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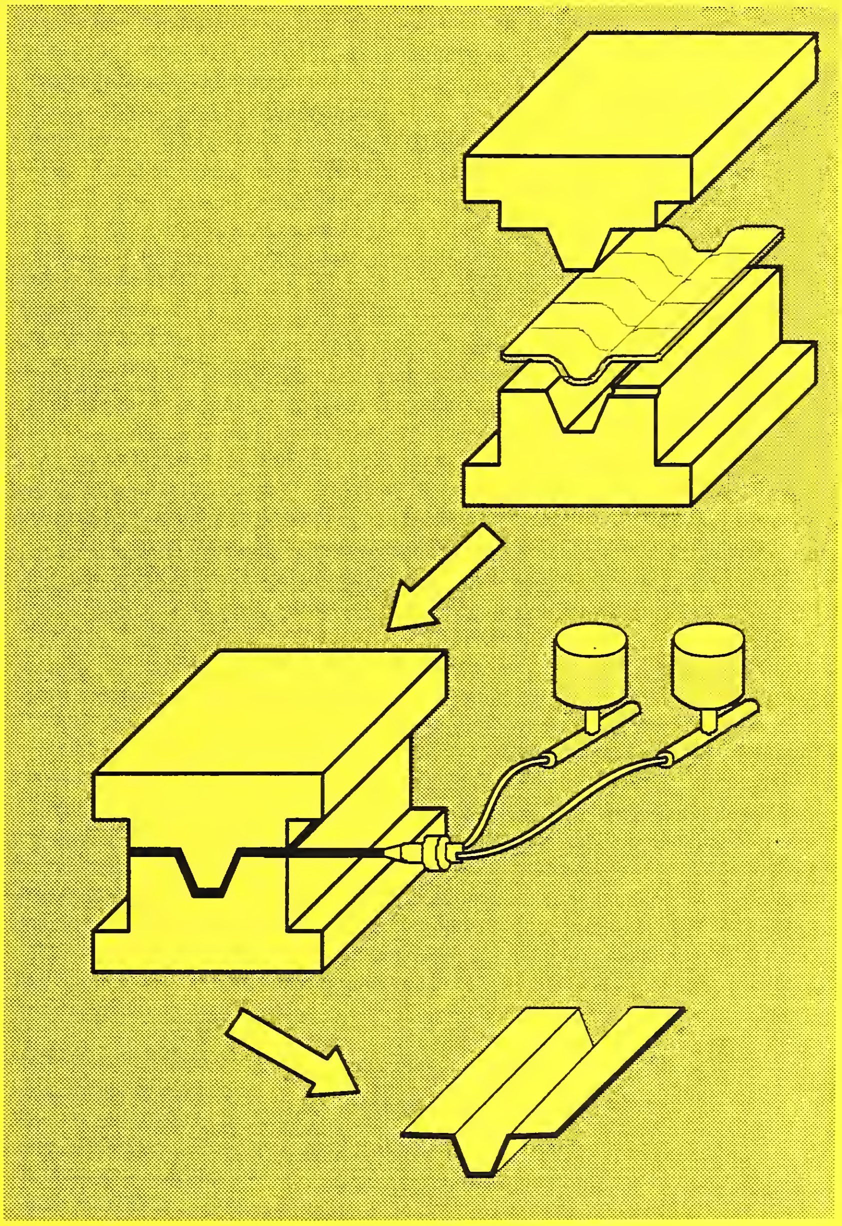
Materials Science and Engineering Laboratory

POLYMERS



NAS-NRC
Assessment Panel
February 13-14, 1992

NISTIR 4696
U.S. Department of Commerce
National Institute of Standards
and Technology

Technical Activities
1991

Fabricating composites by resin transfer molding has the potential for high speed and low cost. NIST is cooperating with the Automotive Composites Consortium to obtain the scientific understanding needed to realize this potential.

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POLYMERS

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

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U.S. DEPARTMENT OF COMMERCE, Robert A. Mosbacher,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 is responsible for providing 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. An assessment of the industry was made during the past year, and became part of the long range plan of the Materials Science and Engineering Laboratory.

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.

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.

The 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, automotive 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. This year we completed development of computer simulations of the flow of polymers in transfer molding processing of thick cross-section structures. Such processes inject a reacting thermoset mixture into a mold containing a fiber preform and the challenge is to predict the pressures and flow front positions in a complex geometry under process conditions. This modeling capability will allow the more rapid and cost effective production of composite parts for many user industries.

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 59 Research Associates and 83 Guest Scientists who together spent over 47 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 7 patents granted or pending on subjects given in the Appendix.

Polymer standards continue to be one of our most important outputs and new standards are under development. One Reference Material was issued last year as described in the Appendix and the development of others are described in the body of the report. 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.

- As part of a Cooperative Research and Development Agreement with the Automotive Composites Consortium, a computer simulation was performed to model resin flow in liquid molding of the front end structure of a Ford Escort. The initial results show the ability of the simulation to predict features like venting locations and clamping forces as a function of injection gate positions, resin viscosity, and preform permeability. Such results provide the information necessary for process optimization.

- A NIST/industry workshop on new measurement technology for polymer processing was carried out. From this workshop, the nucleus of an NIST/industry consortium has evolved for the purpose of developing in-line measurement technology based on optical and fluorescence methods.

- A combined light scattering photometer/rheometer has been constructed to examine phase separation behavior of polymer blends and solutions under the influence of a simple shear field. This device utilizes a cone and plate geometry to generate the shear gradient for torque and normal force measurement and utilizes a special lens system, a charge coupled array detector and an optical multichannel analyzer for steady shear as well as time resolved 2-d light scattering detection. Steady shear as well as kinetics of mixing/demixing after starting and cessation of shear can be studied.

- A unique new tool has been developed to study the physics involved in the adhesion between a polymer and a solid surface like glass. The technique, based on neutron reflectivity, was shown to provide data on the density of molecular segments near such an interface. The theoretical framework to interpret the reflectivity results has also been developed.

- The distribution of polarization in poly(vinylidene fluoride) poled by corona discharge rather than by contacting electrodes indicates positive charge injection near the surface. This effect is expected to be of significance in non-linear optic materials which are usually poled in a corona discharge.

- Proton spin diffusion results indicated domain sizes in poly(butylmethacrylate)/ hydroxy modified polystyrene blends with minimum dimensions in the 6 - 10 nm range and stoichiometries of the order of 75/25.

- Novel, siloxane-containing difunctional and multifunctional vinyl monomers were prepared based on a modification of the method used for the synthesis of analogous hydrocarbon and fluorocarbon cyclopolymerizable monomers.

- The apparent "shift" in polymer blend phase separation temperature, T_c, under shear flow has been interpreted with the mode-coupling theory for mean-field polymer blend systems. This hydrodynamics theory predicts no true shift of T_c; the apparent shift of T_c along the flow direction arises from suppression of fluctuations along the direction of flow. Upon dilution of the polymer blend, fluctuation effects become important and mean-field theory no longer applies. The shift in T_c in diluted blends is consistent with a crossover from mean-field to Ising critical behavior upon dilution.

The combination of detailed scattering data and the hydrodynamic theory allows for a rational interpretation of polymer blend phase separation subject to deformation.

