.48 Gpa, diam.=8 μm). The polymer, a commercial bisphenol-A polycarbonate (PC), is a slow crystallizing polymer which can be readily quenched from the melt to an amorphous state by rapid cooling to room temperature. The glass transition temperature of PC is about 150°C. In preliminary experiments, in which PC films containing short lengths (circa 1mm) of the HMS4 were crystallized isothermally from the melt using a hot-stage-equipped light microscope, it was seen that the polymer underwent transcrystallization at the surface of the fibers. The outer growth of the transcrystalline sheath from the fiber surface and the evolution of spherulites in the bulk of the polymer matrix could be readily arrested by rapidly cooling the polymer from the crystallization temperature (e.g. 180°C-190°C) to room temperature at different times. These observations were used as a guide for preparing specimens for the fragmentation tests using a hot press.

The polymer in the form of two 0.6mm thick sheets sandwiching individual carbon filaments was melted and subsequently either quenched rapidly to room temperature to prevent any crystallization, or was crystallized isothermally at 190°C for about four days followed by rapid quenching to room temperature. In the latter samples a transcrystalline sheath about 2μm thick was formed at 190°C along the entire length of the filaments. Well dispersed incipient spherulites of comparable dimensions were formed in the surrounding matrix, the remaining bulk of which remained uncrystallized and was quenched as such in the final cooling cycle. In initial experiments, melting was carried out at 240°C for one hour. Many of the samples exhibited residual stresses and filament breakage occurred often. Both of these effects were reduced but not eliminated by melting at 280°C for one hour.

Elastoplastic Finite Element Analysis of an Adhesive Joint

Polymeric resins are widely used in a variety of important technological applications including adhesive bonding, composite materials, coatings and microlaminations. Under severe spatial constraint, the mechanical properties of the binding phase, in particular the fracture toughness, may be greatly affected by its thickness. Currently, the fracture behavior of interlayer films is generally evaluated based on linear elastic fracture mechanics concepts. However, recent tests have shown that the ultimate shear strain of brittle epoxies in thin bond lines may increase by over 30 fold, being as large as 300%, when the interlayer thickness is decreased to the micrometer level. A meaningful fracture analysis of such configurations clearly necessitates, at least, an elastoplastic crack tip analysis.

The present research effort is concerned with developing and implementing numerical techniques for elucidating the detailed distribution of plastic stresses and strains at the crack tip in adhesive bonds loaded in shear, and with attempting to correlate local tip parameters with ultimate material properties as obtained from tests on the unflawed adhesive.

The adhesive thickness is the main input variable, ranging from a few micrometers up to values large enough to expose the bulk material behavior. For this purpose, the large-deformation finite-element code Abaqus is employed. The material constitutive relationships needed in the analysis were previously generated using the "napkin ring" shear tests. It should be noted that these relationships are greatly affected by the interlayer thickness. A number of flow rules are investigated, including Von-Mises and Drucker-Prager. At this time the main concern is with code development aspects such as mesh generation, convergence of the crack tip parameters and film-substrate contact laws. Preliminary results pertaining to global quantities such as critical length of plastic zone and average shear strain at the crack tip agree well with experimental data. Correlation of local field quantities is not as good, and further exploratory work is necessary.

POLYMER COMPOSITES

Polymer composites are light-weight, high-strength materials whose properties can be extensively tailor within a part. By using these advantages, companies can make dramatically improve products which are more competitive in world markets. Unfortunately, this potential remains largely unrealized, particularly in mass-market, commercial applications. There are two critical barriers hindering the wide spread use of polymer composites: (1) the need to improve the speed, reliability, and cost effectiveness of fabrication, and (2) the need to develop a better understanding and predictive capability for long term performance (durability). Research in the Composites Group focuses on the first topic while the second area is addressed by activities in the Mechanical Performance Group. A number of programs overlap the two areas, and this results in cooperative efforts between the two Groups.

The critical need for improved manufacturing, particularly in commercial applications, can be illustrated by comparing the fabrication of structural parts for a defense/aerospace application and an automotive application. The manufacturing time for an aerospace part is generally in the range of days while the goal in the automotive industry is to manufacture a part in minutes. This represents a 2 to 3 order of magnitude difference. A second comparison involves the value gained by saving weight. In a defense/aerospace application, a 1 kg savings is often said to be worth several hundred dollars or more over the life of the part. In an automotive application, that same savings is worth only 1 to 2 dollars. Again, the difference is 2 to 3 orders of magnitude. Manufacturing is critical in this regard since it can often represent more than 70% of the cost for the part. Clearly, for composites to be viable for commercial applications like automotive, new manufacturing methods are essential. Moreover, these methods must be understood on a basic scientific level so that they can be optimized for speed and reliability. In fact, even in the defense and aerospace industries, the need to significantly lower cost is now a major driving force for improved processing.

The programs in the Composites Group seek to address this challenge with activities in three thrust areas: **Liquid Molding, Process Monitoring and Control, and Interface Science.** During the past year, however, most of the effort has been on topics one and three. The Group has interests in four processing methods: advanced autoclave cure, filament placement, press molding, and liquid molding (LM), but the major focus is on LM, which includes resin transfer molding and structural reaction injection molding. This emphasis is based on the advice of industry obtained through a variety of mechanisms, including NIST sponsored Industry Workshops. The consensus was that LM offers the best possibility to achieve the goals outlined above. The Process Monitoring and Control thrust area addresses the need to develop both a basic understanding of the events that occur during processing and the technology to control these events in real time. The need applies not only to liquid molding but also to any other composite fabrication method. The work focuses on the development, understanding, and implementation of process monitoring and control sensors. The third thrust area is interface science. The fiber-matrix interface is probably the least understood aspect of most composites and yet most critical to features like long term durability. The objective in this thrust is to develop measurement capabilities that can characterize the interface region, and apply these capabilities to understand how the interface region is formed during processing and what are the consequences for long term performance.

During the past year, the programs have been assisted by interactions with a number of outside organizations. In the liquid molding area, the cooperating groups included the Automotive Composites Consortium, General Electric, Ford, Grumman, Boeing, Johns Hopkins University, and the University of Delaware. Ford and the University of Delaware also participated in the interface science programs along with DuPont. Dow cooperated in the effort on toughening. S. Matsukawa from Nihon University in Japan completed his sabbatical at NIST during the past year, and M. Shioya from Tokyo Institute of Technology began a sabbatical working in the interface program. Finally, two graduate students are conducting part of their thesis research at NIST in the Group's programs: D. Levy from Johns Hopkins University, and P. Chin from the University of Delaware.

The discussion below begins with a list of major accomplishments, and then five sections describe the activities during the past year. The first section is a short summary of the results from the 3rd Industry Workshop on Polymer Composite Processing sponsored by NIST. The next three sections cover the three major thrust areas. The final section discusses activities which draw upon expertise in the Group but are outside the major thrust areas.

FY 92 Significant Accomplishments

- The third Industry Workshop on Polymer Composite Processing brought together 22 industry experts to review the NIST research program and to provide guidance for future program planning. The attendees strongly supported the current effort in liquid molding of composites and encouraged the development of new activities in process monitoring and control technology, and preform preparation.

- A versatile flow animation program was developed to analyze the results from finite element programs for mold filling in the liquid molding process. The animation makes it easy to observe filling behavior from all angles and stop the flow simulation at any point for detailed examinations. This represents a major advancement in the analysis of flow simulations.

- A micro-model for flow through porous media successfully predicted the permeability of a unidirectional fiber preform with impenetrable fiber tows. The shape and geometric arrangement of the tows have been modelled, and this provides an important first step towards goal of scientifically designing preform microstructure to optimize processing and performance.

- By application of neutron reflectivity, the concentration of absorbed water in a polyimide near an interface with a solid surface (silicon) was quantitatively determined for the first time. The results show that the water content within the first 25Å of the interface is more than 6 times the value in bulk polymer. This measurement is a critical step in understanding the problem of environmental attack on interfaces.

- The diffusion between polymer layers on a solid surface was characterized using neutron reflectivity. It was shown that the interface significantly reduced the rate of diffusion for an adsorbed layer, and this has important consequences for the behavior near interfaces during processing.

THIRD INDUSTRY WORKSHOP ON POLYMER COMPOSITE PROCESSING

In May, 1992, a group of 22 industry experts gathered at NIST for the 3rd in a series of workshops designed to seek guidance from industry for future program planning and to provide industry with a overview of the latest NIST results. The attendees represented automotive, aerospace, and electronic companies, as well as organizations involved in materials supply, part manufacturing, and design. Through extensive discussions, the attendees identified four critical issues hindering more cost effective fabrication of composites. These issues are the needs for: improved process monitoring and control, a better understanding of the fiber-matrix interface, advances in recycling, and standardized test methods and data reporting procedures (data bases). The Workshop paid particular attention to fabrication by liquid molding because this technique had been rated as most important for the future in the two previous Workshops. For this method, the attendees concluded that process simulation models and preform fabrication technology are vital and that the characterization data required by the simulation models, for example preform permeability, are badly needed.

The priorities determined in the workshop fit very well with the existing NIST program, and the attendees were very supportive of the current effort. Some of the companies represented already have cooperative interactions with NIST, and several others are now negotiating joint programs based on the discussions at the workshop.

LIQUID MOLDING

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Research in liquid molding (LM) involves two areas: Modeling and Experimental Studies. There is significant interaction between the two areas and topics discussed under one heading often involve significant contributions from the other. The effort on modeling approaches the problem on both macro- and micro-scales. The former treats global behavior like mold filling while the latter is needed to predict properties like void formation and permeability that depend on the detailed microstructure. The experimental work provides characterization of material properties like permeability, studies of the physics of flow through porous media, and results to test and refine the simulation models.

Modeling the Liquid Molding Process

The long range plan for modeling involves three phases: the first addresses mold filling under isothermal conditions; the second models thermal and cure effects without flow; and the third combines all parameters in a single program. Phase one is near completion as will be outlined below. Work on the second phase has just begun and will not be discussed here. Another active area not covered here is the development of models for viscoelastic flow in porous media. This topic has been discussed in previous Annual Reports. The presentation here will cover: (1) improvements to the existing computer program for simulating mold filling, (2) development of an interactive graphics animation program for interpreting results from these simulations; and (3) permeability prediction via the modeling of flow at the micro-scale level in fibrous porous media and comparison of these predictions with experimental results.

Modeling of Mold Filling: Previous work has developed two finite element programs to simulate mold filling. The first models flow in 2.5D geometries. These are shell structures which may be highly complex in 3D space, but which have a thickness direction throughout that is thin enough that the entire geometry can be treated as locally two-dimensional. Thus, in a 2.5D simulation it is assumed that there is no flow in the thickness direction. This simulation uses linear triangular elements to solve for the pressure. The second program is for fully 3D flows, and uses linear tetrahedral elements. Together, these programs enable simulations for a variety of conditions of commercial interest including multiple injection gates, anisotropic and multi-ply preforms, thick sections, and regions of variable packing.

During the past year, several significant improvements to these simulation capabilities have been made. The first improvement was to combine the two separate programs into one comprehensive program called RTMFill. During this process, new code was incorporated which enables RTMFill to do simulations with an arbitrary mixing of element types. For example, 3D elements can be employed near inlets, or in thick sections where it is expected that 3D flow effects are important, while simultaneously using 2D elements which are less computationally expensive in areas of the mold where there is no significant through-thickness flow.

A second important improvement to RTMFill was the addition of new element types: 1D rod elements, 2D quadrilaterals, and 3D pentahedrons and hexahedrons (all linear). The linear

1D rod elements permit modeling of flow in runners, which are narrow channels cut into the mold wall above the preform material extending from the injection point. Fluid flows very rapidly through the runners in comparison to flow into the preform, and this effectively provides a greater surface area for injection. The result is a lower resistance to filling and greater fluid distribution. This is important for applications like automotive where rapid filling (25 kg/min) is required. The 1D element types also permits modeling of edge effects where fluid "race tracks" ahead of the rest of the flow front do to a poor fit between preform and the mold wall. The new 3D elements types facilitate modeling of 3D structures. Although RTMFill already had 3D capability with tetrahedral elements, the pentahedral and hexahedral element types permit RTMFill to use meshes generated with the majority of the current commercial pre/post-processing packages.

A number of cooperative programs with industry are underway to test and refine these computer programs by comparing predictions with data on the fabrication of actual parts. One example is the CRDA with the Automotive Composites Consortium (ACC); the ACC is a coordinated effort by Ford, General Motors, and Chrysler to address the technical problems hindering the use of polymer composites for structural automotive parts. The NIST/ACC cooperation is currently focusing on two parts: the front end structure in an Escort and the cross-member in an Aerostar van. The 3D elements described above are particularly important for the cross-member which has extremely thick preform sections that probably require 3D flow to simulate the fill. Some results for the front end are described in the next section. Another interaction designed to test the models was initiated last year through a CRDA with Grumman. This program will investigate application of RTMFill to commercial aerospace parts. Some preliminary cooperation involving both modeling and permeability measurements is also underway with Boeing.

Graphics Animation Program: To complement RTMFill, a new program called RTMView has been developed. RTMView is a graphics program written using the SGI IRIS Graphics Library (IrisGL) to display the results from RTMFill mold filling simulations as 3D contour lines. The program has two key features. The first is the graphics interface which enables rapid "point and click" rotation, translation and zoom of the mesh geometry; the second is the ability to display an animation of the flow front movement predicted by RTMFill. The ability to quickly view the dynamics of the filling process at different angles enables rapid examination and interpretation of results even from simulations in very complicated geometries. An example is shown in Figure 1, which is a still from RTMView for the filling of the Ford Escort front end structure in the region around the shock tower. The Figure shows that several flow fronts are about to merge around the base of the shock tower causing an area at the top to be closed off from the flow. This is a potential air entrapment mechanism. The dynamic view of these events provided by RTMView makes such features much easier to see than they are in standard still pictures with contour lines.

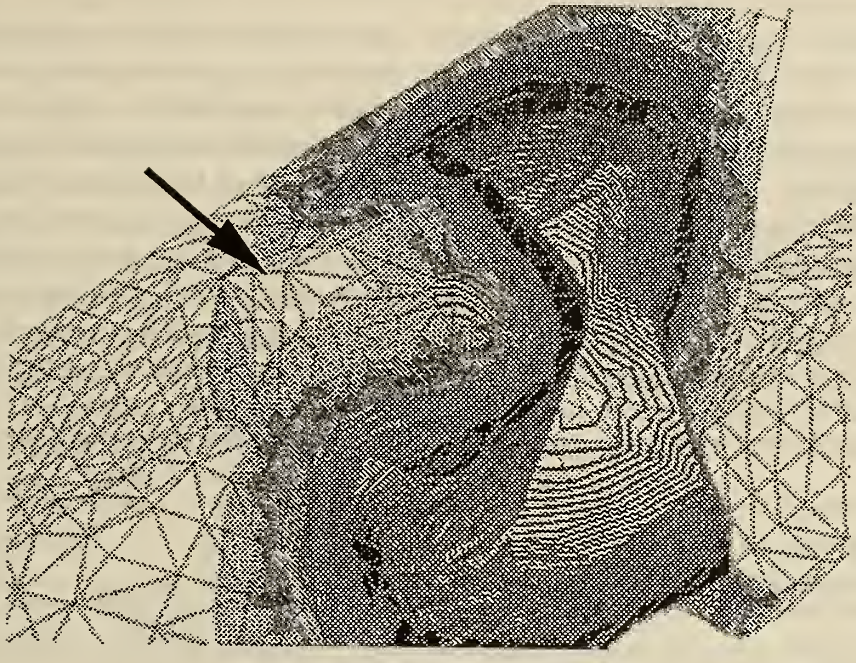

Figure 1: Predicted injection pattern in the front end structure for the region around the shock tower. The arrow indicates a region that is closed off by the flow and hence a region of air entrapment unless a vent is positioned at this point in the mold.