- The two common methods to measure permeability, radial flow experiments and unidirectional flow experiments, have for the first time been shown to produce equivalent results. In tests with a number of different preform materials, the radial flow behavior was successfully predicted from measurements in unidirectional flow.

- An exposure technique that rapidly determines whether or not a polymer is biodegradable has been developed. The method gives positive or negative results in less than one week as compared to the several weeks or months required for other exposure techniques.

- Instrumentation has been set up and calibrated to measure the dielectric constant of thin polymer films at high electric fields. A two-fluid capacitance cell which yields data on dielectric constant and thickness of polymer films proved valuable in providing films of known properties for calibration.

- A viscoelastic model of stresses in porcelain-metal strips has shown a relationship between the temperature at which stress first develops in porcelain and the differences in thermal expansion between porcelain and metal.

RESEARCH STAFF

Antonucci, Joseph M.	o Synthetic and polymer chemistry o Dental composites and cements 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
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, Laurence 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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* Research Associate

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
Douglas, Jack F.	o Theory on polymer solutions 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
Eidelman, Naomi N.*	o Atherosclerotic plaque

*Research Associate

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
Goodman, Claude[*]	o Gas plasma sterilization
G'Sell, Christian J.[+]	o Mechanical behavior of polymer glasses o Thermosets
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

[*] Research Associate
[+] Guest Scientist

Herrera-Franco, Pedro[+]	o Composite mechanical properties o Stress analysis o Composite failure behavior
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 X-ray diffraction o X-ray line shape analysis o Structure of physical gels o Microcellular foams morphology
Jameson, A. Keith[+]	o ^{129}Xe NMR of porous materials
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 o Bioprocessing
Johnston, Allen D.[*]	o Nuclear magnetic resonance o Mossbauer studies o Chemical adhesion

[*] Research Associate
[+] Guest Scientist

Keeny III, Spurgeon M.	o Gas plasma sterilization o Mechanical testing o Tribiology, dental materials o Polymerization shrinkage o Fluorescence studies o Curing of polymers o Coupling agents
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
Kikuchi, Hisaji[+]	o Dental composites
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
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

[*] Research Associate
[+] Guest Scientist

Matsukawa, Shiochiro[+]	o Fracture behavior of polymers o Structure-property relationships o Dental materials
Matsuya, S.[+]	o Calcium phosphate cement o Adhesion
Matsuya, Yoko[+]	o Dental cements
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
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
Muller, Robert[*]	o Denture base materials o Soft liners

[*] Research Associate
[+] Guest Scientist

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
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

[*] Research Associate
[+] Guest Scientist

Rupp, Nelson W.[*]	o Clinical dentistry o Amalgams o Direct golds o Dental standards o Composites o Titanium castings 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
Schen, Michael A.	o Living polymer synthesis o Polymers for non-linear optics o Molecular electronics o Optical spectroscopy
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

[*] Research Associate
[+] Guest Scientist

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
Tilstra, Luanne F.	o Polymer biodegradation o Time-resolved fluorescence spectroscopy o Solution properties of polymers o Biotransformation of polymeric materials
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
Venz, Sabine*	o Clinical dentistry o Dental composites o Dental polymers
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

*Research Associate

Waldow, Dean A.	o Shear light scattering o Forced Rayleigh light scattering o Polymer blends o Polymer diffusion
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
Zapas, Louis J.	o Continuum mechanics and rheology o Non-linear mechanical behavior of polymers o Static fatigue of plastics o Finite elasticity (rubbers)

SPECIALTY POLYMERS

The task of the Specialty Polymers Group is to characterize the properties of polymers for special applications as well as to synthesize new polymers for specific applications. Examples of research on polymers for special applications include electric cable insulation, high energy density capacitors, new resins for intaglio printing inks, polymer systems for non-linear optics, and piezoelectric and pyroelectric polymers. Two measurement techniques developed at NIST play a central role in these investigations, namely the time domain dielectric spectrometer and the thermal pulse apparatus for determining charge or polarization distribution in dielectric films. Improvements in the instrumentation are being made concurrently with use of the instruments for research.

Changes in dielectric spectra at frequencies between 10^4 and 10^{-3} Hz which are readily accessible in the time domain measurement, have proven especially useful for detecting damage in electrical cable insulation and for following the cure of thermosetting resins. Changes in cable insulation subjected to ac voltage stresses have been detected by measurement of voltage-induced charge injection and the kinetics of its subsequent decay in the thermal pulse apparatus. The sign and quantity of charge injected into polymer films can be modified by the introduction of additives designed to reduce the formation of electrical trees. These investigations on electrical insulation have been carried out as part of other-agency contracts and through cooperative research programs with industry and universities.

In two programs sponsored by the Bureau of Engraving and Printing, BEP, resins are designed and synthesized for cylinder wipe, air-dry intaglio printing inks*and the use of gel permeation chromatography is explored to detect differences in production inks which might also correlate with performance during printing and with durability of the printed currency. Considerable progress has been made in determining the composition of alkyd resins required to impart water-dispersibility, acceptable air-dry kinetics, and appropriate viscosity. Other requirements for an acceptable ink can be met by additives commonly used in ink formulations such as wax to improve set-off characteristics and tung oil to increase cross-linking and improved resistance to alkali. Full scale press trials using a NIST-developed resin showed that it performed satisfactorily as an intaglio ink varnish when properly formulated. Resins based on this composition are believed to be ready for further scale-up production which must be done in an industrial pilot plant. In the chromatography investigation, differences between resins in some batches of ink can be distinguished clearly, but no attempts have yet been made to correlate these results with performance on the press, or the durability of the printed currency.

Certain commercial materials and equipment are identified in this report to specify the experimental procedures. In no instance does such identification imply recommendation or endorsement by the National Institute of Standards and Technology or that the materials and equipment identified are necessarily the best available for the purpose.

Second order, non-linear optical properties are being imparted to polymers by dissolving in them molecules with known NLO properties, or by incorporating appropriate moieties as side chains in glassy amorphous polymers. In either case, asymmetry must be introduced by application of high electric fields at temperatures above T_g which preferentially aligns the dipoles of the NLO component. This alignment is frozen in by cooling below T_g before removing the electric field. Dielectric properties obtained from time domain spectroscopy are used to predict the degree of alignment that should be achievable as well as to study the kinetics of the dipole orientation. Thermal pulse measurements are used to assess the distribution of alignment (polarization) across the thickness of the polymer film as a function of the poling conditions and subsequent ageing conditions. An understanding is sought of the factors which determine the long term stability of dipolar alignment which is very important to the development of NLO polymers.

The electronics for measuring hysteresis loops on ferroelectric polymers has now been interfaced to a personal computer. During the past year, the equipment has been used in a cooperative program with the Naval Surface Warfare Center to study polarization in polymorphic crystal forms of Nylon 11. Poled films of Nylon 7 and Nylon 11 offer the possibility of higher temperatures of use than poly(vinylidene fluoride), PVDF, transducers.

FY 91 Significant Accomplishments

- The 55-gallon drum of NIST-developed resin supplied to BEP for press trials as an intaglio ink by Superior Varnish and Drier Co. did not have the desired high molecular weight components because the time-temperature regimen specified could not be met in the scaled-up synthesis. Nevertheless, an intaglio ink with acceptable press characteristics and satisfactory resistance was prepared by formulation with tung oil and wax, components that are frequently used in printing inks.