Micro-flow Modeling for Permeability Prediction: The final area of numerical modeling work involves flow simulation at the level of the preform tow structure in order to predict permeability. In this work, flow inside the tows is modeled using the Brinkman-volume averaged momentum equation (BVAME), which is given by

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

where $\boldsymbol{v}$ is average fluid velocity, $\boldsymbol{K}$ is the permeability tensor, $\boldsymbol{\mu}$ is the viscosity, and $\boldsymbol{P}$ is the pressure. Flow outside the tows is modeled using the Stokes Equation. This approach was used to simulate unidirectional flow in a variety of model arrays for fiber porous media. The effect of tow shape, packing, and porosity on the overall permeability was predicted numerically. The predictions for axial flow in a periodic array of porous elliptical rods were considered first, and the results compared with permeability measurements on unidirectional material which had tow cross sections that were very nearly elliptical. The first tests used a

Knytex D155 knit material manufactured by Hexcel Corp. and provided by the Ford Motor Co. This was a good material to start with since the fibrils in the tows are glued together with a binder material, thus making them act effectively as solids; this eliminated the effect of tow porosity. Careful measurements were done under a microscope to determine the shape of the tows, and the inter-tow spacing. Permeability measurements were then conducted for fiber volume fractions of 52%, 59.65%, and 69.9%. When the results were compared with the numerical calculations, the experimental results were almost an order of magnitude too low. One possible source of this discrepancy was the few warp threads that hold the preform together. To test this, the experiments for the case of 52% fiber fraction were repeated, but this time with all the transverse warp threads removed except those at the very ends so that the material could still be handled without losing its integrity. This experiment yielded a permeability value within 5% of that predicted numerically. A summary of both the experimental and numerical data is shown in the table below.

Table I: Comparison of Permeability Values

Number of Preform Layers	Determination Method	Crossing Threads	Permeability Value (cm^2)
25	Experimental	yes	5.42×10^{-6}
25	Experimental	no	3.42×10^{-5}
25	Numerical	no	3.56×10^{-5}
31	Experimental	yes	2.98×10^{-6}
35	Experimental	yes	4.11×10^{-7}

Although the crossing threads in the original material account for only 2% by weight, they exert an enormous effect on the permeability because of the position they occupy in the flow channel between the tows. Consequently, such fibers must be considered in any simulation that attempts to predict permeability as a function of structure.

The next step in the comparison of modeling and experiment will be to repeat the tests, but with a material in which the fibrils that make up the tows are not glued together with a binder material. This will make it possible to examine the role of tow permeability in the overall permeability of the media.

Experimental Studies in Liquid Molding

The major experimental studies fall into two categories: Permeability Research and Permeability Characterization. Work in the first area seeks to develop appropriate test methods for permeability and conducts visualization experiments to understand the flow behavior and test the simulation models. Permeability Characterization provides property data and reference materials for both in-house and outside efforts in LM.

Permeability Research: A major effort, which began in 1990, is comparing the two most widely used methods for measuring the in-plane permeability of composite reinforcements: the radial flow technique and one-dimensional flow measurements. This work is a collaboration with the Corporate Research & Development Laboratory of General Electric, and a CRDA was recently signed to extend the work to a broader range of materials. Four woven glass fabrics have now been examined, and for three of them the agreement between the two testing methods is excellent (see table II). The flow orientation is the direction of maximum permeability in the fabric plane relative to the direction of the fill fibers while K_{xx}/K_{yy} is the ratio of the minimum permeability to the maximum permeability in the plane. With the fourth fabric tested, significant discrepancies were found. These discrepancies are thought to be due to a unique micro-structure of that material which resulted in the permeability measurements having great sensitivity to the way in which the material is packed into the mold.

Table II: Permeability Data for Fabrics

Fabric	Radial Flow K_{xx}/K_{yy}	Radial Flow Orientation	1-D Flow K_{xx}/K_{yy}	1-D Flow Orientation
8-harness[1]	0.85	107	0.72	103
8-harness[2]	0.83	79	0.83	75
5-harness[2]	0.61	90	0.85	121
Crowfoot[2]	0.60	90	0.61	94

[1] J. P. Stevens, [2] Carolina Narrow Fabric

The radial flow experiments were imaged for digital analysis, and the results showed an important result. The flow length, or time scale, required to achieve a steady state in the shape of the flow front was very long. In fact, it was much longer than current theories predict. Concurrent with the transient in the flow front shape, the expansion of the flow front through the porous material appeared to slow more quickly than predicted by Darcy's law. Previous work modeling one-dimensional flow geometries indicated that the heterogeneous nature of the reinforcement material could be responsible for both observations. Additional work is needed, however, to substantiate the link between the long term transients, the excess front slowdown, and the microstructure of the porous media. In the long time limit, the flow orientation and the permeability ratio measured in the radial flow experiments converged to those obtained from the one-dimensional flow tests. The quantitative determination of the individual components of the permeability tensor from the radial flow experiments will be performed as part of the CRDA with GE, and this will permit direct comparisons of the K's.

A new experimental program started in collaboration with the University of Delaware is designed to test and improve upon assumptions commonly used in modeling the liquid molding process. It is desirable to use a 2D model for flow if possible because 3D models involve considerable additional computational time. Even in shell like structures, however, it is common to use a fiber preform constructed by combining two or more layers of different materials. The question then is whether an average permeability for this layered structure can be predicted if the individual materials have been characterized. The study began with a simple two layer system, and the compressibility of each material was measured so that its fiber volume fraction in the combined preform could be calculated. The materials were found to exhibit a nonlinear but elastic behavior so the fiber volume fraction of each individual material in the preform can be calculated.

In the two cases tested for permeability to date, the saturated flow behavior conformed to what was predicted using a simple averaging scheme derived from Darcy's law for in-plane flow. The unsaturated flow behavior, however, deviated considerably from what was predicted, presumably due to flow in the through-thickness direction. A 3D flow model is expected to properly describe the observed behavior, and this will be tested in the coming year. It is hoped that this work can identify those cases where an averaging scheme and a 2D model can provide adequate results as well as those situations where a full 3D analysis is required. This would make it possible to use only the resources necessary to obtain a good simulation of the process.

Permeability Characterization: During the course of the past year, a number of materials have been characterized for permeability. In addition to the work with GE described above, materials for the Ford/GE collaboration funded under the Advanced Technology Program are being measured by NIST. Finally, materials of interest to the ACC have been characterized for permeability. These materials include a random continuous mat, a two-dimensionally braided material, and a +-45° stitched fabric. They are to be used in liquid modeling applications, including the front-end structure and the cross-member. The in-plane permeability tensors of the materials were measured, and there are plans to determine the through-thickness permeability once testing is completed on a newly built flow system. An important use for this permeability characterization data is input for the NIST flow model so the process and mold design can be optimized in the joint NIST/ACC program. The generation of data for all of these materials provides an opportunity to create a permeability data base. It is hoped that work on such a project can begin next year.

An outgrowth of the permeability characterization effort is a new program to develop standard reference materials (SRM) for permeability. Initially, it is envisioned that this would involve two samples. The random continuous mat fabric, of interest to the ACC, was chosen as the first because of its simplicity. The in-plane permeability of that material is very nearly isotropic over a broad range of fiber volume fractions. The second sample has been designed and will be characterized in the coming year. It is expected to be anisotropic in the plane of the material. Once characterized, an SRM which contains a sample of each material will be released for sale. In the future, additional materials may be added as the need arises.

PROCESS MONITORING AND CONTROL

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In previous years, the Process Monitoring and Control Thrust Area has been quite active. During that period, an extensive capability was developed with 10 different process monitoring techniques and the corresponding expertise to use them effectively. These techniques include both laboratory methods and the most common on-line techniques: ultrasonics, dielectrics, optical, and spectroscopic measurements. During the past year, activity in this area have been low but included the planning and initiation of a new program which will significantly increase research effort in the future. This program will apply process monitoring to the liquid molding process and, thereby, take advantage of the capabilities and expertise developed previously while also complimenting the research in the Liquid Molding Thrust. A second activity in process monitoring involved extending previous studies on the effect of processing cycle on properties to a resin system of interest to the automotive industry.

Process Monitoring for Liquid Molding

The program to implement process monitoring and control in liquid molding will begin by considering the application of fluorescence spectroscopy implemented through a fiber optic probe. This method was chosen for its high potential to sense both the position of the fluid flow front during injection into the mold and the resin cure state after the mold is filled. In addition, this method has a unique capability to make measurements inside the preform with a minimal perturbation to the system. The project is being conducted in collaboration with the Johns Hopkins University. A special heated mold has been designed and built to permit inclusion of a variety of fiber configurations in the mold. The optical bench is currently being designed to interface with the liquid molding system.

To make optimal use of the fluorescence signal obtained from the fiber optic probe as well as other processing information, data acquisition and control software is been written and implemented on a laboratory computer. The software is intended to automate the entire liquid molding process as well as the permeability measurements associated with preform characterization. The software is menu driven and allows the user to configure up to eight feedback controllers as desired. Control is implemented in a hierarchical manner, with standard PID single input/single output feedback loops comprising the base level controllers. Cascade flow and temperature control is being implemented by using the computer based control programs to manipulate the setpoints on the external controllers. In addition, a special, state-of-the-art, high-capacity LM pump with internal microprocessor control of flow, shot size, and ratio of the two fluid components has been installed and can be interfaced to the computer controllers via an RS-232 port. Higher level control algorithms based upon real-time models are currently under design, and will provide the basis for a control system. The multi-input/multi-output nature of the high-level controller provides maximum flexibility and the tools to optimize the LM process for each part produced.

Process Cycle Dependency of Glass Transition Temperature for an Automotive Resin System

Previous studies have shown that the ultimate glass transition temperature in a homopolymer of diglycidyl ether of bisphenol A (DGEBA) can vary by as much as 50°C depending on the processing conditions. During the past year, an important resin system for the automotive industry, vinyl ester resin, was studied for the influence of processing conditions as well as compositional changes. The results show that the properties of this resin system are much less dependent on formulation and processing history than the epoxy resin system previously tested. This was attributed to the high activation energy and the self-acceleration of the reaction. For a fixed vinyl ester/styrene composition, changing processing conditions such as heating rate and ultimate cure temperature over a wide range of values altered the ultimate glass transition temperature by less than 15°C. Compositional changes from 15 to 50% styrene content change the glass transition temperature by only 20°C. On the other hand, the characteristics of the glass transition, such as the magnitude of the C_p discontinuity, were changed drastically as a function of composition. This has important consequences for process monitoring because it may affect things such as the sensitivity of different measuring methods.

INTERFACE SCIENCE

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The interface is a major area of study in the composites program. The work focuses on microstructural characterization of the interface region and measurement of interface strength. In the first area, the studies consider not only the fiber-matrix interface in composites but also the implications for adhesives, coatings, and layered systems of importance for electronic packaging. Efforts in the second area have concentrated on the fiber-matrix interface during the past year.

Microstructure Characterization

This work is exploring the use of the technique developed previously to characterize the interface region between polymers and solid substrates using neutron reflectivity (NR). Three different aspects of polymer/solid interfaces have been studied. First, the polymer segmental density near the substrate was investigated as a function of temperature. This work represents an initial step in addressing the question of polymer packing near a flat surface, and how it develops during processing. The second area of study addresses how the diffusion of polymers near an interface is affected by the presence of that interface. The third area involves the measurement of moisture near an interface in samples exposed to water. This is a critical issue for durability, but no previous technique had the ability to characterize this feature.

Polymer Segment Density near Interface with Solid Substrate: The way polymer molecules arrange themselves and pack together when in contact with a solid is an important subject because it plays a major role in interface adhesion. Adhesion is critical for performances of adhesive joints and polymeric composites. Considerable progress in predicting the polymer density near a surface using computer modelling has been made in recent years; however, experimental data in this area is rather scarce.

To examine this question, NR has been applied to characterize the interface region between poly(methyl methacrylate), PMMA, and a silicon wafer. The PMMA has a glass transition temperature of 115°C as determined by differential scanning calorimetry (DSC). The (100) surface of silicon single-crystal wafers was used as the substrate. The neutron reflectivity result from the silicon/air surface indicated a roughness of 4Å RMS (root mean square). A PMMA film of 0.5mm thickness was prepared in vacuum at 150°C in direct contact with the polished surface of a wafer. This polymer/silicon sample was then placed between two aluminum plates in contact with a heating block.

The reflectivity results were obtained at six different temperatures (80 to 144°C) and were fitted with theoretical curves based on an error function profile. Two variables were allowed: the thickness of the interface region, and Q_c^2, the square of the critical Q in $Å^{-1}$, which is linearly proportional to the polymer density remote from the interface. The interface region is the space over which the polymer density transitions from zero at the substrate boundary to a plateau value away from the interface. Q is the momentum transfer between the reflected and the incident beams.

The most striking feature revealed by these results was the temperature dependence of thickness of the interface region. It is very narrow (1-3Å) below T_g, but broadens significantly (20Å) at higher temperatures. This thermal transition is completely reversible. The polymer densities were calculated based on Q_c^2 and compared with values determined from the literature for bulk samples. At the lower temperatures, the bulk values were significantly lower than the densities calculated from the NR results. The reverse was true, however, at 144°C. Additional studies are needed to explain these density results.

The experiments described above were repeated with spin coated PMMA films that were 2700Å thick on the (111) surface of silicon single-crystal wafers. The results, although similar to those discussed above for the thick films, were different quantitatively. The transition from a steep to a gradual density profile took place at somewhat higher temperature, and the width of the interface region at high temperatures was narrower, in the range of 10Å instead of 20Å. These observations point to the complexities of interface problems; the structure is rather sensitive to the sample preparation technique as well as other details such as the crystalline orientation of the substrate.

<u>Polymer Diffusion near a Polymer/Solid Interface</u>: The presence of a flat surface which has short range interaction with polymers may affect not only the local density of polymer segments but also the diffusion dynamics of the polymer. To study this, the self diffusion of chains adsorbed onto a flat surface was investigated. In the system studied here, a single layer of deuterated poly(methyl methacrylate) (dPMMA) was adsorbed onto a silicon disk, and then a second layer of hydrogenated PMMA (hPMMA) was applied on top. This bilayer was then annealed for 15 minutes at various temperatures above T_g (106°C), and the interchain diffusion between the deuterated the protonated species was followed by NR.

The results show a significant decrease in reflected intensity with annealing time, and this reflects the interchain diffusion of deuterated and hydrogenated chains near the silicon surface. Fitting the results provides density profiles which indicate that the original layer of deuterated material is 42Å thick while the total thickness of the bilayer is 840Å. Annealing does not change the total thickness but broadens and dilutes the deuterated layer. Despite the interdiffusion, however, the concentration of dPMMA near the interface remains surprisingly high for all three annealing temperatures. Compositions are 84, 76 and 68% deuterated polymer for annealing temperatures of 114, 146, and 161°C respectively. This suggests a remarkable difference in the time scales for the diffusion between adsorbed polymer chains and those existing in a bulk melt. Based on diffusivity values for PMMA at 161°C, the centers of mass of the deuterated chains would have moved nearly 900Å in a bulk sample. Yet, there was still 68% of the deuterated species within 150Å of the surface. This has important consequences for the behavior of thin surface layers, sizings, surface finishes, etc. during processing. More research is required, however, to understand the mechanics of this remarkably slow exchange at the polymer melt/solid interface.

<u>Characterization of Moisture Profiles near a Polymer/Solid Interface</u>: The existence of an unexpectedly high concentration of moisture in a polymer adjacent to a solid interface has long been postulated to explain various moisture related problems encountered in composites, protective coatings, and electronic packagings. Unfortunately, despite the importance of this effect, there is little direct evidence for it. The work here not only provides the first direct evidence but also permits quantification of the effect.