- Time domain dielectric spectroscopy has been used to study the sub T_g relaxation of NLO dyes in PMMA and PS. The time scale and temperature dependence of the "guest" dye relaxation are essentially the same as those observed for the polymer "host" matrix.

- The distribution of polarization in PVDF poled by corona rather than by contacting electrodes indicates positive charge injection near the surface. This effect is expected to be of significance in non-linear optic materials which are usually poled in a corona discharge.

- Instrumentation has been set up and calibrated to measure dielectric constant of thin polymer films at high electric field. A two-fluid capacitance cell which yields data on dielectric constant and thickness of polymer films proved valuable in providing films of known properties for the calibration.

AUTOMATED DIELECTRIC MEASUREMENTS

F. I. Mopsik

Instrumentation

The increased use of the NIST-designed and built Time Domain Spectrometer has added emphasis to the program to modernize the data acquisition and control of the instrument.

The work this year has centered around the design and construction of a replacement interface box. The design of this box has now progressed so that the entire measurement can take place under its control without any computer supervision except for setting up its configuration and starting a measurement. This capability has become more desirable with the newer high-speed acquisition card that now has true dual-port data memory that can be accessed at any time by the PC no matter what the state of the board. This memory is more than sufficient to hold an entire data set. Transfer rates in excess of 2 Mb/s have been demonstrated with this board. It now allows the computer to act only as a supervisor, checking the current status of the measurement without any difficult real-time demands. It has also greatly simplified the program requirements for acquisition and transfer of data. The interface box has been redesigned for this board to ensure compatibility with the new board's I/O bus. It is awaiting final test of the address decoder circuits which will mark completion of all hardware tasks. The new software for the board has been written and tested. Also, the screen graphics programs, including the necessary printer dumps for data presentation for the running acquisition program have been completed.

Thin Films

This year, tasks have arisen that require calibration of electrical measurements on thin films. The two-fluid thin-film dielectric cell has been restored to provide this capability. By means of four capacitance measurements: air, air+sample, second liquid, second liquid+sample, the film thickness and dielectric constant can be derived. No independent, contacting means for determining the thickness is required.

This cell has rigid, guarded electrodes with a well-defined area. The spacing is rigidly maintained by a set of shims so that the gap can be adjusted. Also, the cell body can act as a fluid reservoir and is grooved so that a film holder can be used to reproducibly insert a film sample between the electrodes. Film holders were designed and built. An analysis was made for the propagation of error in the measurement so that confidence limits for any given measurement combination of sample thickness, sample dielectric constant and second fluid dielectric constant could be evaluated. Several films varying in dielectric constant from that of polypropylene (2.2) to that of poly(vinylidene fluoride) (10.5) were measured and the results used to calibrate other measurement configurations.

Finally, instrumentation was designed so that high field dielectric constants of films could be measured in a three-terminal configuration with a charge amplifier as the detector. The system has been assembled and calibrated with an overall estimate of accuracy of 5%.

Reactor Cable Insulation Testing

The measurements on a set of cables furnished by Électricité de France, EDF, that had been subjected to both thermal and δ irradiation induced aging was completed. The results, obtained by means of the dielectric spectrometer, showed that there was a well defined signature relaxation process in olefin type polymers as a function of radiation aging. This loss process definitely increased with increasing dose and was not overly affected by thermal aging. Re-examination of older data, even where the insulation had large filler induced losses, showed that this loss could be detected. These results indicate that time-domain measurements can be used to assess radiation aging in polymeric insulation of the type used in reactors.

These results have been presented before the Nuclear Regulatory Commission, NRC, and a draft report, incorporating mechanical measurements by EDF has been sent to NRC and EDF for comment.

NONLINEAR OPTICAL MATERIALS

M. A. Schen, A. S. DeReggi, and F. I. Mopsik

The focus of the nonlinear optical (NLO) materials research program in the Polymers Division has been changed to include materials characterization of second-order NLO polymers, while at the same time, de-emphasizing the synthesis of new third-order NLO materials. Most recently, activities have focused on polymer relaxation dynamics as it relates to the diminution of second-order nonlinear optical activity during physical ageing; a phenomenon observed with most second-order NLO polymers.

For some time now, it has been known that non-centrosymmetric assemblies of organic molecules containing highly delocalized, charge correlated π-electrons will exhibit an intensity dependent refractive index as a consequence of a nonlinear polarization of the molecular electron cloud when subjected to high energy pulsed laser radiation. "Benchmark" NLO dye molecules containing intramolecular electron donating and accepting groups that show large second order NLO activity include methylnitroaniline (MNA) and 4-[N-dimethylamino]-4'-nitrostilbene (DANS), for example. Efforts to incorporate molecules such as these into amorphous polymers include the preparation of guest-host or dye-polymer blends and functionalized copolymers.

Numerous reports have shown that for amorphous guest/host or dye functionalized second order (χ^2) NLO polymers, the intensity of the second harmonic signal arising from the preferentially aligned dye molecules diminishes with time after the electric poling field is removed. It is well recognized that the glass transition phenomenon characteristic of amorphous polymers plays a role in affecting the orientational stability of χ^2 dipoles. Results from various groups examining a wide range of guest/host and functionalized materials reveal multi-exponential second harmonic generation, SHG, intensity decay profiles. Torkelson and coworkers conclude that dye orientational mobility relies on the local mobility and free volume within the glass.

Time domain dielectric spectroscopy is used to study the dielectric relaxations of χ^2 nonlinear optical polymers. In these experiments, the real and imaginary components of the complex dielectric permittivity (ε^*) are determined by taking the numerical transform of the sample charge response to an applied step voltage. Our focus has been on the relaxation of DANS, MNA and other χ^2 dyes in poly(methylmethacrylate) (PMMA) and polystyrene (PS) below T_g. PS is viewed to be a near ideal matrix in which to study the dielectric relaxations of χ^2 dyes, such as DANS, because of its nearly non-polar nature and inherently low loss in the glassy state.

Our initial work using PMMA as the host and incorporating ca. 0.2 mole % DANS revealed that inherent sub-T_g losses of the polymer alone precluded direct observation of the dye relaxation. Analysis of the polymer β-relaxation with and without dye did not show strong evidence of dye interaction with the ester group of the polymer. On the other hand, in our studies of PS containing ca. 0.2 mole % DANS and Disperse Red 1 (DR1) - another χ^2 dye - a clearly distinguishable relaxation, ascribed to the dye, can be observed. The studies have shown that the sub-T_g β-relaxation of the dye occurs on the same time scale as the β loss characteristic of the polymer. For DANS, the activation energy for the rate at which this loss is occurring is within error of the reported values for the PS β-transition.

The variation of the β-relaxation with temperature was also found not to follow T^{-1} behavior as predicted by the Onsager equation. At temperatures about 20° below T_g, the dielectric loss begins to rapidly increase indicating that either more dye molecules are participating in the relaxation process or that the angular variation over which each dye molecule is relaxing is increasing. Assuming a mechanism involving the first process, comparison of the experimentally found dielectric loss versus the maximum possible loss assuming free rotation of non-interacting dye molecules indicates that below T_g, 17-20% of dye orientation is lost within a second of ageing due to a β loss process.

Examination of physical ageing at ca. 20° of undercooling for DR1 in PS shows that with ageing time, the β relaxation associated with the dye becomes a more clearly defined semi-circular arc when plotted in a Cole-Cole fashion, implying a narrowing of the relaxation distribution function for the dye. Relative to the decrease in the loss amplitude at low frequencies, which is taken as a measure of the polymer α-transition, it is seen that the amplitude of the sub-T_g dye relaxation for DR1 decreases approximately 10 times more slowly. Consequently, the retention of dye orientation after poling for a polymer guest/host system depends more heavily on the annealing out of long-range, T_g relaxations to longer times or higher temperatures than the diminution of sub-T_g relaxations associated with local segmental motions. Only by choosing very carefully both the chemical structure and molecular architecture of the dye and polymer alike may sub-T_g relaxation amplitudes be reduced.

Currently these studies are continuing by investigating dye functionalized linear copolymers in cooperation with outside investigators. It is our expectation that time domain dielectric spectrometry will continue to be a powerful tool for the study of sub-T_g and T_g relaxations as newer, compositionally more complex NLO materials evolve.

DESIGN AND SYNTHESIS OF INTAGLIO INKS RESINS

B. Dickens, B. J. Bauer, W. R. Blair and R. E. Lowry

NIST is developing prototype ink vehicles for intaglio printing of security documents such as currency at the Bureau of Engraving and Printing, BEP. Because intaglio printing is used only in special cases, commercial activity in developing intaglio inks is limited. Security document inks should cure by crosslinking rather than by solvent evaporation. Current emphasis at BEP is on intaglio ink systems that crosslink on exposure to air. The objective of this project is to provide information on the design and synthesis of resins suitable for such intaglio inks. The air-dry systems are based on drying oil technology.

The properties required of an intaglio resin for adequate performance on the printing presses are: resin viscosity in the region of 6 to 60 Pascal seconds (1 Pa s = 10 poise); inks made from the resin disperse in 1% aqueous sodium hydroxide to which 1% w/w of surfactant has been added; the resin disperses the pigments and other solid fillers to form a stable suspension; uncured inks do not transfer between adjacent sheets of printed paper; and ink ingredients, including resins, are to be of acceptably low toxicity. Low toxicity is an important reason for the emphasis on air-dry technology. In addition, the formulated ink must transfer acceptably from the engraved cylinder to the paper substrate, and, when cured, be resistant to solvents and chemical attack.

Two series of air-dry intaglio inks have already been developed and the best candidate resin in each group has been refined to give acceptable performance in laboratory tests. The first series is based on molecules which resemble extra large drying oil molecules. They were synthesized by esterifying a high polyhydric alcohol (tripentaerythritol) with linseed oil fatty acids and subsequently reacting excess alcohol groups with acid anhydrides to give pendant acid groups. The second series is based on lower polyhydric alcohols which have been made into alkyds.

Dispersion in the alkaline medium used to clean the roller system on the printing press is highly dependent on the formulation of the ink (i.e., on the identity and amounts of the other ingredients) and on the acid number of the resin. The cure is dependent on many factors. Several members of each series of resin passed laboratory tests when formulated into trial air-dry intaglio inks by BEP.

A patent application has been filed for resins based on the first system. The resins in the second system have shown considerable promise. A sample was synthesized industrially in 55-gallon quantity and performed well in press trials at BEP, except that the resistance of the cured film to aqueous caustic was not sufficiently high. Investigation revealed that the industrial synthesis had not been able to follow the temperature program of the laboratory synthesis and had produced a material of too low molecular weight. Recent work has concentrated on incorporating tung oil fatty acids in the resin molecules, changing the temperatures in the two steps of the synthesis of the alkyd to produce a synthesis which is optimized for stability and reproducibility of the product rather than for speed of production, and increasing the molecular weight and viscosity of the resins.

CHROMATOGRAPHIC EXAMINATION OF INTAGLIO INKS, RESINS AND VARNISHES

B. J. Bauer, B. Dickens, and W. R. Blair

Gel Permeation Chromatography, GPC, is investigated as a potential quality control procedure for intaglio printing inks. It has been used to examine soluble ink components in more than one hundred intaglio ink samples supplied by the Bureau of Engraving and Printing (BEP). The ink samples were of black and green intaglio, cylinder wipe inks used in the printing of currency. Currently, the BEP purchases fully formulated inks for printing security documents such as currency and stamps. Many of the quality control tests insuring that the printed documents are acceptable have to conducted on products of a full production run. Failure to pass tests at this stage means destruction of the full press run at considerable expense. If correlations between chromatograms and ink quality can be found, GPC will offer a quick and efficient way of characterizing large molecular size components in ink extracts before the production runs.

Several modifications of equipment and procedures have been made to improve the sensitivity and reliability of chromatographic evaluation of ink extracts. The mass evaporative detector has been upgraded, giving it greatly increased sensitivity. This detector can be used to estimate the amount of extractable, nonvolatile material in the ink resins. For best results, the upgraded detector's sensitivity requires that the tetrahydrofuran (THF) used contain no stabilizer (generally butylated hydroxy toluene). This inhibitor-free solvent stream also gives increased UV sensitivity. However, there was some indication that ink components extracted by unstabilized THF slowly changed over a period of hours, increasing the amount of large molecules. When the extracts were made with stabilized THF, the chromatograms did not change over a period of hours. For this reason stabilized THF is used as the solvent in extractions.

A new UV detector allows for four wavelengths to be monitored continuously from the ink extracts that are being separated by molecular size. The ratios of the output at 230, 240, 254, and 275 nm continuously change in the high molecular size region, indicating that the chemical composition of these large molecules is changing with molecular size. It may be that the ink resins are made up of several components, each with a different chemical composition. The multiple wavelength UV detector and the mass evaporative detector each see a different characteristic of the resin, and thus reveal variations in the ink due to different amounts of different components.

Each batch of commercial ink sent to BEP is packaged in two drums and has a unique identification number. For each batch of ink delivered, a small metal container containing a sample of the ink known as a "retain" sample is sent for the convenience of BEP in running tests. It is assumed that the material in the small containers accurately represents the drum material that is used in the printing of currency. Ink is known to change slowly with time, changing the printing and curing properties. Earlier work in the Polymers Division used GPC techniques to show that over a three month period, there can be important changes in the molecular size of the extractable components. If material in the "retain" samples ages at a different rate than the drum material, then the study of "retains" will not give an accurate picture of the properties of printed ink. Eleven pairs of "retain" and press inks were studied. GPC chromatograms were compared and match factors calculated for every pair. Chromatograms of the ink pairs produced match factors much higher than comparisons of unmatched pairs. Therefore, variations in batch to batch inks are much greater than variations between the "retains" and press samples from the same batch. Thus, there seems to be little advantage to collecting inks from the press for these quality control studies, since the "retains" are similar to the inks in the drums.

Many samples of the current black and green cylinder wipe currency inks were examined by chromatography. The chromatograms were quite different and could be easily used to distinguish between the black and green inks. This suggests that different resins are used to formulate these two different inks. Recently a new green ink formulation was supplied to BEP to replace the old formulation. The new formulation seems more similar to the black formulation than to the old green formulation. Such changes in formulations may be easily detectible by GPC.