The initial studies utilized a polyimide (PI) supplied by DuPont as part of a cooperative program begun under a recent CRDA. Two micrometer thick polyimide were prepared on silicon single-crystal wafers by spin-coating. Since the silicon surface is covered with an oxide layer, it should have a high affinity for moisture. NR measurements were conducted on dry samples and samples placed in an atmosphere saturated with deuterated water vapor for a week at 23°C. A significant difference in the NR results was observed between the dry and the wet samples. This difference can be accounted for by the presence of a moisture rich layer about 25Å thick near the PI/silicon interface in the wet sample. The water content within this thin layer reached 16% by volume as compared to the bulk saturation level in PI of 2.4% (see Figure 2).

Future work will focus on two questions. First, what is the explanation for this high local concentration of moisture, and what factors control it. Of particular interest are the effects of surface treatments and coupling agents on the concentration. The second question is how this moisture affects performance, particularly durability. This couples with the work described below and efforts in the Mechanical Performance Group.

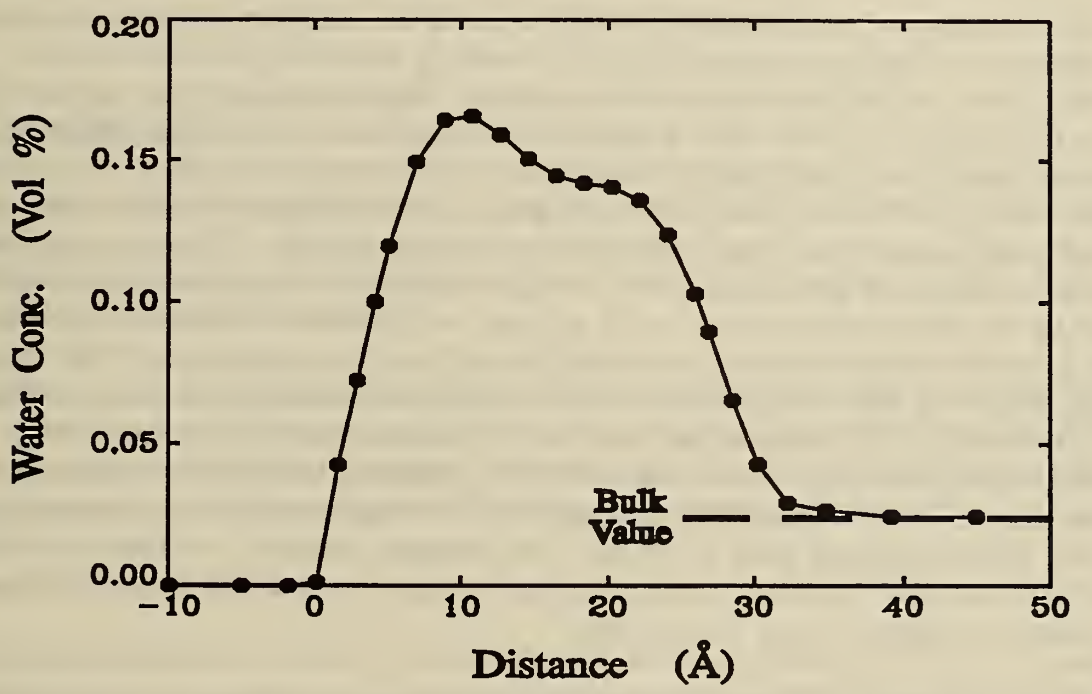

Figure 2: The concentration of water is shown as a function of distance from the silicon interface. The initial rise corresponds approximately to the surface roughness of the silicon. Above 35Å the concentration approaches that for saturated polyimide.

Measurement of Interface Strength

The second aspect of the interface program involves measurement of the fiber-matrix interface strength. This builds on previous work in which apparatuses were assembled and measurements made with two of the most common test methods: the single fiber fragmentation measurement and the micro-drop pull-off test. There are two objectives in this research: (1) to evaluate and improve the test methods, and (2) to use them to assess how composition and processing affect interface strength.

Evaluation and Improvement of Test Methods: The two measurement techniques are being evaluated through analysis of the assumptions made in the tests and improved by automation of the equipment. The analysis involves finite element studies of the tests and comparing the results with experimental observations. The effects of many features including plasticity, failure mode, residual stresses, geometric details, and the presence of an "interphase" region have been studied. The work is in cooperation with the Mechanical Performance Group.

Improved automation of the equipment involved updating the computer programs and adding video capabilities. The importance of this can be seen by examining how the tests are conducted. In the single fiber fragmentation technique, dog-bone-shaped resin sample is cast around a single fiber. A tensile load is applied to the dog bone, and an interfacial shear mechanism transfers the forces through the interface to the encapsulated fiber. The load is increased causing the fiber to break repeatedly until a limiting fragment length is reached. The lengths are measured and used to calculate an interface strength. The micro-drop pull-off technique consists of embedding a fiber through a droplet of resin, holding the droplet, and loading the free end of the fiber until it is pulled out of the resin droplet. The average strength of the interface is obtained by dividing the pull-out force by the area of the fiber-matrix interface. In both cases, a large number of data points is needed to obtain a reliable result. Previously, a filar eyepiece had been used to measure the fiber diameters and embedded lengths, but this is tedious and slow. The procedure has now been replaced with a video micrometer system connected to a computer. This improves accuracy, reduces eye strain, and greatly increases speed of testing. The computer programs for data acquisition and analysis have been modified to take advantage of this new capability and to include other improvements developed during the past year.

Effects of Composition and Processing on Interface Strength: Experiments using the interface strength measurement equipment have now begun in three areas. The first is a collaboration with Ford Motor Co. to examine the effects of through-thickness stitching in a fabric-reinforced composite. Ford is investigating the use of stitching to improve composite properties in crash energy management tests. They made a number of hollow columns with square cross-sections using a 0/90/random mat construction. For some samples, the three reinforcement layers were stitched together with poly(ethylene terephthalate), PET, thread. Unfortunately, the stitched samples showed extensive cracking, and one suggestion was that poor adhesion between the matrix and thread was responsible. In the joint program, the micro-drop pull-off test at NIST was used to assess the interface strength of test materials provided by Ford. Glass and PET fibers subjected to a variety of fiber surface treatments were used. The results show that the interface strength varied considerably for the different fibers and surface treatments. Column samples are now being prepared to see if a correlation between interface strength and cracking is observed.

The other two projects use the interface test facilities in cooperative efforts with the Mechanical Performance Group. One project measures the effect of the environment, specifically moisture, on the durability of composite. Material systems of interest to the automotive industry are included, and the work is being coordinated with studies by researchers associated with the Automotive Composites Consortium. The program involves exposing test specimens to moisture for various lengths of time and measuring the degradation of interface strength. The other project is examining the effect of transcrystallinity on the interface strength of carbon fiber/polycarbonate samples. By changing the thermal history of the sample, the amount of transcrystallinity can be changed without altering the resin or the fiber. As a result, it should be possible to assess the effects of transcrystallinity on interface strength. This would be very useful for optimizing properties of composites capable of forming such morphologies.

OTHER ACTIVITIES

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In addition to the activities described above, there are two programs that draw upon expertise in the Group but fall outside the major thrust areas. The first is an effort with the Office of Consular Affairs at the State Department to develop tests for passport laminates. The second is a joint program with Dow Chemical Company on toughening of thermosets.

Testing of Passport Laminates

The Office of Consular Affairs of the State Department is responsible for the U.S. passports, including the plastic laminate used to protect the photograph and the descriptive information inside the cover. This laminate must resist dirt, spills, abrasion, etc. encountered in normal use as well as any illegal attempts to tamper with the information on the passport. In order for the State Department to obtain the best balance of performance and cost in a laminate, it is essential to have effective test methods. This is challenging because there are many different approaches to laminate construction. NIST is working with the State Department and the companies involved in the security laminate business to identify tests that are both effective and fair. A second goal in this program is to provide feedback to the companies on the performance of their products so they can develop better security laminates for the future.

As part of this program, a Workshop has been planned for early FY93. Interested companies and other government agencies with similar applications will meet with personnel from NIST and the State Department to discuss existing laminate test methods and possible ways to improve these tests in the future.

Thermoset Toughening

A second program that draws on expertise and experience in the Group addresses toughening of thermoset resins. These materials generally consist of a cross-linked matrix, often epoxy, containing small elastomeric or thermoplastic particles dispersed in the matrix. The work here addressed both the physical aging characteristics and structure-property relationships in toughened resins. In the area of aging, the behavior of a toughened system was shown to be identical to that obtained previously by McKenna and Lee for a brittle epoxy. This is consistent with other work that shows the behavior of brittle and toughened systems to be quite similar in the range of small deformations even though it differs substantially at the large deformations associated with fracture.

The most important feature of toughened systems is their high fracture energy. Although their toughness depends on morphological characteristics like the particle size and size distribution, the structure-property relations involved are not well understood. The challenge is to systematically change the morphology in a controlled manner. To accomplish this, a cooperative program was initiated with Dow Chemical Company and takes advantage of some innovative new materials developed there. These materials contain preformed rubber particles dispersed in a liquid epoxy. By diluting these samples with various amounts of additional epoxy before cure, it should be possible to change the particle concentration without altering the particles size and size distribution. Moreover, since the starting materials can be made with different size particles, comparisons should be possible at the same concentration of rubber but different particles sizes. Experiments conducted during the past year have shown that samples made in this way have a range of fracture behaviors. Studies are now underway to characterize the morphologies so structure-property relationships can be developed.

POLYMER BLENDS AND SOLUTIONS

The goal of the Polymer Blends and Solutions Group is to develop fundamental understanding, measurement techniques and characterization methods for the phase behavior of polymer blends and polymer solutions. Polymer molecular weight SRM's are also produced.

The importance of polymer blends is evident from their ubiquitous presence in consumer products in recent years. These products include automobile and airplane parts, business machines, appliances, furniture, packaging materials, housewares, toys and clothing materials. Blending and alloying technology has significantly expanded the number of grades and types of plastics available, providing a wide variety of property profiles for applications needs. The worldwide consumption of polymer blends and alloys is expected to increase from 0.72 Tg (1.6 billion pounds) in 1989 to 1.08 Tg (2.4 billion pounds) by 1994, at an annual growth rate of over 8%, not including elastomer blends.

Similar to metal alloys, polymer blends are mixtures of two or more polymers which form plastic alloys with new properties. Many important materials properties, such as mechanical properties, flame retardancy, processibility, and barrier properties can be improved through blending. High value engineering plastics with special properties can often be obtained by blending low cost polymers. Several techniques are commonly used in the blending of polymers: (1) single phase materials formed by using miscible polymer pairs; (2) phase separated morphology and structure obtained through chemically bonded block copolymers; (3) phase separated morphology obtained through compatibilization by crosslinking and grafting of the polymer pairs; (4) morphology controlled through flow field and the use of interfacial modifiers such as block copolymers; (5) combinations of the above mentioned techniques.

Although miscibility in polymer blends is neither an absolute requirement nor always desirable for improving material properties, the phase separated alloy often gives inferior properties if structure, morphology and interfacial adhesion are not controlled. Often an order of magnitude improvement of properties can be achieved through the synergistic effect of a well-controlled phase separated alloying process. In general, the science and technology of polymer blends and alloys involves the following areas:

1. Single chain characterization.
2. Equilibrium phase diagrams, binary interaction potentials and other thermodynamic properties.
3. Kinetics of phase separation and coarsening.
4. Effect of chemical crosslinking on the statics and dynamics of phase separation/morphology stabilization.
5 Effect of mechanical energy and flow on the statics and dynamics.
6. Interfacial modification and its effect on the phase equilibria, kinetics, and materials properties.

Experimental and theoretical studies of polymer/solvent and polymer/polymer systems are actively pursued. Emphasis is on characterization of the static and dynamic properties of the single polymer chain, the phase behavior of polymer blends with and without crosslinking, the mixing and demixing kinetics of polymer blends especially in the non-linear (late stage) region, the shear rate and strain dependence of the mixing/demixing process, and the coarsening of the phase separated structure after shear mixing.

Polymer SRM's certified for molecular weight are needed by the polymer industry to calibrate gel permeation chromatographs which are used routinely to measure polymer molecular weights and molecular weight distributions. The latter are the most important molecular characteristics in determining processibility and end-use properties of polymers.

Measurement techniques employed in the Group include classical characterization methods used to obtain absolute molecular weights of polymers for SRM production, as well as small angle neutron scattering (SANS) and time resolved temperature-jump light scattering (TJLS) to obtain information on phase diagrams and demixing kinetics of blends. In addition to the last two mentioned techniques, forced Rayleigh scattering (FRS), and electron and optical microscopy are used in polymer blend studies. A flow device has been constructed which allows SANS studies of polymer blends under various shear conditions in situ. A similar device for light scattering has also been constructed which extends the study to structures of larger size and also allows the needed time resolved measurement capability for mixing/demixing studies at the start and the cessation of flow perturbation.

FY 92 Significant Accomplishments

- Significant advancement in the understanding of the influence of shear flow on the static and dynamics of phase behavior has been achieved. Experimental studies of the molecular weight effect on the Ginzburg criterion of cross-over from mean-field to Ising critical behavior as well as the shear rate dependence of the system behavior cross-over from weak to strong shear dependence were carried out. Results compared favorably with theoretical predictions.

- Theoretical calculations for the kinetics of demixing/mixing in the unstable two phase region has been carried out. These results which include polymer specific effects are applicable for the intermediate stages of spinodal decomposition and the dissolution of inhomogeneities formed during spinodal decomposition include polymer specific effects for polymer blends applications. Experimental results have been analyzed successfully using this theory.

- Time-resolved small angle neutron scattering techniques have been developed to measure the phase diagram of blend systems which are normally inaccessible experimentally due to the interference of glass transition temperatures.

- A NIST/industry workshop was organized and held to review the current scientific understanding and technology of polymer blends processing. A consortium involving industry and NIST is being formed to develop the scientific basis of processing blends/alloys, especially interfacial characterization and control.

- SRM 1475 and SRM 1484, polyethylene standards, were recertified this year. SRM 1484 is a narrow molecular weight polyethylene used to calibrate high temperature Size Exclusion Chromatography (SEC) equipment. SRM 1475 is a broader molecular weight polyethylene used to calibrate high temperature SEC and melt flow equipment following ASTM D1238.

EXPERIMENTAL

C. C. Han, A. I. Nakatani, D.W. Hair, E. K. Hobbie, B. J. Bauer, C. M. Guttman, K. L. Jewett, D. Johnsonbaugh, J. Douglas, B. Hamouda[1], A.Z. Akcasu[2], H. Jinnai[3], H. Hasegawa[3], T. Hashimoto[3], M. Motowoka[3], Y. Qui[4], Y. Feng[4], R. M. Briber[5], T. Tanaka[6], M. Shibayama[7], C. Cohen[8], N.P. Balsara[9], L. J. Fetters[9], N. Hadjichristidis[9], D. J. Lohse[9], W. W. Graessley[10] R. Krishnamoorti[10], Y. B. Ban[11], H. Yajima[12], H. Yoon[13]

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1. Single Chain Characterization

Conformational Changes in Polystyrene/Poly(vinylmethylether) Blends at Low Polystyrene Composition: Small angle neutron scattering measurements were made of binary polymer blends of deuterated polystyrene and poly(vinylmethyl- ether) at low polystyrene compositions. The Zimm plot was used to extrapolate to zero polystyrene content and radii of gyration and virial coefficients were calculated for the blends between 80°C and 160°C. The polystyrene radius of gyration decreased with increased temperature by about 10%. The second virial coefficient also changed steadily with temperature, being positive at low temperatures and finally becoming slightly negative at 160°C.

2. Equilibrium Phase Behavior

Deviation from Mean-field Behavior in a Low Molecular Weight Critical Polymer Blends: It is well established that simple binary fluids show static critical behavior characteristic of the three dimensional Ising ($d=3$, $n=1$) universality class. Although phase separation in binary polymer mixtures has the same inherent Ising symmetry, de Gennes used the Ginzburg criterion to argue that for sufficiently high degrees of polymerization, the critical regime is confined to a vanishingly small window and T_c and the mean-field (Flory-Huggins) model is adequate to describe the transition. Small angle neutron scattering (SANS) studies of high molecular weight polymer blends have confirmed this prediction. In light of this, it is reasonable to expect that a crossover from mean-field to Ising behavior might be observable in polymer blends with sufficiently low molecular weight. A number of groups have recently reported observing such a crossover using small angle scattering. However, there is some disagreement between their results.

SANS measurements of the susceptibility and correlation length were carried out as a function of temperature near the phase boundary of a low molecular weight critical mixture of polystyrene and polybutadiene. The Ginzburg criterion was re-examined for polymer blends. With a proper expression of the Ginzburg criterion and the use of experimentally observed values for the bare-correlation length, ξ_o, and the binary interaction parameter, χ, the cross-over from mean-field to Ising critical behavior of our results, as well as those in the literature, can be described consistently. The modified Ginzburg expression derived for polymer mixtures is readily applicable to blends of any molecular weight, but its validity in higher molecular weight blends remains to be tested.

Critical Dynamics of an Asymmetric Binary Polymer Mixture: The critical dynamics of small molecule binary mixtures has been studied in great detail, and the experimental results have been in remarkable agreement with the modern mode-coupling and renormalization-group theories of dynamic critical phenomena. In the present work the critical dynamics near the consolute point were studied for a relatively low molecular weight asymmetric critical binary mixture of polystyrene and polybutadiene with dynamic light scattering technique. Bimodal relaxation was observed from the intensity-correlation function of this blend. This bimodality was interpreted as the eigenvalues due to the coupling of the order parameter fluctuation and the thermal fluctuation. The thermal fluctuation is an additional long wavelength diffusive mode resulting from a linear combination of mass densities and the energy density. From the temperature dependence of the "fast" and "slow" modes obtained from the dynamic light scattering measurements, the corresponding diffusion coefficient and dynamic correlation length due to the order parameter fluctuation have been obtained. The critical slowing down of this order parameter fluctuation in the vicinity of T_c is consistent with a crossover between asymptotic mode-coupling and conventional behaviors. The nondissipative coupling between the order parameter and the transverse part of the momentum density has been observed and examined.

Inversion of Phase Diagram from UCST to LCST in Deuterated Polybutadiene and Protonated Polybutadiene Blends: The miscibility of amorphous mixture of normal (protonated) and perdeuterated polybutadiene (hereafter being refereed as HPB and DPB, respectively) has been extensively studied and was characterized by an upper critical solution temperature (UCST). Some literature reports have interpreted the partial miscibility of isotopic polymer blend in terms of the reduction in carbon-hydrogen bond length resulting from substituting deuterium for hydrogen (isotope effect). For the DPB/HPB blend, however, since polybutadiene consists of a 1,2-unit(vinyl) and a 1,4-unit, the microstructure in the blend should play an important part in the miscibility of the blend. An earlier study in our group separated the isotope effect from the microstructure effect through a systematic small angle neutron scattering (SANS) study on the DPB/HPB blends with various vinyl contents on the basis of random copolymer mixtures theory. By regarding the DPB/HPB blend as a blend of A-B copolymer (A and B are the 1,2-unit and the 1,4-unit for DPB, respectively) and C-D copolymer (C and D are the 1,2-unit and the 1,4-unit for HPB, respectively), it was shown that the main contribution for miscibility in the blend is due to the intramolecular pairs of A/B and C/D rather than the isotope pairs of A/C and B/D. These intramolecular interactions account for the observation of negative χ's (χ is the binary interaction parameter) for one of the DPB/HPB blend pairs, while the isotope effect can only explain positive χ's. Therefore, it is extremely important to clarify the effect of the microstructure on the miscibility of the DPB/HPB blends.

In this study, SANS measurements for a series of DPB/HPB blends were carried out. By holding the vinyl content of the DPB component constant, experimental evidence for the inversion of phase diagram from a UCST to a lower critical solution temperature, LCST, by increasing the vinyl content of HPB was obtained. This inversion is caused by the difference in temperature coefficients for individual pair interaction parameters. Although all individual pair interaction parameters have positive temperature coefficients (in terms of 1/T) which implies an UCST system, the difference between intermolecular and intramolecular interactions could change the sign of the over all χ which results in an inversion from UCST to LCST.

Thermodynamic Interactions in Model Polyolefin Blends Obtained by Small Angle Neutron Scattering: The dependence of Flory-Huggins interaction parameter χ on temperature, composition and chain length was investigated for binary blends of amorphous model polyolefins which are structurally analogous to copolymers of ethylene and butene-1. The components were prepared by saturating the double bonds of nearly monodisperse polybutadienes (78%, 88% and 97% vinyl content) with H_2 and D_2, the latter to provide contrast for small angle neutron scattering (SANS) experiments. Values of χ were extracted from SANS data in the single-phase region for two series of blends, H97/D88 and H88/D78, using the random phase approximation and the Flory-Huggins expression for free energy of mixing. These values were found to be insensitive to chain length and to the component volume fractions for $\phi=0.25$, 0.50, and 0.75. The temperature dependence of the χ's (27°-170°C) obeys the form $\chi(T)=A/T+B$ with coefficients that connote upper critical solution behavior, yielding a $T_c \sim 40°C$ for one blend series (H97A/D88) and a $T_c \sim 60°$ for another (H88/D78). These estimates are consistent with SANS pattern changes and supplemental light scattering results that indicate two-phase morphologies at lower temperatures. The $\chi(T)$ coefficients for the two series are also consistent with the prediction of random copolymer theory.

Liquid Crystalline Polymer Phase Behavior in Solutions: Optical microscopy has been used to determine the approximate temperature-concentration phase diagram of a solution of poly (γ-benzyl L-glutamate) (PBLG) in benzyl alcohol (BA). Once the approximate phase diagram was determined, small angle neutron scattering (SANS) and small angle light scattering (SALS) were used to pinpoint the transition temperature of the polymer in solution. The phase transitions of an 8 wt %, 10 wt % and 14 wt % solution of PBLG in BA have been identified. Next, the kinetics of the isotropic to biphasic (8 and 10 wt.% solution), isotropic to liquid crystalline (tentatively 12 wt.%), and liquid crystalline to biphasic (14 wt. % solution) transitions will be studied with temperature jump light scattering. The effect of shear on the temperature and the kinetics of these transitions will also be studied.

3. Kinetics of Phase Separation

Theoretical and Experimental Study of Dissolution of Inhomogeneities: The kinetics of phase separation in binary mixtures has received much attention in the fields of metallurgy, ceramics, and polymers, and has been an important subject of many theoretical and experimental studies in the past three decades. The motivation for these studies was the possibility of controlling the morphology, especially the possibility of forming co-continuous materials, through phase separation in the unstable two-phase region. The analysis of the kinetics of phase separation has been centered around the early stage of spinodal decomposition process (SD), the intermediate mode-coupling stage, and the late stage scaling analysis.

Although the time resolved light scattering studies of polymer systems have enjoyed success in comparing and verifying the linear theory of Cahn-Hilliard-Cook in the early stage of SD and the scaling analysis in late stage of SD, a quantitative comparison between experiments and theory is still lacking in the intermediate region. The nonlinear theory of Langer, Bar-on, and Miller is probably the most comprehensive mode-coupling calculation available describing the intermediate time region of the SD process. However, this theory is intended for small molecular systems, and does not include the polymeric nature of long chain molecules. Nonlinear calculations have been carried out for the intermediate stages of spinodal decomposition which modifies the theory of Langer, Bar-on and Miller to include polymer effects through mode coupling and fluctuation.

Time resolved light scattering results obtained from dissolution (mixing) of inhomogeneities formed during spinodal decomposition of polystyrene/poly(vinylmethylether) blend have been analyzed according to this theoretical model successfully.

Phase Separation in Deuterated Polycarbonate/poly(methyl-methacrylate) Blend Near Glass Transition Temperature: A small angle neutron scattering study of a deuterated bisphenol-A polycarbonate/poly(methylmethacrylate) (dpc/PMMA) blend near and above its T_g has been carried out.

It is clear from time resolved SANS studies that 50/50 blend of dPC/PMMA is immiscible above its glass transition temperature. A trapped miscible state can be obtained through fast solution casting of thin film ($\sim 50 \mu m$) in THF. A slow spinodal kinetics has been studied by SANS techniques by heating the solvent casted specimen to a temperature above its T_g. At this temperature the mobility, M, of the interdiffusion is still slow enough to keep the interdiffusion coefficient, D_{int} ($D_{int} = M\, \partial^2 \Delta f / \partial \phi_o^2$), small enough for the time resolved SANS study.

The SANS experiment covers a q-range which encompasses the single chain dimension, i.e. from $qR_g > 1$ to $qR_g < 1$. Thus the time dependent structure factor thus obtained provides unequivocal quantitative measure of the virtual structure factor, $S(q, \infty)$ the relationship of q_m and q_c through rate of growth, Cahn-plot analysis and singularity in $S(q, \infty)$ the growth of fluctuation at $qR_g < 1$ and intra-chain relaxation at $qR_g > 1$ and finally a clear proof of CHC theory in the very early stage of spinodal decomposition.

This procedure provided a technique of obtaining the functional form of the free energy of mixing of immiscible blends by measuring the temperature dependence of χ parameters at various compositions and final temperatures through measurements of the kinetics of spinodal decomposition. The phase diagram which is inaccessible due to the interference of T_g line, can be obtained through temperature extrapolation of χ parameter. The intra-chain relaxation can in principle be studied from the time and q dependence of S(q) in the region of $q\, R_g > 1$.

4. Effects of Crosslinking on the Phase Behavior

Effect of Crosslinks on the Miscibility of a Deuterated Polybutadiene and Protonated Polybutadiene Blend: The effect of peroxide crosslinking on the phase diagram and the scattering function for a critical mixture of perdeuterated polybutadiene (DPB) and protonated polybutadiene (HPB) has been examined by small-angle neutron scattering as a function of temperature. The scattering curves for the crosslinked blends were essentially temperature independent. It was found that even at temperatures (T) below the critical temperature (T_c) of the uncrosslinked (linear) blend (e.g., T = 0°C; T_c=99.2°C) the crosslinked blends remained single phase and did not undergo microphase separation. The calculation of the reduced temperature, ϵ, for the crosslinked blends also implied that crosslinking greatly increased the single phase region of the phase diagram. By comparing the scattering for the crosslinked blend with that of the linear blend at the crosslinking temperature (150°C), a suppression in the scattering was observed due to the presence of the crosslinks. However, it was found experimentally that the concentration fluctuations present at the temperature of crosslinking dominate the scattering, and this made it difficult to verify the prediction on the scattering function made by de Gennes.

Small Angle Neutron Scattering Study on Poly(N-Isopropyl Acrylamide) Gels Near Their Volume-Phase Transition Temperature: The small angle neutron scattering experiments were conducted on N-isopropyl acrylamide (NIPA) gels in D_2O and on the corresponding NIPA solutions. The NIPA gels underwent a sharp, but a continuous volume phase transition at 34.6°C from a swollen state to a shrunken state with increasing temperature. In the case of the gels, an excess scattering due to the presence of crosslinks was observed at low q region ($q < 0.02 Å^{-1}$). The scattered intensity function for the gel was well described with a combination of Gauss and Lorentz type function, i.e., $I(q) = I_G(0)\exp[-\Xi^2 q^2] + I_L(0)/(1+\xi^2 q^2)$ as proposed by Geissler et al. The Gaussian part results from solid-like inhomogeneity, having a characteristic size of Ξ, and is due to the introduction of crosslinks into the system. The Lorentzian part originated from the liquid nature of the local concentration fluctuation of the gel characterized with a thermal blob of dimension ξ. Ξ decreases systematically with polymer volume fraction, ϕ, indicating the nature of Ξ as the solid-like inhomogeneity. On the other hand, the intensity function for solutions was well fitted with the Ornstein-Zernike (OZ) equation (a Lorentzian function), i.e., $I(q) = I_L(O)/(1 + \xi^2 q^2)$. It was found that both ξ and $I_L(0)$ diverged at the spinodal temperature, T_s. The critical exponents, ν and γ, for the temperature dependence of ξ and $I_L(0)$, were estimated to be ca.0.60 and 1.2 for the gel, respectively, and were larger than the values for the solution of the same polymers ($\nu=0.45$ and $\gamma=0.8$). The concentration dependence of ξ and $I_L(0)$ was also well described with a power law relationship, i.e., $\xi \sim \phi^{\nu_\phi}$ and $I_L(0) \sim \phi^{\gamma_\phi}$. The values of ν_ϕ and γ_ϕ at 23°C are -3/4 and ca. -1/4, respectively, for the NIPA solutions, and this is in good agreement with the theoretical prediction for polymer solutions in a good solvent.

Small-Angle Neutron Scattering Study on Weakly Charged Temperature Sensitive Polymer Gels: The static structure factor for poly(N-isopropylacrylamide-co-acrylic acid) (NIPA/AAc) gels was investigated in terms of small-angle neutron scattering (SANS). The NIPA/AAc gels underwent a discrete volume phase transition at 50.8°C from swollen to shrunken states as temperature increased. The static structure factors for NIPA/AAc gels were well described by a Lorentz type scattered intensity function at temperatures below 34°C which was near the so-called Θ temperature of NIPA in D_2O. At higher temperatures, the static structure factor had a distinct scattering maximum although the gel was still in the highly swollen state. The scattering maximum was located around $q=0.02Å$ and was temperature and concentration dependent. The appearance of the peak indicates the strong concentration fluctuations that create polymer rich and poor regions in the system. The contrast in the concentrations appeared to result from the competing interactions in the network, i.e., the electrostatic repulsive interaction between AAc segments. The static structure factors were analyzed quantitatively with the theory of Borue and Erkhimovich for polyelectrolyte solutions in a poor solvent. It is found that the concentration fluctuation leads to a microphase separation between polymer rich and poor domains before the system undergoes the volume phase transition.

Small Angle Neutron Scattering Studies of Blends Containing Linear and Crosslinked Polymers: Previous work on blends with crosslinked components used samples synthesized by dissolving a linear polymer (PVME or PSH) in a mixture of vinyl and divinyl monomers (styrene and divinylbenzene). In all cases increased crosslink density destabilized the system, eventually causing phase separation. Polymerizations of vinyl and divinyl monomers can lead to very broad molecular weight distributions between crosslinks, and hence, a heterogeneous network structure can form.

In FY 92 work was done in collaboration with Professor Claude Cohen in the Chemical Engineering Department of Cornell University in which siloxane networks were formed around linear, deuterated siloxanes. The data were consistent with the previous results from vinyl/divinyl polymerizations, in that the zero angle scattering intensity increasing with increased crosslink density. The polydispersity of the siloxane network chains was Mw/Mn $\approx$ 1.3 compared to the expected value of
Mw/Mn > 2 for the vinyl/divinyl chains. Thus, polydispersity alone cannot account for the destabilization.

5. Effect of Flow Field

Crossover to Strong Shear in a Low Molecular Weight Critical Polymer Blend: Small-angle neutron scattering has been used to measure the influence of shear flow (γ) on a low-molecular-weight polymer blend near the critical point. When combined with light scattering measurements of the equilibrium ($\gamma=0$) critical dynamics, these measurements reveal that the long-range critical fluctuations begin to break apart when the shear rate becomes comparable to the characteristic relaxation rate τ_c^{-1}, where τ_c is the equilibrium lifetime of the critical fluctuations. In our experiment, $\tau_c=\xi^2/D_c$, for a polystyrene/polybutadiene blend at critical composition. The correlation length ξ was measured by SANS and D_c was obtained from the dynamic light scattering (DLS) experiments. The static structure factor S(q) at various temperatures and shear rates was measured in-situ by SANS experiment. The universal behavior of the shear rate dependence of structure factor or correlation length as a function of reduced shear rate, ($\gamma\tau_c$), can be directly related to the decrease in the critical temperature caused by the flow. Our experimental results are found to be in very good agreement with the theoretical predictions of Onuki and Kawasaki.