A data base is being formed from the chromatograms of many ink extracts which are nominally the same. Comparisons will be made between these chromatographic results and BEP quality control results on the same inks.

ELECTRICAL HYSTERESIS AND FERROELECTRIC POLARIZATION OF POLYMER FILMS

A. S. DeReggi, B. Dickens, and E. Balizer[1]

[1]Naval Surface Warfare Center (NSWC)

Large piezoelectric and pyroelectric coefficients in materials provide the basis of sensors sensitive to heat and pressure. The existence of large piezoelectric and pyroelectric effects in poly(vinylidene fluoride) (PVDF) films is known to be related to preferential alignment of dipoles. Preferential alignment of dipoles is induced by applying an appropriately large electric field perpendicular to the film surface. Such orientation is known as remanent polarization if it persists when the aligning electrical field is removed and can only occur in crystallographically non-centrosymmetric phases.

The polyamides made from alpha-omega amino acids containing odd numbers of carbons are known as the odd nylons. Odd nylons crystallize in at least three non-centrosymmetric crystalline phases. Nylon 11 and nylon 7 have been reported to have even larger piezoelectric and pyroelectric coefficients than PVDF at temperatures above the T_g of the nylons (approximately 50°C). Remanent polarization in the odd nylons persists to temperatures significantly above ambient and in this respect the odd nylons are also better than PVDF. Prior to this work, it was supposed that hydrogen bonding in the odd nylons limited the induction of remanent polarization. An investigation of remanent polarization in nylon 11 containing hydrogenated and deuterated amide groups was begun in cooperation with the Naval Surface Warfare Center.

The conditions necessary to produce the cold-drawn alpha, quenched delta, and gamma phases (extension ratio of three) of nylon 11 were elucidated and the drawn and non-drawn phases were subjected to remanent polarization characterization. An apparatus consisting of a programmable high voltage power supply and a current amplifier was automated using an in-house system of programs written for a personal computer. The computer programs allow programmed poling and automated routine determination of the remanent polarization (milliCoulombs/square meter) and coercive field (MV/m) for both non-conducting and conducting samples. The conductivity must however be sufficiently low that the coercive field of the sample can be attained at currents below about 1 mA.

Ferroelectric polarization was induced for the first time in the oriented gamma phase of nylon 11, but not in the unoriented gamma phase. Ferroelectric polarization was similarly induced in the oriented quenched delta phase. No significant polarization could be induced in the alpha phase. The remanent polarizations and coercive fields in the three phases alpha, quenched delta and gamma are in inverse relation to the strength of the hydrogen bonding in these phases (the hydrogen bonding strength was determined from FTIR examination of the deuterated phases). Deuteration of the amide group in nylon 11 seems to have no effect on the polarization values. These two findings suggest that hydrogen bonding is of secondary importance in limiting the ability of the dipoles in a film of nylon 11 to align under the action of an imposed electrical field. The primary determining factor appears to be steric hindrance of the amide groups.

THERMAL PULSE MEASUREMENT OF POLARIZATION PROFILES

A. S. DeReggi and B. Dickens

The thermal pulse method continues to be a major tool for characterizing electroactive dielectrics. A laser-induced thermal pulse is applied to the surface of a metallized specimen and the electrical response is measured as the heat in the thermal pulse diffuses across the thickness. Analysis of the response yields the polarization or charge profile, that is, the distribution of polarization or charge density as a function of depth from the thermally pulsed surface. Improvements in the measuring apparatus include the acquisition of a new transient digitizer which can operate with 12-bit accuracy up to a 10 MHz digitizing rate and a new computer matching the onboard computer in the digitizer to reduce data transfer times. Reprogramming of the software is still in process.

New measurements have been undertaken on corona-poled samples of poly(vinylidene fluoride) (PVDF) in collaboration with Prof. Jose Giacometti of the "Grupo de Eletretos Prof. Bernhard Gross" at the University of Sao Paulo in San Carlo, Brazil. Professor Giacometti spent two months in the Polymers Division as a guest scientist for the purpose of studying the polarization profile obtained by corona-poling. Corona-poling is assuming importance in nonlinear optics and integrated optics technology in that it allows the application of a poling electric field to a sample without hardwired electrical connections to it, hence without the necessity of poling electrodes on its surfaces. The drawback of this method is that even though the voltage producing the corona is known, the voltage actually across the specimen is not reliably inferred. The corona triode pioneered at the University of Sao Paulo is a recent development which provides data from which the voltage across the sample can be inferred. Recent data show that polarization-voltage hysteresis curves derived from corona-triode data are in good agreement with similar curves obtained by conventional means. A simplified corona-triode poling set-up was assembled at NIST and the polarization profiles of PVDF poled with this set-up in atmospheric air were measured using the thermal pulse facility. A systematic dependence of the polarization profile on the corona polarity was observed in a set of measurements on samples that were first poled to saturation with one corona polarity and then were reverse poled incrementally using the opposite polarity and progressively increased reversed voltages. These measurements show conclusively that positive ions penetrate the samples when the corona is positive. The positive ion penetration is manifested by an asymmetric polarization profile. No ionic injection is apparent when the corona is negative. The corona-poling process appears to be more complicated than assumed in models where corona charge is to the sample surfaces where it is blocked. These results should be useful to manufacturers of nonlinear optical and integrated optics devices. A report of the above results is in preparation.

The thermal pulse work on nonpolar polymeric insulators suggested the existence of a charging steady state in which the charge injected by an applied voltage and which remains stored for a time in an insulator is an approximately linear function of the applied voltage over a wide range of conditions. The possibility that the slope of the charge-voltage curve is a "charging constant" which characterizes a particular material is being investigated in light of recent work by Dr. Le Gressus of Saclay seeking to show a fundamental connection between the charging behavior of insulators and catastrophic phenomena.

CHEMICAL PERFORMANCE

The goal of the Chemical Performance Group is to develop measurement methods, data, and models for the control of polymer processing and bioprocessing and to carry out supportive long-range research on polymer characterization and chemical performance properties.

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 measurement 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.

Investigations in the bioprocessing program involve the use of microorganisms and their metabolic products for the upgrading, synthesis, recovery and degradation of materials, and the development of methods for monitoring biotic transformations of a variety of substrates. With support from the Standard Reference Materials Program, a rapid and reproducible test method has been developed to measure the biodegradability of polymers. In addition, candidate reference materials for polymer biodegradability calibration have been assembled.

The objective of the metal-polymer interactions program is to determine the mechanisms of reactions involving toxic species and the 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. A liquid chromatography method has been developed to determine known cellular metabolites of arsenic such as arsenite, arsonate, and methanearsonate.

FY 91 Significant Accomplishments

- The fluorescence anisotropy of a tagged polymeric probe molecule doped into a polymer matrix and its dependence on applied shear stress were measured. A model to describe the observed effects was developed.

- A method of detecting simultaneously phase transitions and measuring temperature in polymers during processing was developed in collaboration with Drexel University. The method utilizes the dependence of the fluorescence behavior of molecular rotors and excimer producing dyes on microviscosity and temperature.