Polystyrene/DOP Solutions - Single Chain Behavior Under Shear: Experiments to examine the single chain scattering behavior during shear for a 3% solution of polystyrene in dioctyl phthalate were conducted. Three samples were utilized, each containing 3% total polymer with varying ratios of deuterated to protonated chains (10:90, 20:80, and 30:70). Experiments were performed on the 8 m SANS instrument, at shear rates ranging between 107 and 815 s^{-1}. In contrast to the results obtained previously on the 30 m SANS instrument, where no anisotropy was observed, all samples under all shearing conditions displayed some anisotropic scattering. At low rates ($<190\ s^{-1}$), the scattered intensity parallel to the flow direction is suppressed relative to the quiescent scattered intensity. With increasing rates, the low q scattering increases while the intermediate q range scattering remains suppressed. At the highest rate, the low q scattering for the sheared sample is greater than the quiescent sample, yet the intermediate q range scattering is still lower than the quiescent sample. Normal to the flow direction, an enhancement of the scattering is observed at rates greater than $190\ s^{-1}$. The enhancement increases with increasing shear rate, however the q value where the scattering diverges does not change with shear rate.

An estimate of the radius of gyration (R_g) components as a function of shear rate was made using the random phase approximation for polymer solutions. The fits to the structure factors show R_g increases both parallel and normal to the flow. The increase along the flow direction is greater than the increase perpendicular to flow. The ratio of $R_{g\parallel}$ to $R_{g\perp}$ is approximately constant (1.1) for the shear rates examined. Due to the fact that the condition $qR_g < 1$ is not satisfied for our experimental conditions, attempts to measure the radius of gyration components parallel and normal to flow using the "high concentration" method and the Zimm plot were unsuccessful.

Polystyrene/Polybutadiene/DOP Solutions - Off Critical Shear Rate Behavior: The steady shear SANS behavior was studied for the off-critical blend solution that was also examined with the shear light scattering instrument. These results will complement each other to provide a complete picture of the shear induced homogenization observed in this sample. A suppression of concentration fluctuations parallel to the flow direction is observed with the application of sufficiently large shear rates. Normal to the flow direction there is no effect of shear on the fluctuation size. The structure factors were fit to the Ornstein-Zernike function to extract values of the correlation length, ξ, and $S(q=0)$ as a function of temperature and shear rate. By assuming the system is mean-field in nature and plotting ξ^{-2} versus 1/T, an apparent spinodal temperature may be determined by extrapolating to infinite correlation length. There is a decrease in the apparent spinodal temperature parallel to flow and no change in the apparent spinodal temperature normal to flow. The shear rate dependence of ΔT is much stronger for this off-critical mixture than is predicted by Onuki and Kawasaki for critical mixtures. However, as pointed out by Douglas, due to the mean field nature of the system there is no true shift in the spinodal temperature with shear rate, and these results are a reflection of the distortion of the concentration fluctuations with shear.

An attempt was made to determine the smallest concentration fluctuation which is affected by a given shear rate in a manner similar to that used in the analysis of SANS from polymer blends under shear. The critical size is related to q_c, which is determined as the divergence point between sheared and quiescent structure factors. By plotting log q_c versus log $\dot{\gamma}$, power law behavior was observed for different temperatures. However, these power law exponents were less than the 1/3 predicted by mode coupling theory and observed for critical compositions of two component polymer blends. This study highlights the differences between critical and off-critical mixtures and indicates that more work in the area of off-critical mixtures is necessary.

6. Interfacial Modification

Competition of Phase Separation and Transesterification in D-Polycarbonate/Co-Polyester Blends: Time and temperature dependence of transesterification and phase separation in blends of bisphenol A d-polycarbonate/random copolyester of cyclohexanedimethanol and ethylenediol with terephthalic acid were studied with small angle neutron scattering technique. Radius of gyration and the exponent x in $I \propto q^{-x}$, where q is scattering wave number, showed that phase separation is dominant below 180°C while transesterification becomes dominant above 220°C. In the intermediate temperature, both processes compete so that the interface first becomes very sharp due to phase separation and then broadened by transesterification. It is concluded that relative rates of both processes determine the structure coarsening, melting and stabilization mechanisms.

Molecular Composites Through Hydrogen Bonding: Rod-Like Polymers in Blends: The feasibility of creating a molecular composite through the blending of a rod-like polymer with a hydrogen bonding coiled polymer is being investigated. The miscibility of a blend of a polystyrene that contains about 1% (1,1,1,3,3,3-hexaflouro-2-hydroxyisopropyl) α-methylstyrene with polypeptides has been investigated using optical microscopy. Polypeptides that are being studied are poly(γ-benzyl L-glutamate) (PBLG), poly (ϵ-carbobenzoxy L-lysine) (PCBZL), poly (hydroxypropyl L-glutamine) (PHOPG), and poly (ϵ-carbobenzoxy L-ornithine) (PCBZO). Optical microscopy and DSC results show that some mixing is possible over the complete concentration range. PHOPG shows the most favorable results exhibiting miscibility at room temperature after annealing above the glass transition temperature of the blend for concentrations less than 50 wt.% PHOPG. Temperature jump light scattering and SANS are being implemented to determine the complete phase diagram (binodal and spinodal) as well as study the kinetics of the phase behavior of these blends.

7. Technical Collaboration and Technology Transfer to Industries and Other Agencies on Polymer Blends and Characterizations

Protection of Archival Records: Protection of records stored in the National Archives and Records Administration (NARA) from atmospheric pollutants has been a matter of long time concern. This research program currently involves the study of shielding mechanisms of containers commonly used in protecting archival materials from such atmospheric pollutants as sulfur dioxide and the nitrogen oxides.

The diffusion constants of SO_2 for the six types of boxboard used to make archival boxes were measured. For the two samples provided by NARA diffusion constants were found to be about 1×10^{-3} cm^2/sec. Four samples obtained from a commercial manufacturer had diffusion constants of less than 1×10^{-5} to 3×10^{-3} cm^2/sec. These data suggest that in many cases, diffusion of SO_2 through boxboard is mediated by that glue used to laminate the boxboard.

The diffusion constants of NO for boxboard used to make archival boxes were measured. For the two samples provided by NARA diffusion constants were found to be about 2 x 10^{-3} cm^2/sec.

The absorption of SO_2 by boxboard was found to be very dependent upon the nature of the boxboard sample. Both permanent and nonpermanent binding of SO_2 were observed.

Interpenetrating Inorganic/Organic Polymer Networks for the Printed Wiring board Applications: Collaboration among NIST, Sandia Laboratories and the National Center for Manufacturing Sciences have been developed to study the phase separated inorganic/organic interpenetrating networks for possible future printed wiring board application. In this study tetraethoxysilane (TEOS) or related silane derivatives will be used to form SiO2 network together with organic network formed from epoxy or glassy polymeric materials. In situ SANS and LS characterization of the materials are being carried out at NIST.

Workshop and Consortium on Polymer Blends: A NIST/Industry workshop on polymer blends was held on April 20-21, 1992. Current blends technology and science background have been reviewed through a set of invited lectures and posters. 27 scientists representing 13 industrial companies and three universities together with 23 NIST representatives have attended this workshop. A consensus emerged from this workshop that a NIST/Industry consortium should be organized to study the science/technology of polymer blends/alloys processing with emphasis on the interfacial modification and characterization. This NIST/Industry consortium is currently being organized.

THEORY

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Translational Friction on an Arbitrarily Shaped Brownian Particle

Hydrodynamic measurements are a primary source of polymer molecular parameters (molecular weight, size, shape). These measurements include the translational diffusion coefficient, rotational diffusion coefficient, intrinsic viscosity and the sedimentation coefficient. It is shown that the scalar transational friction of an arbitrarily shaped particle is related to the electrostatic capacity of the same body. This hydrodynamic-electrostatic "analogy" allows for the analytical calculation of the translational friction in many new cases (short circular cylinders, cube, ...) and provides fundamental new theoretical insight into the physical origin of friction. The Stokes paradox and the critical dimension $d=4$ for random coil polymers follow simply from the recurrence properties of random walks. The connection between translational friction and capacity also allows the calculation of friction through the methods of probabilistic potential theory. Random walks are launched from a large shell surrounding the body and the capacity of the arbitrary point set (and thus the friction) is calculated simply from an accounting of the hit statistics. This method has been tested numerically by Dr. Huan-Xiang Zhou at the National Institute of Diabetes and Digestive and Kidney Diseases, NIH with excellent results for cubes, two spheres and random coil polymers with and without excluded volume. The method is very promising for proteins and dendrimer polymers where classical slender body calculations (Kirkwood-Riseman theory) are not accurate or appropriate.

Important results have also been obtained for rotational friction coefficients and the intrinsic viscosity of bodies of general shape. An exact relation of the rotational friction of an arbitrarily shaped axisymmetric body to the capacity has been found and useful approximate relations for the intrinsic viscosity have been obtained in terms of the average polarization and capacity. The new formal results are readily implemented through function space integration method and are well suited to parallel computation methods on a computer.

Geometrical Properties of Polymers in Dilute Solution

The problem of the characterization of polymers through the measurement of dilute solution properties (radius of gyration, etc.) and the comparison with molecular models is basic to all activities in polymer science involving quantitative measurement. Unfortunately, the exact solution of the geometrical properties of interacting polymers ("excluded volume") has resisted all attempts. The difficulty of the problem is not surprising once the close relation between the interacting polymer problem and the Ising model and other intractable problems is recognized.

A direct attack on the problem of the geometrical properties of self-avoiding walks is made by exactly enumerating all configurations of self-avoiding chains of a given length n ($n \leq 12$) on hypercubic lattices of variable dimension ($d=1$-6). The configurations are sorted according to the number of nearest-neighbor contact number which allows energetics to be incorporated in the model. Many of the most basic properties of the interacting polymers are obtained from our exact results for the polymer partition function, and end-to-end distance $\langle R^2 \rangle$ of interacting chains in variable spatial dimension d. The critical exponents γ and ν, for example, are calculated for chains in good solvents and theta solvents and thermodynamic properties are also calculated (entropy, free-energy, specific heat). The first lattice model calculations of the critical exponents in variable dimensions are given and are compared with estimates from continuum field theory. Similar calculations are in progress for the Ising model which are relevant to phase separation in polymeric systems. The effect of finite size of confining boundaries on the theta temperature of a polymer is also being considered as a step toward the related problem of finite size effects on phase separation in thin polymer blend films and other second order phase transitions. Monte Carlo methods are also being utilized in the pursuit of these fundamental problems.

Mixing Strong and Weak Bonds in a Polymer Blend

The question of how a mix of strong bonds and weak bonds affects polymer behavior is of interest in a blend of two polymers attracted to each other by a few very strong bonds per chain and repelled by many weak bonds per chain. What is the result of this competition? To approach this problem the case of a polymer that has many weak and few strong bonds onto a surface is treated . The adsorption is very different from adsorption of a homopolymer with the average value of attractive energy. The next problem is to calculate the attraction of two chains of the above type to each other. These two examples should provide insight into the blend problem. A method used previously for adsorption of homopolymers to the adsorption of copolymers of all types has been generalized to comb and star molecules.

Adsorption of Polymer Rings

An analytic treatment of a ring polymer adsorbed onto a surface has been formulated. For the case of a body centered cubic lattice the partition function has been obtained from which the thermodynamic formulae are deduced. For other lattices the problem reduces to summing up the $i=j$ terms of the series $Q(L,R) = \sum A_{ij}L^{i}R^{j}$ where the form of Q is known but not the double-summed Taylor series.

Dynamics of Polymer Chains and Blends

The processibility and the final characteristics of blends and other plastics depend in large part upon the relaxation behavior of the high-polymer chains of which these materials are primarily composed. Better theoretical treatments of polymer melts and blends will lead to more efficient processing and better fabricated end products. A major shortcoming of present theories is their inability to treat excluded volume and chain entanglement effects in a realistic way. Present work is aimed primarily at the study of these effects, using a combination of analytical and computer simulation techniques. The simulation results provide data on simple model systems which serve to guide the development of better theoretical treatments.

Better understanding of chain dynamics is also important to improving the characterization of polymers. Size exclusion chromatography, widely used for the estimation of distribution in molecular weight, is a dynamical, nonequilibrium technique which depends upon the relaxation of polymer chains. Present theories do not allow the calculation of molecular weight directly from measured quantities; a series of calibrants of known molecular weight is required. Improvements in the theory could reduce or even remove the need for calibrants, allowing the determination of molecular weight distribution of polymers for which calibrants are not available.

Present efforts in this project are in two areas. First is a study of the effects of the size or "bulkiness" of chain monomers upon equilibrium and relaxation behavior. This work is intended primarily to separate the effects of excluded volume expansion from those of chain self-entanglement. The results will provide a critical test of some of the theoretical treatments currently in use. Some results have been published; papers describing other results are in preparation. This part of the work is essentially a study of the behavior of isolated chains (dilute solution limit). As such, it is a necessary preliminary to the second part, a study of phase separation in polymer blends, expected to be the major continuing emphasis in this project. Computer programs for simulating phase separation in polymer blends and for sampling scattering functions in the blends systems have been written and tested on the Cray computing system at NIST. Simulations have been carried out at a variety of densities and "temperatures", in order to estimate internal relaxation times over the phase diagram for the determination of appropriate time scales for sampling phase separation behavior. Quenching simulations have also been carried out, again primarily to estimate time scales for future studies.

The Geometry of Self-Avoiding Walks

Self-avoid walks (SAWS) model coil-like polymers very well. The geometry of self-avoiding walks can be shown to correlate with thermodynamic quantities of a polymer chain. Using Monte Carlo simulation, the number of nonbonded next nearest neighbors, $<Z>$, of SAWS in 2 and 3 dimensions has been calculated for chains of varying length, n. The relation of $<Z>$ to n is used to determine the first order correction exponent, Δ. It has been found that $\Delta=1.0$ in both two and three dimensions, contrary to previous predictions.

The Evolution of the Isotropic Phase of a Liquid Crystal in the Presence of an Adsorbing Surface

A study of the evolution of the isotropic phase from a nematic phase in the presence of an adsorbing surface is being studied using Monte Carlo simulation. A computer program has been written to follow the evolution of the isotropic phase. This will be characterized by monitoring the order parameter, S^2, as a function of distance from the adsorbing surface as the system undergoes the nematic-isotropic transition. The model for this system has three energies, the adsorbing energy, ϵ_a, the intramolecular bending energy, ϵ_b, and the intermolecular ordering energy, ϵ_p. The relationship of these three energies is an important parameter in this study. Results to date include calculation of the order parameter of the complete system, the order parameter as a function of distance, and heat capacity C_v for the systems with $\epsilon_a=50\epsilon_p=50\epsilon_b$, $\epsilon_a=\epsilon_p=\epsilon_b$, and $\epsilon_a=10\epsilon_b$.

STANDARD REFERENCE MATERIALS

C. C. Han, C. M. Guttman, J. R. Maurey and P. H. Verdier

Development of Polyurethane Characterization Techniques and Standards

There is growing need for better methods of characterizing the commercial polyurethanes used in medical devices, both before use and after degradation following implantation. Because of the wide variations in the compositions of these block copolymer systems, the usual methods for determining molecular weight distribution (MWD) are of limited applicability and are difficult to interpret. With support from the Food and Drug Administration and Standard Reference Materials Program, we are undertaking a program to produce polyurethane Standard Reference Materials (SRM) and to develop improved methods for characterizing these and other block copolymer systems.

One polyurethane SRM has been produced with weight-average molecular weight determined by light scattering and the limiting viscosity numbers determined under the conditions commonly used for the estimation of MWD by gel permeation chromatography. This low molecular weight SRM is not one of the usual commercial polyurethanes, but rather is a model compound to which the usual techniques for determining molecular weights of homopolymers can be applied.

Light scattering is used to measure the weight average molecular weight of the SRM, 4.3×10^4 g/mole. The intrinsic viscosity of this material in tetrahydrofuran is also measured.

Two NISTIR's have been written describing this work and a SRM certificate has been issued.

Polyolefin Melt Flow Rate Standards

Melt flow rate and melt index measurements are used in specification of polymers in the polymer industry. NIST SRM's with certified melt flow rates are used to check equipment stipulated by the ASTM D-1238 voluntary standards.

A branched polyethylene, SRM-1473, with a melt flow rate of about 2.0 g/10 min was recertified and a report was issued this year. This work is supported by SRMP.

Work on the certification of a polypropylene with a melt flow rate of about 11 g/10 min is currently going on using ASTM method D-1238 condition 230/1.2. The need for this material has been established through consultation with the members of the subcommittee of ASTM D-20 in charge of Method D-1238. Support for this work came from a group of polymer companies represented on the ASTM subcommittee.

Aqueous SEC Molecular Weight Standards

No SRM's are presently available for water-soluble high polymers. Water soluble polymers are industrially important in such areas as adhesives, coatings, paints, lubricants, oil resistant plastics, etc. The need for such standards for these materials has been noted by Visiting Committees, during staff visits to industrial characterization laboratories, and in the responses to market surveys.

By far the most pressing need for water-soluble molecular-weight polymer SRM's is for calibration standards for aqueous size exclusion chromatography (SEC). For this purpose, absolute molecular weight measurements are being made on two narrow molecular weight distribution polyethylene oxides. The polyethylene oxide SRM's should be usable on most aqueous SEC columns without special column conditioning.

Two Polyethylene SRM's Recertified

SRM 1475 and SRM 1484, two polyethylene molecular weight standards commonly used in SEC calibration and melt index work were recertified this year. The old and new materials were checked against one another using SEC for both polymers. The melt index on SRM 1475 was also measured.

DENTAL AND MEDICAL MATERIALS

The objective of this Group is to provide basic materials science, engineering, and test methods which may be used by sectors of the health-care industry or profession for the development of new or improved materials, delivery systems, and standards.

New monomer systems that shrink less, are more resistant to oral fluids and with the potential to bond to teeth and other materials are the object of intense investigations. These monomers may find their applications for improved dental composite restoratives, adhesives and cements. Durability is assessed by evaluating properties such as hardness, flexure strength, and wear resistance following immersion in food simulating liquids. Studies of the basic chemistry of calcium phosphate compounds as they relate to mineralization, demineralization and remineralization are pursued. The analysis of the failure of ceramic and ceramic-metal restorations is being conducted with the objective of defining tougher material systems. Fractography coupled with Weibull analysis of failures is employed. Finite element analysis and modeling of multicomponent systems is used to identify the states of stress in restorations and model test systems.

The group has extensive interactions with other organizations to further strengthen the impact of its programs. The American Dental Associations Paffenbarger Research Center maintains it staff at NIST to carry out cooperative research. The Center of Excellence for Materials Science Research at NIST, one of three such research entities currently funded by the National Institute of Dental Research, is directed by Dr. Rafael L. Bowen and co-directed by Dr. John A. Tesk, Leader of the Dental and Medical Materials Group at NIST. Five research projects are being pursued by scientists in the Dental and Medical Materials Group and the American Dental Association Health Foundation/Paffenbarger Research Center through 1994. Four research associates from the intramural research program of the National Institute of Dental Research plus guest scientists from the United States Navy and the Public Health Service form an important part of the dental program.

FY 92 Significant Accomplishments

- Ethyl 4-dimethylaminobenzoate (4EDMAB), which is used both in UV and visible light initiated polymerization of acrylic monomers, was found to be an effective fluorescent probe for monitoring the degree of cure of dental resin systems.

- Collaboration with a Naval guest scientist identified a more efficient method of analysis and testing for the indentation fracture toughness of ceramics.

- Better routes to low shrinkage resins were developed using cationic polymerization initiators which were shown to yield 100% ring-opening. The cationic initiators can be used in conjunction with free radical initiators to provide dual cures for methacrylate-spiro resin systems.

- A novel method of rapid remineralization was developed by research associates from the American Dental Association Health Foundation. The method involves the use of a carbon dioxide aerosol to prevent and repair incipient dental caries, to desensitize dentin and to aid in dentin bonding procedures.

- A guest scientist agreement was drawn with a prominent dental company for the purpose of investigating patented NIST technology on cyclopolymerizable monomers with a view toward licensing.

- Depolymerization, rather than removal of mineral-binding ligands, was found to be responsible for the enzymatic reversal of the inhibition of apatite formation by polysaccharides such as chondroitin sulfate.

DURABILITY, CLINICAL STUDIES AND RELATED PROPERTIES OF DENTAL COMPOSITES, AMALGAMS, AND CEMENTS

J. M. Antonucci, S. M. Keeny III[1], J. E. McKinney[1], J. A. Tesk, R. L. Bowen[2], F. C. Eichmiller[2], N. E. Rupp[2], A. Ly[2], S. Venz[2], K. Miyazaki[3], S. Takagi[2], L. C. Chow[2], Y. Matsuya[4], S. Matsuya[4], and D. Lashmore[5]

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The transfer to industry of Paffenbarger Research Center (PRC) adhesive technology resulted in an improved dentin-enamel adhesive and a metal adhesive, both introduced by one company. Another company is in the process of evaluating the improvements and is expected to be introducing new products in the near future.

A project on the development of radiation shielding materials has resulted in elastomeric materials, similar to impression putty, that are capable of blocking significant amounts of radiation energy. Current materials have demonstrated the ability to block over 40% of ^{60}Co gamma-rays and 10 MeV X-rays and almost 100% of 7 MeV electron beams with thicknesses of 2 cm and less. Experiments completed in the past year have determined the effective thickness needed for several higher energies of electron beams. The addition of this data will make it possible to give reliable recommendations for use in clinical trials. Arrangements are currently under way with several hospitals within the Veterans Administration to develop formal trials. Contacts have also been made with one commercial dental material company that is showing a strong interest in producing a product from this technology. This material would have significant usefulness in shielding soft tissues and salivary glands during high-energy radiation therapy of head and neck tumors and during electron therapy for skin and mucosal carcinomas. A patent is expected to issue in 1992.

A pilot project began exploring the application of super strong electrodeposited alloys for use in dental prostheses. Possible applications include resin retained bridges, precision attachment prostheses, and implant superstructure prostheses. These applications require an extreme degree of precision as well as high material strength, and electrodeposited glass-metal alloys enhance precision and possess high material strength.

Beta quartz glass-ceramic inserts have been successfully licensed to industry and products are being marketed. The clinical program has been instrumental in developing the instructions, instrumentation, and protocols necessary for placement of the inserts. Clinical studies have been initiated at several U.S. and foreign universities under the guidance and review of the PRC clinical program.

DENTAL POLYMER, COMPOSITE, CEMENT, SEALANT, AND ADHESION CHEMISTRY

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Polymerization shrinkage is considered to be a major detriment to improved performance of dental composites, adhesives and sealants. New resin systems that reduce shrinkage are being developed. These include monomers that either: expand on polymerization by ring opening, cyclopolymerize with volume occupying rings, or that have higher molecular weights. Fluorinated polymers also can improve performance.

Cyclopolymerizable monomers and oligomers were prepared from hydrophilic precursors. Polyethylene glycol (PEG) chains of various molecular weights were used to link together the cyclopolymerizable reactive sites in multifunctional oligomers. The oligomers ranged from water dispersible to water soluble as the PEG chain length was increased. The oligomers readily polymerized to highly crosslinked polymers which exhibited rapid water uptake. The amount and rate of water uptake was related to the length of the PEG chain.

Other hydrophilic cyclopolymerizable monomers were prepared with tetrahydrofurfuryl (THF) end groups. The resulting crosslinked polymers had a dry modulus of ~ 3 GPa (comparable to unfilled dental resins) and a wet modulus of ~ 2 GPa. Water uptake was rapid and could be controlled between approximately 5 and 50% based on the inclusion of various amounts of a very hydrophilic monomer with the THF functional group. Proposed applications for the hydrophilic cyclopolymers include resin modified cements and adhesion promoting bonding agents.

Fluorinated multifunctional oligomers were prepared by the formaldehyde reaction with acrylates. The polymerization of several bulky oxybismethacrylates was conducted. Very high degrees of cyclopolymerization were attained due to the bulky ester group functionality.

The formaldehyde reaction was used with a triacrylate to prepare a unique 3-dimensional multifunctional network. This material has a mixture of 1,6-diene groups capable of cyclopolymerization and terminal hydroxymethyl acrylate groups. The material is hydrophilic and may be useful in reinforced cements as well as many other applications.

The synthesis of difunctional spiro monomers was undertaken so that crosslinked polymers could be prepared exclusively by ring-opening. Initial work with a 1,2-diol starting material lead to polymers with excessive amounts of single ring-opening with elimination of a cyclic carbonate fragment. The triaryl sulfonium salt photocationic initiator was found to be very effective in the double ring-opening polymerization of vinyl-substituted spiro monomers which are based on a 1,3-diol starting material.

A methacrylate-substituted spiro orthocarbonate was evaluated in polymerizations under a variety of conditions. A mixed-mode radical/cationic photocure process give the optimum degree of conversion for both the methacrylate and spiro vinyl groups. However, this method resulted in shrinkage of ~ 6-7%. By free radical polymerization alone, the shrinkage was ~ 9-11% while with only cationic initiation, the shrinkage was only ~ 2%. The molecular weight of the cationic-formed polymer was low and the material lacked any significant mechanical strength.

Bonding to tooth structures is important for restoratives to become intimate with the tooth. This can be accomplished by a number of methods. L-Ascorbic acid or vitamin C, a unique enolic acid with antioxidant properties, was evaluated as an etchant/conditioner for preparing cut dentin for bonding to resin based materials. Dentin surfaces were treated with various ascorbic acid aqueous solutions (10-32 w/w%) for times ranging from 15-120 seconds. After rinsing with distilled water and drying, the conditioned dentinal surfaces were examined by SEM for the degree of smear layer removal. The optimal time for smear layer removal for a 17.6 w/w % aqueous solution of ascorbic acid was 60 seconds. Significant tensile bond strengths between ascorbic acid etched/conditioned dentin and a chemically cured composite were obtained after sequential application of acetone solutions of N-phenylglycine and carboxylic acid containing methacrylates such as mono(2-methacryloyloxy) ethyl phthalate.

PMDM (a pyromellitic anhydride / hydroxyethyl methacrylate adduct) is one component of a dentin bonding agent. Spontaneous polymerization of PMDM has been observed on dentin preconditioned with acidic agents and surface-active amines. The origin of this surface-initiated, autopolymerization remains unknown. Understanding the mechanism of these self-initiated polymerizations will aid in designing optimal dentin adhesive and dual cure initiator systems. A plausible mechanism for this may involve interaction of the acid groups (CO_2H) of PMDM with the amine to form an ammonium salt which converts to initiating radicals via a charge-transfer complex. To test this hypothesis separate resin formulations with CO_2H groups (A), from e.g. acid monomers, organic acids, etc. were mixed with resins with various types of amines (B). Concentrations of CO_2H and the amine components of A and B were varied and polymerizations were conducted at 23°C, 37°C and 60°C. Rotational hardening times (RHTs) were determined by mixing equal parts of A and B between crossed glass slides and noting the time to immobilization. RHTs varied inversely with temperature and with the concentrations of amine and acid and acid strength (pKa); O_2 inhibited the polymerization. Aromatic amines that are effective activators for the decomposition of benzoyl peroxide also are effective in activating the polymerization of CO_2H resins. ^1H NMR spectroscopy indicated ammonium salt formation as well as changes which may due to charge-transfer reactions. ESR indicates the formation of biradical species. The results suggest a radical polymerization mechanism involving acid-amine complexation and electron transfer.

Advancing adhesion and resin technologies have aided the efforts this year toward providing the dentist with means to apply aesthetic or transparent protective polymeric coatings to tooth surfaces. This may be especially important to prevent root caries in the exposed root surfaces of the teeth of older patients. Analogous to the protective coatings on houses, automobiles, and other structures against the damaging effects of environment, the application of protective coatings on the entire exposed surfaces of patients' teeth may be a new and valuable service that dentistry can provide. Results to date indicate that experimental formulations of these new PRC materials can successfully adhere to the whole tooth and withstand challenges simulating those of the oral environment.

DENTAL ALLOYS, CERAMICS, METROLOGY, AND ANALYSIS

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Computer simulations of porcelain fused-to-metal slabs indicate that the use of crystalline-like materials (i.e., without glass transition temperatures) as opaque layers should lead to tougher systems. Stresses within the opaque layer, at the opaque porcelain-body porcelain interface, should be rendered smaller and more compressive while having a minimal influence on the stresses in the body porcelain itself. Experimental studies are in progress to confirm this effect.

Studies continued during the past year on new alloys patented by the ADAHF/PRC that are expected to produce fracture-resistant prosthetic devices having excellent biocompatibility. Evidence obtained suggests that microscopic crack propagation is inhibited in alloys containing zirconium, ruthenium and palladium by the occurrence of stress-induced atomic shear transformations. Small transformed platelets are apparently formed near the ends of growing cracks that are regions of high stress normally leading to fracture. High stresses applied to the surface of these alloys, e.g., by cutting or machining, produce a tough, fibrous surface layer on the transformed materials that creates extraordinary wear resistance. The unique mechanical behavior of these alloys and their excellent corrosion resistance are expected to ensure their use in a variety of dental and nondental applications.

The formulation of direct-filling metallic pastes (based on a NIST patent application) that can be readily manipulated and hardened at mouth temperature has traditionally required the presence of a liquid metal, most specifically, mercury. Corrosion, discoloration of restored teeth, and questions regarding biocompatibility of compounds containing virtually all liquid metallic elements have motivated innovative research on alternatives for dental amalgam. Exploratory studies have been undertaken on powders of relatively soft metals that can be condensed directly in the manner of gold foil, but with handling characteristics more like amalgam. Preliminary studies are focusing on an evaluation of the forces of condensation and the time required to produce satisfactory restorations.

Monte-Carlo simulations of indentation cracks for the measurement of fracture toughness of ceramic materials have shown that the best and most consistent estimate of the fracture toughness is obtained by using a slope averaging method. It consists of fitting a linear least squares analysis to the crack length as a function of indentation load and forcing the result through the origin. Very good estimates are obtained with data from only ten indents, better than using 50 indents and a mean averaging method. A publication in the NIST Journal of Research will provide the details.

Beta quartz glass-ceramic inserts have been successfully licensed and products are being marketed. Many of the limitations of composite resins are due to the properties of the resin, and increasing the amount of inorganic reinforcing filler material can make such restorations more closely resemble the properties of the natural tooth crowns. The insertion of a "megafiller" that fills as much of the cavity as possible in effect reduces the amount of resin. Dentists are thereby provided with a material for forming a composite restoration that has overall less resin and more "filler" than would be otherwise possible. The product has been well received and should result in a significant improvement in the properties of directly placed composite restorations. Laboratory development of the glass-ceramic material for casting and CAD-CAM applications is continuing.