- An NIST/industry workshop on New Measurement Technology for Polymer Processing was organized and held. From this workshop, the nucleus of an NIST/industry consortium has evolved for the purpose of developing in-line measurement technology based on optical and fluorescence methods.

- An exposure technique that rapidly determines the biodegradability of polymers was developed. The method gives positive or negative results in less than one week as compared to the several weeks or months required for other exposure techniques.

- A long-term exposure method was improved to permit aseptic recycling of growth media; this modification increases the effectiveness of the exposure condition for long (greater than one month) exposures. The modification also permits regulation of air supply, and observation of microorganism growth via a carbon dioxide production monitor.

- The storage stabilities of three lead solutions (50, 250 and 1000 ppm) have been determined for over 12 weeks. Irrespective of concentration, all solutions showed no significant differences from their originally determined concentrations. As part of a collaborative effort with the University of Maryland at Baltimore these solutions will now be periodically delivered with high quality assurance to act as a critical element in a study on the mechanisms of lead poisoning in mammals.

- Speciation of several health and environmentally significant arsenic compounds has been accomplished using high performance liquid chromatography coupled to a graphite furnace atomic absorption spectrophotometer. Using ion exchange chromatography with an in-line micro cell (for monitoring the pH of eluant solutions), analytes are separated based on their ionicity at selected conditions.

POLYMER PROCESSING

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

[1]Drexel University

The objective is to develop in-line measurement technology based on optical measurement methods to monitor important polymer properties during processing. The major optical method employed involves the detection of fluorescence spectra from fluorescent dyes which have been doped into the processed polymer material. Characteristics of the fluorescence, i.e. intensity, polarization, and wavelength distribution, yield information about the state of the polymer. The work concentrates on developing concepts and methods to measure molecular orientation, shear and extension stress, shear and extension strain rate, non-Newtonian viscosity, velocity, flow instabilities, quality-of-mix of ingredients, residence time distribution, the onset of the glass transition and the liquid to crystal transition. Work on quality-of-mix, residence time distribution and flow instabilities, carried out in collaboration with the Naval Surface Warfare Center, has been completed. In collaboration with Drexel University, fluorescent probes are used to monitor temperature and phase transitions. Significant progress has been made in developing relationships between fluorescence anisotropy and shear stress, non-Newtonian viscosity, and molecular orientation.

Over the past year specific objectives have been to develop a model of the relationship between fluorescence anisotropy and molecular orientation factors, to examine the temperature dependence of fluorescence from molecular rotor dyes and excimer producing dyes, to conduct a workshop on new measurement technology for polymer processing involving the participation of industry scientists, and to establish an NIST/Industry consortium to develop in-line measurement technology for polymer processing.

Fluorescence Anisotropy Measurements

This measurement involves the use of polarized light to determine the anisotropy of a fluorescent dye molecule which has been doped into a polymer matrix at low concentrations. The objective is to determine shear stress, molecular orientation, and non-Newtonian viscosity. Laboratory confirmation of this measurement concept and an extensive experimental study of anisotropy using a polymeric fluorescent dye have been carried out. The polymeric dye (or molecular probe) is an anthracene tagged polybutadiene which was synthesized in our laboratory. The dye was doped into a polybutadiene matrix and anisotropy was measured as a function of the applied shear stress using an optically instrumented rheometer. The anisotropy was found to decrease with increasing shear stress, an observation opposite to that which occurred when the polymer was stressed in extension. The difference between the shear and extensional effects was examined by developing a model for the relationship between anisotropy, molecular orientation factors and shear stress. It was found that, if a reasonable orientation distribution function $f(\theta,\phi)$ (θ and ϕ are polar coordinates) is assumed, then the model predicts that anisotropy decreases with applied shear stress.

Temperature Dependence of Fluorescence

Two types of fluorescent dyes have been used in this study, an excimer producing dye and a molecular rotor. The excimer producing dye, 1,3-bis-(pyrene) propane (BPP), consists of two fluorescently active pyrene rings separated by a flexible trimethylene link. When one pyrene molecule absorbs excitation energy at 340 nm, two paths of fluorescence decay are possible, one, by monomer decay at 380 and 400 nm, i.e. the pyrene molecule displays its characteristic fluorescence without interaction with the other pyrene, and two, by excimer decay in the range 450 to 550 nm which occurs when the excited pyrene forms an excimer with its unexcited pyrene neighbor by rotating to a position of close molecular contact. The probability that the excited pyrene can rotate into the proper position to form an excimer before its own decay occurs is dependent on the τ_r, the intramolecular rotational relaxation time of the dye, which is proportional to the ratio η/T. η is a microscopic or molecular viscosity and T is temperature. Fluorescence decay from molecular rotor dyes is also influenced by its intramolecular rotational relaxation. Upon absorbing excitation energy, a molecular rotor can decay to its ground state via fluorescence radiation or by radiationless decay, i.e. energy transferred to molecular vibrations or rotations. The amount of radiationless decay is regulated by intramolecular bond rotations. Intramolecular rotational motion creates potential radiationless decay paths if its relaxation time, τ_r, is shorter than or approximately equal to the fluorescence decay time τ_f of the dye, usually tens of nanoseconds. For $\tau_r >> \tau_f$, maximum fluorescence radiation and minimum radiationless decay is observed. Since $\tau_r \propto \eta/T$, fluorescence intensity will be a function of temperature. Thus, for excimer producing dyes as well as for molecular rotors, rotational relaxation time plays a prominent role in the production of fluorescence radiation.

The temperature dependence of the ratio of excimer to monomer fluorescence intensity for BPP doped into polystyrene is shown in Figure 1. The onset of the glass transition, T_g, is clearly indicated by the knee in the curve at 105°C. Below T_g, the lack of rotational mobility inhibits the formation of excimers, but as the temperature increases above T_g, the excimer fluorescence intensity increases. These data indicate how BPP can be used as a phase transition marker and a temperature sensing probe.

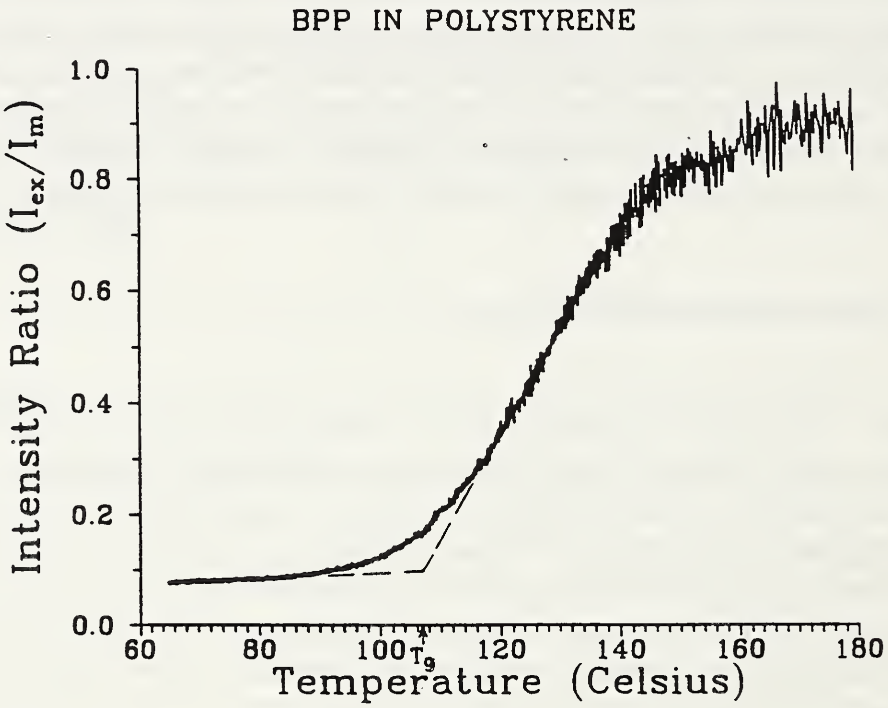

Figure 1. The ratio of excimer to monomer fluorescence is plotted versus temperature for polystyrene doped with BPP. The glass transition of polystyrene, indicated by the arrow at approximately 105°C, was obtained from the intersection of the linear extrapolations from high and low temperature. The excitation wavelength was 340 nm.