CALCIUM PHOSPHATE CHEMISTRY, BIOCHEMISTRY, STRUCTURE AND CLINICAL IMPLICATIONS

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A novel method of rapid remineralization was developed at the PRC to prevent and repair incipient dental caries, to desensitize dentin, and for application to etched dentin during dentin bonding procedures. Solutions containing high concentrations of calcium phosphate were obtained at lowered pH, produced by the presence of carbonic acid formed from dissolved CO_2 (carbon dioxide) in water under pressurized CO_2 atmosphere. When an aerosol was used to apply the experimental solution to teeth, ions diffused into the teeth, and the Ph of the applied solution increased due to the evaporation of the CO_2. The solution precipitated amorphous calcium phosphate (ACP) that then converted to tooth mineral. The precipitation was followed by the pH change in the solution, and the solids were analyzed by x-ray powder diffraction, infrared spectroscopy and chemical analysis. Application of the experimental solution on etched dentin during dentin bonding yielded high bond strengths. This new method of rapid remineralization overcomes the problems of present remineralization solutions, i.e., low concentrations, low diffusion rates, and the low precipitation rate of apatite.

Investigations of octacalcium phosphate (OCP) and its role in biomineralization have continued. Crystal structures of several calcium dicarboxylates have been determined. These are being used to develop a general OCP-dicarboxylate salts structural model that can provide a better understanding of the properties and mechanisms of the formation of biominerals.

Artificial lipid vesicles (liposomes) continued to be used as in vitro models for studying proteoglycan (PG) inhibition of biomineralization in cartilage where matrix vesicles are the nidi for initial mineral deposition. Unlike the intact PG molecule and its two major components, chondroitin sulfate (CS) and core protein, the products of enzymatic degradation of these latter two components were found not to inhibit mineral formation. Since the products of the CS digestion were the repeating disaccharide units, depolymerization of this component rather than removal of mineral-binding ligands was responsible for the enzymatic reversal of the inhibition in this case.

Studies were continued on the solution hydrolysis (to apatite) of anhydrous dicalcium phosphate ($CaHPO_4$), a major component of calcium phosphate cements. Results suggest that

$CaHPO_4$ initiated the formation of the apatitic phase by surface nucleation. On the other hand, solution parameters, such as pH and supersaturation, controlled the time required to complete the hydrolysis as well as governed the crystalline texture of the apatitic product.

Previous infrared and Raman vibrational assignments of the biologically important compound octacalcium phosphate (OCP) were reevaluated; new assignments and reassignments of many bands were made. These assignments were utilized to establish details of OCP structurally modified by incorporation of foreign ions. This study also revealed that two polymorphic forms of OCP may exist.

A series of new biologically relevant compounds, octacalcium phosphate carboxylate (OCPC) containing six different structurally incorporated carboxylates (succinate, adipate, suberate, sebacate, fumarate, and citrate), were characterized in detail by x-ray diffraction, infrared and Raman spectroscopy, scanning electron microscopy, and chemical and thermogravimetric analyses. Some of these OCPCs, ones containing carboxylates that are in the Krebs cycle, may form in vivo and may have important biological roles.

Recently, it was shown that fast-setting, strong cements could be prepared from calcium phosphate cement (CPC) powders (mixtures of tetracalcium phosphate and dicalcium phosphate) and poly(alkenoic acids), e.g., poly(acrylic acid). Additives were required to control the fast rate of setting of this new cement. In a more recent study, the aqueous based reactions of CPC powders with a less reactive polyacid, the hydrolyzed version of a 1:1 copolymer of methyl vinyl ether and maleic anhydride, were investigated. Several new types of polymeric calcium phosphate cements (PCPC) were derived from the acid-base reaction of the carboxylic acid segment of the poly(methyl vinyl ether-maleic acid), PMVE-Ma, and CPC powder. Cements prepared from the CPC powder and 30% w/w aqueous solutions of PMVE-Ma were tough and had high diametral tensile strengths, e.g., 13.6(1.2) MPa, and compressive strengths, e.g., 65.8(4.4) MPa, after 24 hours storage in distilled water at 37°C. The setting times, which were longer than those of poly(acrylic acid) based PCPC, were dependent on the concentration of the aqueous polymer, the composition of the powder and the powder/liquid ratio. The formation of hydroxyapatite in reacted PCPC was not detected by powder x-ray diffraction methods and was apparently inhibited as a result of the competing setting reaction of PMVE-Ma with CPC powder.

OUTPUTS/INTERACTIONS

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Technical and Professional Committees: Leadership Activities

Academy for Dental Materials
    J.A. Tesk, Member, Long Range Planning Committee

Academy of Operational Dentistry
    F.C. Eichmiller, Chairman of Research Committee

Adhesion Society
    D.L. Hunston, Vice President

American Academy of Gold Foil Operators
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American Academy of Implant Dentistry
    J.A. Tesk, J. Oral Implantology, Editorial Board

American Association for Dental Research - Washington Section
    F.C. Eichmiller, Past President

American Ceramic Society
    L.A. George, Member, Pre-College Education Committee

American Chemical Society
    J.M. Antonucci, Councilor

American National Standards Committee, MD 156, Dental Materials, Instruments, and Equipment
- J.M. Antonucci
  - Observer-Participant, Task Force on Posterior Composites
  - Observer, Task Force on Dental Gloves
- R.L. Bowen
  - Secretary, Subcommittee on Biological Evaluation of Dental Materials
  - Member, Subcommittee on Direct Filling Resins
- F.C. Eichmiller, Chairman, Subcommittee #39 on Pit and Fissure Sealants
- J.R. Kelly, Chairman, Subcommittee #38 on Porcelain-Metal Systems
- J.A. Tesk
  - Member, MD 156
  - Member, Subcommittee #38 on Porcelain-Metal Systems
  - Chairman, #14, Base Metal Casting Alloys
  - Observer, #5, Dental Casting Alloys
  - Observer, #40, Dental Implants
  - Member, Task Force on Posterior Composites

Vice Chairman, Terminology

American National Standards Institute
  J.A. Tesk, Member, Medical Device Standards Board

American Physical Society
  G.B. McKenna, Past-Chairman, Division of High Polymer Physics
  C.C. Han, Executive Committee, Division of High Polymer Physics

American Society for Composites
  D.L. Hunston, Member, Executive Board

American Society for Testing and Materials (ASTM)
  F.E. Brinckman
    Member, E-34 Occupational Health and Safety
    Member, E-47 Biological Effects and Environmental Fate
    Member, E-48 Biotechnology
    Member, E-48.03-07 Subcommittee on Ore Bioleaching
  F.W. Wang
    Member, D-20 Plastics
    Member, D-20.95 Recycled Plastics
    Member, D-20.96 Environmentally Degradable Plastics
    Member, G-3 Durability of Non-Metallic Materials
    Member, G-3.05 Reference Materials for Exposure Tests
  S.S. Chang
    Member, D37 Thermal Measurements
    Member, D37.01 Test Methods
    Member, D37.05 Thermophysical Properties
  M. Farahani
    Voting Member, E10.01
    Referee for "Radiation Physics and Chemistry Journal"
    Referee for "Journal of the European Society for Therapeutic Radiology and Oncology"
  C.M. Guttman
    Member, D20.30 Thermal Properties
    Member, D20.70 Analytical Methods
    Member, E-37 Subcommittee on Thermal Analysis
    Chairman, Task Group on Purity Standards and Methods
  D.L. Hunston
    Member, D30 High Modulus Fibers & Their Composites
  G.B. McKenna
    Member, D-11 Rubber and Rubber-like Materials
    Member, E-9 Fatigue

Applied Organometallic Chemistry, International Journal
    F.E. Brinckman, Member, Editorial Board

ASM International
    R.M. Waterstrat, Fellow
        Member, MSD Thermodynamics and Phase Diagrams Committee

Armstrong World Industry
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Calcified Tissue International
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Center for Molecular and Microstructure of Composites
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        Member, Long Range Planning Committee

Chesapeake Bay Research Consortium, Inc.
    F.E. Brinckman, Member, Toxics Research and Development Panel

Comite International Permanent pour La Recherche Sur La Preservation des Materiaux en Milieu Marin (COIPM)
    F.E. Brinckman, NIST Delegate
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Composite Manufacturing
    D.L. Hunston
        Member, International Editorial Advisory Board

Defense Nuclear Agency
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Drexel University
    A.J. Bur, Member, Injection Molding Thesis Review Committee

Gordon Research Conference: Science of Adhesion
    J.M. Antonucci

Member of the Council of the Gordon Research Conferences

Gordon Research Conference: Calcium Phosphates
- L.C. Chow, Co-chairperson, 1992

Great Lakes Composites Consortium
- D.L. Hunston, Member, Technical Advisory Board

Institute of Electrical and Electronic Engineers (IEEE)
Conference on Electrical Insulation and Dielectric Phenomena
- A.S. DeReggi
  - Member, Board of Directors
  - Member, Executive Committee
  - Chairman, Digest Committee
  - Editor, Digest of Literature on Dielectrics

Interagency Oral Health Research Group
- J.A. Tesk, Member
- F.C. Eichmiller, Member

International Association for Dental Research
- J.M. Antonucci
  - Member, Executive Committee, Dental Materials Group
  - Archivist, Dental Materials Group
  - Member, Souder Award Committee
- N.W. Rupp, Past President, Dental Materials Group
- J.A. Tesk, Treasurer, Dental Materials Group

International Council on Alloy Phase Diagrams
- R.M. Waterstrat, Member

International Journal of Adhesion & Adhesives
- D.L. Hunston, Member, International Advisory Editorial Board

International Journal of Chemical Speciation and Bioavailability
- F.E. Brinckman, Member, Editorial Board

International Standards Organization
TC106, Dental Materials and Devices
- F.C. Eichmiller, Pit and Fissure Sealants
- J.A. Tesk
  - Member, U.S. Expert, SC-2, WG-1 on Porcelain-Metal Systems

TC150, SC-2 on Cardiovascular Implants, Advisor to TAG

Journal of Alloys and Compounds
    R.M. Waterstrat, Member, Editorial Board

Journal of Operative Dentistry
    F.C. Eichmiller, Member, Editorial Review Board
    P.S. Bennett, Member, Editorial Review Board

Journal of Polymer Science, Physics Edition
    G.B. McKenna, Member, Editorial Review Board
    C.C. Han, Member, Advisory Board

Journal of Rheology
    G.B. McKenna, Member, Editorial Review Board

Materials Research Society
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Measurements for Polymer Processing Consortium
    A.J. Bur, Member, Oversight Board

Metallurgical Society AIME
    R.M. Waterstrat, Member, Committee on Alloy Phases

National Academy of Science/National Research Council
Organotin Research Panel
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National Cancer Institute
    J.A. Tesk, Consultant

National Institute Dental Research
    J.M. Antonucci
        AD HOC Reviewer of NIDR Grants
        Chairman, Special Study Sections for Small Business Innovative Research
        (SBIR) Grant Applications, Reviewer for SBIR Site Visits

National Institutes of Health
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National Science Foundation Advisory Board, Regional NMR Facility at Colorado State University
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National Society of Professional Engineers

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    W.R. Rupp, Lecturer
    F.C. Eichmiller, Lecturer

University of Lowell
    F.W. Wang, Member, Plastics Advisory Group

VAMAS
    D.L. Hunston, Member, Technical Working Party on Polymer Composites

Industrial and Academic Interaction

Industrial

A Cooperative Research Agreement has been signed with **Michigan Molecular Institute** to study the size and shape of polyamidoamine dendrimers by small angle neutron scattering.

A NIST/industry consortium, "New Measurement Technology for Polymer Processing" has been established to develop 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 Flow Vision.**

In collaboration with scientists from **AT&T** a fluorescence technique has been developed to monitor the formation of polyimides from their precursors.

Under a Research Associate Program with **Enimont America** a fluorescence method for in-line monitoring of a microwave cure process is being developed.

The NIST Small Angle X-ray and Pole Figure Facility continues to be a resource for the U.S. Industry. The level of use increased approximately 50% during the past year and projects on various aspects of effects of processing on the SAXS measured structure of polymers were performed with **Amoco, Gillette Research Lab, Hercules, Inc., Hoechst-Celanese, Mobil Chemical Company, Raychem Corporation, Shell Oil Company and Sonoco Corporation.**

Collaborative studies of the yield behavior of glassy polymers were undertaken with **Xerox.**

A Workshop was organized on "Aging, Dimensional Stability and Durability Issues in High Technology Polymers." Participants from **17 U.S. companies** as well as several government agencies, National Labs and private research foundations attended.

In collaboration with **Eastman Kodak Corporation** a project was initiated to study the effects of moisture on the viscoelastic response of poly(ethylene terephthalate)(PET) films.

In cooperation with **IBM Corporation** and **MTI Industries** a non-contact method has been developed for measuring the coefficient of thermal expansion (CTE) in the film thickness direction and for measuring film thicknesses, both quantities of interest in electronic packagings applications.

A guest scientist from **Xerox Corporation** is engaged in a study of the evolution of the yield response of a copolymer glass after a quench from above to below the glass transition. The copolymer, polystyrene-poly(n-butyl methacrylate), is used in toner applications and the yield stress is related to the processing of the polymer into a fine powder for toner applications.

An investigation of interfacial degradation in glass fiber reinforced polymer composites involves the **Automotive Composites Consortium**, in order to define the types of resins, fiber and environment, and **Owens Corning Fiberglass, Dow Chemical** and **Dow Corning** as suppliers of model and industrial grade glass fiber, resin and coupling agent systems, respectively.

NIST and **E. I. duPont de Nemours and Company** have initiated a joint program to study the polymer/solid interface and to address the fundamental problem of packing density and interchain diffusion near a flat substrate. DuPont is supplying specialized model materials for the study which takes advantage of the new interface characterization technique based on neutron reflectivity developed by NIST. The results of the study will help identify processing conditions that optimize interface properties in composites, coatings, adhesives, and electronic packaging systems.

A collaborative program with the **Dow Chemical Company** has been initiated to study the effect of morphology on fracture behavior of the two-phase, toughened thermosets that are important for composites and adhesives. Dow is providing some unique model materials where the morphology can be systematically varied and is characterizing the morphology of these materials. NIST is conducting fracture experiments and utilizing its expertise in toughening mechanisms to help establish structure-property relationships. The results will provide generic guidelines for the development of improved materials.

A joint program was conducted with **Ford Motor Company** to examine the role of stitching threads as possible crack initiation sites in composites made from fabric layers stitched together. Ford believes a poor fiber-matrix bond may be the source of the cracks. NIST is using its facility for measuring the fiber-matrix interface strength to examine samples with different fibers and fiber surface treatments provided by Ford. Ford is examining composites made with these fibers to assess cracking. The results should provide guidelines for producing more crack resistance composites.

An on-going cooperative research program between NIST and **General Electric Corporate Research & Development Laboratory** has been expanded to include interaction with the Advanced Technology Program (ATP) of GE and the **Ford Motor Company**. The ATP effort is seeking to commercialize the technology of a polymerizing thermoplastic matrix material for composites. The process involved is resin transfer molding so accurate measurement of reinforcement permeabilities is essential to optimize the process. The NIST permeability measurement facility and expertise in this area are providing the required test methods and permeability data for the program.

The cooperative program with the Automotive Composites Consortium (ACC) formed by **Ford, Chrysler and General Motors** continues. In this effort, NIST uses its process simulation models to predict mold filling for parts of interest to the ACC. NIST also measures the permeability data required for the analysis. The ACC provides equipment in support of NIST's experimental work, details on the part design, and feedback on the validity of the predictions from the simulation. The goal is to develop the technology needed to optimize tool design and processing conditions through computation rather than expensive and time consuming experiments.

A new program was initiated with **Grumman Aircraft** to extend the process simulation capability for fabrication of structural composite parts by liquid molding to commercial aerospace applications. Grumman will test and evaluate the finite element codes developed by NIST through comparisons with flow visualization experiments and the fabrication of parts. NIST will use the results to refine and improve the models.

NIST is working together with **Chrysler Corporation** to evaluate the applicability of NIST's process simulation models for liquid molding to the injection molding process. Chrysler is providing NIST with feedback on how well the modeling predictions agree with experimental measurements.

A Cooperative Research and Development Agreement has been established with the **National Center for Manufacturing Science** on the nature of the two phase morphology of interpenetrating polymer networks. One of the phases is produced from sol-gel chemistry based on organo-silicon compounds. The potential applications are to produce new materials for printed wiring boards. SANS studies have already started in collaboration with **Sandia Labs**, a consortium member of NCMS.

A Cooperative Research Agreement has been signed with **Armstrong World Industries** to initiate a joint program studying 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 understand viscoelasticity, as it affects extrusion and foaming of rubber foam insulation.

Collaborative research among **Goodyear, Sandia Labs** and NIST on the subject of elastomer blends involves SANS studies of the chemical microstructure effects on the miscibility of elastomer blends. NIST expertise on this subject are heavily relied upon in this technologically important subject.

A NIST/Industry polymer blends consortium is being formed. This consortium will emphasize work on the polymer blend properties of mixing/demixing under shear flow as well as methods of understanding and characterizing the interface. An initial workshop was held in April, 1992 with 49 attendees from industrial companies, NIST and other research institutes. A final meeting for the formation of the consortium is planned for February 26, 1993.

Cooperative research with **GE** on the morphology and phase separation studies of the reactive polymerization system of cyclic polymers has started. **GE** fellow, Dr. Roger

Kambour will spend 8 months in the Division and work with the staff on this technologically important polymer system.

Dentsply International placed a guest scientist to work inthe Dental group to observe processing technology with a view toward future licensing of a patent on cyclopolymerizable monomers.

A Dental Group scientist took a lead role with American dental industry to incorporate changes to an ISO committee draft that had held classes that would have had severe negative impacts on exporting of some American dental casting alloys.

The Dental Group provided the initial leadership for efforts to form a consortium with American dental companies for the development of a mercury free, direct-filling, metallic restorative.

Two dental companies, **BISCO** and **Pulpdent**, signed agreements for licensing of adhesive technology developed by American Dental Association Health Foundation (ADAHF) in the dental group.

Jiniru Pentron provided funding to the ADAHF for work on electroposition of dental alloys.

Enamelon, a new start-up company, licensed a patent from the ADAHF for the marketing of remineralizing chewing gum.

Industrial/Academic

A cooperative research program on the subject of polyolefin blends among NIST, **Exxon** and **Princeton University** has been carried out intensively in the past two years.

Academic

A grant to **Drexel University** supports development of optical and ultrasonic techniques to measure resin flow front velocity, mold filling time, resin solidification, resin temperature, part shrinkage, and resin modulus.

Professor K. F. Lin, **National Taiwan University**, participated in the development of a fluorescence technique, based on frequency shifts, to measure curing of thermosetting resins. The approach has the advantage that no internal standard is needed.

A collaborative project with the **University of Maryland Baltimore** funded by the EPA addresses the stability of well-characterized lead solutions in polycarbonate bottles. The solutions are used in toxicology studies at the **University of Maryland**.

Staff at the **University of Massachusetts Lowell** collaborates on the development of an in-line method for monitoring the uniformity of mixing in blends of recycled plastics.

Professor H. Marand of **Virginia Polytechnic Institute and State University** joins in the study of the fine texture of crystallizable polymer blends.

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 visiting scientist from **Ecole des Mines, Nancy, France** participated in a study of volumetric and viscoelastic responses in polymer glasses subjected to temperature jumps.

A collaboration with **Tel Aviv University** investigates failure mechanisms in adhesive joints by analysis of experimental results by elasto-plastic finite element methods.

A collaborative program has been initiated with the **University of Delaware** to investigate the polymer/solid interface in composites. Pearl Chin, a PhD student of Prof. Roy L. McCullough, uses the NIST-developed neutron reflectivity technique to determine the polymer microstructure near the interface. 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.

NIST cooperates with **Johns Hopkins University** to develop on-line process monitoring for the liquid molding process. Process monitoring is a key technology to facilitate automated process control. Dara Levy, a PhD student with Prof. John Hoffman, is developing a fiber optic fluorescence sensor capable of monitoring both flow front position and cure. The sensor will be installed and tested on the liquid molding equipment at NIST, and NIST's expertise in process monitoring and liquid molding will be used to help develop a viable on-line process control system.

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 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.**

A joint project with Professor N. Tsutsumi of the **Kyoto Institute of Technology** investigates polymer blends as host materials for non-linear optically active guest molecules.

The Dental and Medical Materials Group participated in collaborative reserach efforts with scientists from the following academic institutions: The **University of Geneva** and the **Eidgenossiche Technische Hochschule** (Switzerland), the **University Louis Pasteur** (France), **Nihon University** (Japan), **Fukuoka Dental College** (Japan), **Kyushu University** (Japan), **Tokushima University** (Japan), the **Rudjer Boskovic Institute** (Yugoslavia), the **University of Iowa**, **University of the District of Columbia**, **Northwestern University**, the **University of Maryland**, the **University of Florida**, the **Oregon Health Sciences University**, **Taiwan University**, **Howard University**, the U.S. Navy Dental Research and Development Command, the **University of Strasbourg** (France), **McGill University** (Canada) and the **West China University of Medical Sciences.** Research projects including studies of stress in porcelain-metal and other dental bonded systems, new coupling agents for dental composites, postcure properties of dental composites, polymeric calcium phosphate cements, synthesis and characterization of novel fluoro and siloxane monomers and oligomers, implants biomineralization, and calcium phosphate chemistry.

Associated Activities

Invited Talks

Division personnel presented a total of 93 invited talks on research activities at the following types of organizations and symposia: industrial laboratories, 13; international symposia, 8; universities, 26; topical symposia, 4; national and government laboratories, 15; professional society meetings, 20; and Gordon Conferences, 7.

SRMS and Patents

Method for Detecting Polymer Solidification during Injection Molding. A.J. Bur, F.W. Wang, C.L. Thomas and J. Rose, (Pending)

Dental Resins Comprising Cyclopolymerizable Monomers. J.W. Stansbury. Patent No. 5145374, issued September 8, 1992.

Novel Multifunctional Acrylates and the Synthesis Thereof. J.M. Antonucci, J.W. Stansbury, and Guo Wei Cheng, Patent filed, PTO serial number 828,316.

Optical Sensor for the Measurement of Molecular Orientation and Viscosity of Polymeric Materials Based on Fluorescence Radiation., A.J. Bur, C.L. Thomas, R.E. Lowry, F.W. Wang and S.C. Roth. Patent No. 5,151,748, issued September 29, 1992.

Hydrofluoroalkyl-Substituted Styrenes and Polymeric Compositions Containing Same., C.C. Han, Y. Feng and M. He, Patent filed, PTO serial no. 985,932.

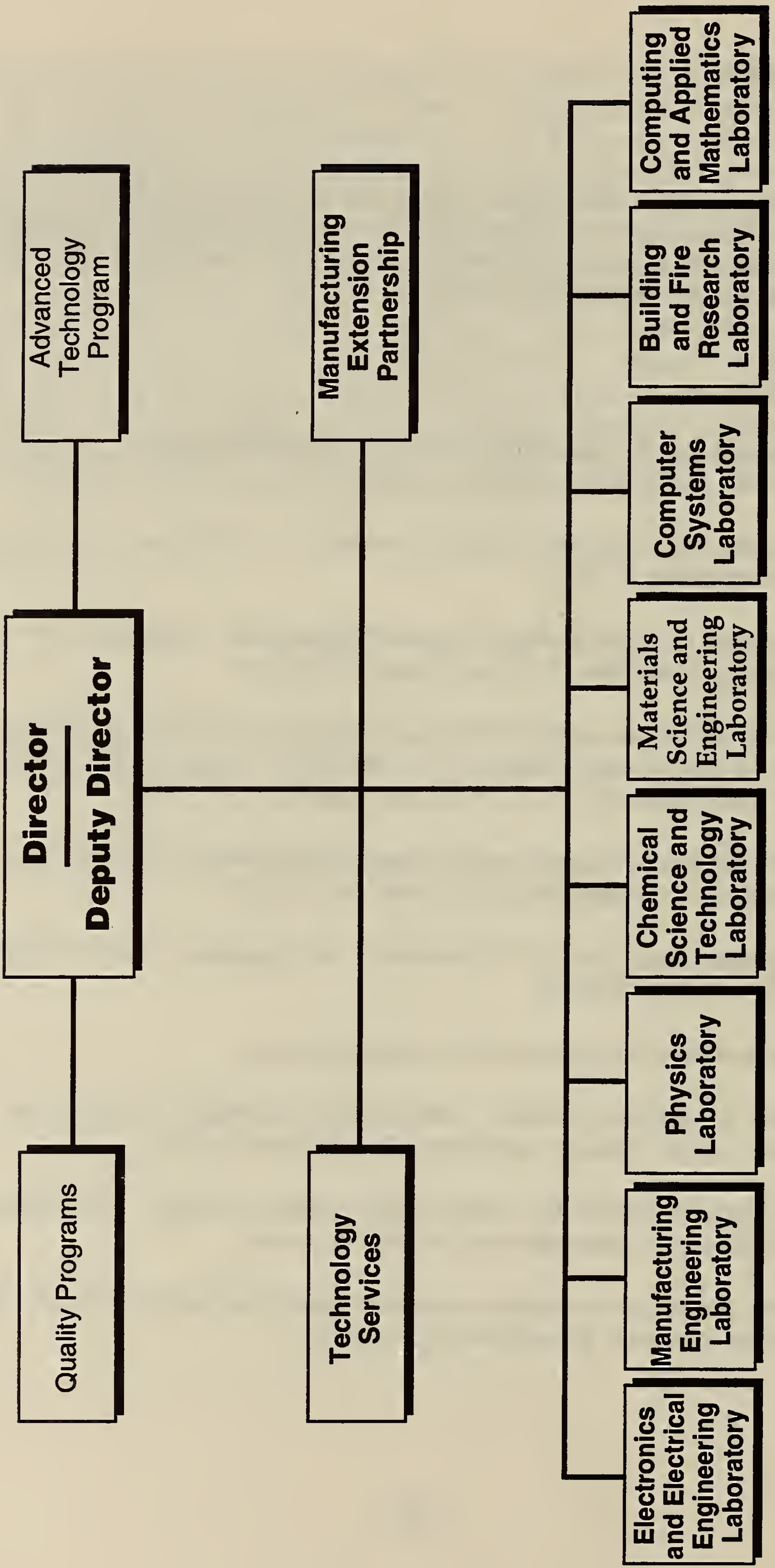
Monomers for Double Ring-Opening Polymerization with Expansion., J.W. Stansbury, Patent filed, PTO serial no. 846,480.

SRM 1473 Branched polyethylene certified for melt flow rate.

SRM 1475 Linear polyethylene, reissued. This material is certified for number and weight average molecular weight, limiting viscosity number and melt flow rate.

SRM 1480 Polyurethane certified for weight average molecular weight. The intrinsic viscosity of this material in tetrahydrofuran was also measured.

SRM 1484 Linear polyethylene of narrow molecular weight distribution reissued. This material is certified for weight average molecular weight.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Deputy Director
Quality Programs
Advanced Technology Program
Technology Services
Manufacturing Extension Partnership
Electronics and Electrical Engineering Laboratory
Manufacturing Engineering Laboratory
Physics Laboratory
Chemical Science and Technology Laboratory
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Computer Systems Laboratory
Building and Fire Research Laboratory
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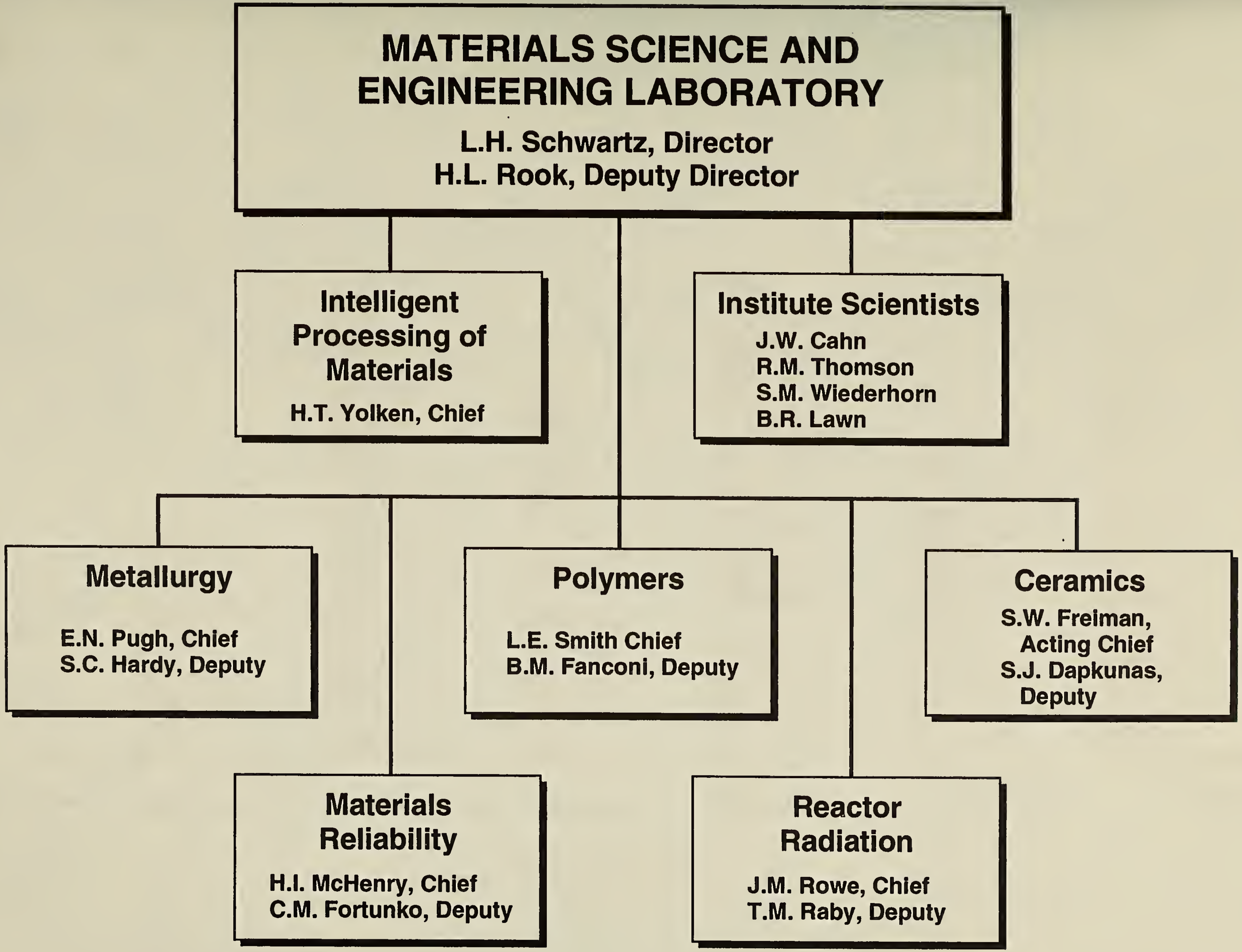
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H.L. Rook, Deputy Director
Intelligent Processing of Materials
H.T. Yolken, Chief
Institute Scientists
J.W. Cahn
R.M. Thomson
S.M. Wiederhorn
B.R. Lawn
Metallurgy
E.N. Pugh, Chief
S.C. Hardy, Deputy
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B.M. Fanconi, Deputy
Ceramics
S.W. Freiman, Acting Chief
S.J. Dapkunas, Deputy
Materials Reliability
H.I. McHenry, Chief
C.M. Fortunko, Deputy
Reactor Radiation
J.M. Rowe, Chief
T.M. Raby, Deputy

October 5, 1992

POLYMERS DIVISION

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