Workshop on New Measurement Technology for Polymer Processing

This workshop was held at NIST on December 3-4, 1990. In attendance were nineteen industry scientists and engineers from polymer processing and instrumentation manufacturing companies. The objectives of the workshop were: (a) to seek industry responses to the question: what on-line, real-time measurements do you need to make during polymer processing but cannot because the measurement technology does not exist? and (b) 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. Tire and rubber manufacturing, thermoplastic compounding, injection molding, film processing, and reactive processing were described with respect to related measurement problems. Workshop discussions yielded a consensus of the following measurement needs: (a) in-line rheological measurements; (b) improved in-line temperature measurements; and, (c) in-line and on-line measurements of polymer morphology. The direct interaction with industry at this workshop has provided the framework for establishing an NIST/industry consortium dedicated to the development of new in-line measurement technology for polymer processing.

BIOPROCESSING AND FLUORESCENCE SPECTROSCOPY

L. F. Tilstra, D. S. Johnsonbaugh, R. E. Lowry and F. W. Wang

Research in bioprocessing investigates the use of microorganisms and their metabolic products for upgrading, synthesis, recovery and degradation of materials and for developing measurement methods and standards to understand mechanisms and rate limiting factors involved in these processes.

Standards for Biodegradation

Degradable plastics may be a partial solution to the problem of reducing the amount of plastic in the solid waste stream. Regulations are appearing at the state and local level mandating use of degradable plastics. In addition, the Federal Trade Commission and the Attorneys General of several states have released statements that require accurate labelling of plastics that are being marketed as being degradable. Although standard testing procedures are being developed by members of the ASTM committee D20.96.01, they have not been rigorously tested. Our research, funded by the NIST Standard Reference Materials Program (SRMP), is investigating the appropriateness of certain materials as standards for biodegradable plastics. In the process, procedures developed in other laboratories are tested and additional procedures are developed.

Polymer samples were exposed to a fungal consortium for five to seven days and the oxygen consumption of the consortium was monitored. Comparison of fungal oxygen consumption in polymer-containing flasks with oxygen consumption in flasks containing no polymer indicates use of the polymer as a food source. Two conclusions from this short-term method are 1) the ability of a fungal consortium to metabolize polycaprolactone is very dependent on which fungi are members of the consortium; and 2) a polymer blend film will give a positive result in this short-term test if the continuous phase of the blend can be metabolized by the consortium. This second conclusion suggests that polymer blends are not ideal candidates for reference materials.

A series of long-term tests, one week to four months, employing the same exposure conditions as the short term tests have been completed. Samples from these longer exposures have been tested for loss of mass, changes in mechanical properties, changes in FTIR spectra, and changes in the molecular weight distribution as detected by gel permeation chromatography. Mass loss is not a good indicator of polymer degradation because of the difficulty involved in completely removing fungal cell mass from the samples. Many samples have an apparent mass gain due to clinging fungal mycelia. Mechanical properties are measured by tensile tests. Tensile strength decreases with increasing exposure duration up to two months, after which no further loss is obtained from this exposure condition. FTIR indicates that amorphous polycaprolactone is preferentially removed from the surface of the film samples. GPC reveals a shift in the molecular weight distribution curve to lower molecular weights. Attempts to quantify GPC results are underway, but qualitative analysis suggests that no further degradation appears after eight weeks exposure.

Because the above long-term method is active for only eight weeks, we have developed a procedure was developed which aseptically replaces growth media every week. In addition, this procedure allows long-term monitoring of CO_2 production. CO_2 production is a measure of metabolic rate and may parallel polymer metabolization. Media recycling minimizes the build-up of metabolic waste and thereby helps to maintain fungal growth. In addition, periodic media collection will allow the identification of predominant organisms and any soluble degradation products, thus facilitating studies of degradation mechanisms.

Two categories of polymer films have been examined for their appropriateness as reference materials. Polycaprolactone and polycaprolactone/polyethylene blends have been tested using both the short and long-term methods described above. Blends tested included those containing 0, 10, 30, 80, and 100% polycaprolactone obtained from Union Carbide. Blends are not good candidates for reference materials if the short-term method is to be employed for the reasons listed above. They may be satisfactory for longer exposures, but it would be preferable to have one set of materials that can apply to a wide variety of exposure tests.

Tests have been initiated on cellulose films which differ by the degree of acetylation of the cellulose. Preliminary results indicate that the biodegradability of these films as measured by loss of mechanical strength is correlated with the degree of acetylation regardless of the exposure method used. These films are expected to be good candidates for reference materials.

Cure Monitoring of Polyurethane Resins by Fluorescence Spectroscopy

The fluorescence spectra of organic dyes dissolved in polyurethane resins are sensitive to local viscosity. The excimer forming dyes are particularly useful as probes since the monomer emission can be used as an internal standard in the measurement. In this case, the probability of excimer formation is related to molecular mobility and hence to the microviscosity. This approach has been successfully used to monitor the cure of polyurethane resins, even the ones containing carbon black and other fillers.

METAL-POLYMER INTERACTIONS

K. L. Jewett, F. E. Brinckman, W. R. Blair, D. S. Johnsonbaugh, and F. W. Wang

In naturally occurring distributions, toxic elements such as arsenic and lead cause few serious health problems to man. However, these elements and their compounds are widely used in industry. This results in localization of high concentrations of toxic materials that may cause many health problems in work and home environments. It is therefore of fundamental and practical interest to determine the mechanisms of reactions involving toxic species and the biopolymer systems with which they interact. Two lines of research are currently addressing these problems.

Intracellular Chemical Speciation of Lead: Relation to Nephrotoxicity

Lead compounds have been used in plumbing fixtures and as pigments in paints. Many cases have been uncovered where the children living in old houses develop lead poisoning by eating paint chips or by ingesting dust containing lead. Detoxification in these cases has been relatively unsuccessful. For the most part the victims of lead poisoning often develop permanent mental and/or physical disabilities. And severe lead poisoning is often fatal.

A multiyear collaborative study with University of Maryland at Baltimore (UMAB) has as its main goal the examination of mechanisms of the interactions between lead and naturally occurring biopolymers.

NIST periodically supplies UMAB with well-characterized lead solutions (50, 250, and 1000 ppm) as feed water to a population of laboratory animals. Stability studies indicated that in polycarbonate containers no appreciable loss in concentrations occurred in more than 11 weeks.

At predetermined intervals NIST will receive tissue samples of selected animals and study the nature of metal-biopolymer binding. Such determinations may ultimately suggest more effective methods to treat lead poisoning.

Toxicity from III-V Semiconductors

Semiconductors made of Group III and Group V elements (*e.g.* gallium arsenide [GaAs] or indium arsenide [InAs]) produce toxic components when interacting with biological systems. During manufacturing processes semiconductor dust particles are produced and may be ingested by workers. Bioconversion of arsenic, a commonly used element in semiconductors, has been demonstrated, but mechanisms of toxication and detoxication are unknown. In this project samples of liver tissue taken from rats which have been treated with semiconductor dust will be studied to determine arsenic binding sites on protein and cellular structures.

A method has been developed to determine known cellular metabolites of arsenic such as arsenite, arsonate, methanearsonate and dimethylarsinate using a high performance liquid chromatograph coupled to a graphite furnace atomic absorption detector (HPLC-GFAA). This method is rapid, sensitive (low ppm range) and species specific. This and other analytical procedure will be employed to gain insight into mechanisms of arsenic toxicity in biopolymer systems.

MECHANICAL PERFORMANCE GROUP

The Mechanical Performance Group conducts research leading to new concepts, measurement methods and data that assist the U.S. polymer industry in maintaining competitiveness. The activities of the group focus on mechanical properties and performance and the interrelationships between properties and microstructure. The group capabilities have emphasized NMR, optical and transmission electron microscopy for microstructural characterization of polymers. The mechanical properties have been characterized in both the linear and nonlinear ranges using rheometry for melts and solutions, servohydraulic testing equipment for solids and a unique dilatometric facility for characterization of the glassy state of polymers. This year the capabilities to characterize the microstructure of polymeric materials was enhanced by the transfer of the NIST x-ray facility to the group. This facility consists of a 10m small angle x-ray camera equipped with a two dimensional position sensitive detector as well as a pole figure apparatus for texture studies. The x-ray facility attracts both academic users who carry out collaborative research and industrial users who come to perform proprietary as well as cooperative research. Internal efforts in the past year have begun to examine the microstructural changes associated with the long time creep deformation response of linear low density polyethylenes.

A concerted effort was made to attract industrial collaboration in studies of physical aging behavior of glassy polymers. Visits were made to Eastman Kodak, Xerox, IBM, GE, Ford, GM, and Dow Chemical to acquaint industrial scientists with our research on physical aging as well as other areas of mechanical properties research and to solicit joint work on aspects of immediate concern to industry. Direct collaborations with the technical staffs of Xerox and Kodak have been established. These focus on physical aging processes in materials and systems of interest to each company. In each case resources and expertise at NIST are shared with personnel from Xerox or Kodak. Expansion of these collaborations and developments of others are anticipated.

The Group has also cooperated extensively with the Composites Group on studies of physical aging of epoxies and transcrystallization, both problems of great interest in composites. These activities are reported under the Composites Group efforts.

Planning activities have centered on polymeric materials used in microelectronic packagings. Increasing foreign competition and the need to develop materials and processes compatible with the ever decreasing feature sizes of microelectronic devices are the motivations for programs in this area. Group scientists have contributed research proposals to two NIST budget initiatives, a FY-92 proposal concerned with packaging at the chip level and an FY-93 initiative dealing with materials for electronic interconnects. Both budget initiatives have received favorable reviews from NIST management and plans are being formulated to initiate activities in both areas.

FY 91 Significant Accomplishments

- Proton spin diffusion results indicated domain sizes in PBMA/PS-OH blends with minimum dimensions in the 6-10 nm range and stoichiometries of the order of 75/25.

- The stoichiometry of the PBI-rich phase in a phase separated PBI-PEI blend was determined from spin diffusion data. It was found that, using annealing times of 1 h, the composition of the PBI-rich phase corresponded to that having a T_g about 40 - 50°C higher than the annealing temperature.

- A workshop was organized and attended by virtually all external users of the X-ray Scattering Facility to discuss needs for additional software and refurbishment of the facility hardware.

- A standard liquid approach to assessing the compatibility of liquid hazardous materials was developed for the U. S. Department of Transportation.

- Xerox Corporation sent an industrial research associate to NIST to collaborate on studies of the influence of physical aging on the performance of copolymer glasses.

- Measurements of the strain energy function at large deformations of concentrated polyisoprene solutions was analyzed according to models of rubber elasticity which contain the classical Neo-Hookean term plus a correction. Preliminary results suggest that both models describe the solution behavior at large deformations better than the classical(Neo-Hookean) theories.

- The kinetics of glass forming substances near to the glass transition have been shown to be altered by confined geometries. As pore size decreased, the glass transition is reduced, while the enthalpy retardation times calculated from annealing measurements at a constant temperature below T_g, are unchanged. However, the aging process is slowed down indicating a changing structure dependence of the retardation process as pore size decreases.

- The time dependent responses of polymeric glasses to temperature jumps has been shown to be "hierarchical" in nature. In a quench from above the glass transition T_g to below it, the volume, viscoelastic properties and the yield response of a polymer glass evolve towards equilibrium at different time scales such that responses cease evolving in the order $t_{viscoelastic} < t_{yield} < t_{volume}$. Furthermore, the times involved with the viscoelastic relaxation processes themselves are different from the thermal evolution time scales. Thus, at a given temperature the volume may take 5 days to recover to equilibrium after a quench, but the stress relaxation modulus for the glass after it has attained equilibrium has a characteristic time of the order of 1 hour.

POLYMER STRUCTURE

D. L. VanderHart, J. D. Barnes, G. C. Campbell, S. J. Kryder, C. C. Han, E. S. Clark,[1] and Y. Feng[2]

[1]University of Tennessee, Knoxville, Tennessee
[2]East China University of Chemical Technology, Shanghai, China

Characterization of the Solid State Structure of Polymers

Previous work in our laboratory established proton spin diffusion (PSD) as a method to estimate the minimum domain dimension (MDD) either for domains possessing contrasting proton multiple pulse (MP) spectra (e.g. many polymer blends) or for domains characterized by anisotropic bulk magnetic susceptibility (ABMS). While the PSD experiments based on domains showing spectral contrast are well understood, those based on regions having ABMS character required further exploration. In the past year the range of application to polymers was investigated. A second major thrust was to identify a proton multiple pulse sequence which could be applied in the presence of magic angle spinning (MAS) to yield a relaxation profile (in the presence of MP) determined primarily by molecular mobility. The long-term goal was to create a polarization gradient for a PSD experiment based on a contrast in molecular mobility between different morphological regions. The ability to generate such a gradient would be an important addition to techniques for conducting PSD experiments. Although techniques are already available for observing relaxation under MP, these techniques have only been tested on static samples. The addition of ^{13}C cross-polarization/MAS techniques to MP relaxation leads to a much more powerful method. The superior detail of ^{13}C spectra, relative to proton MP spectra, would allow a) interpretation of the original gradient in much greater detail and b) PSD experiments on a much larger class of polymer blends.

Investigation of the Level of Mixing in a Compatibilized Blend

One way of creating compatible polymer blends is to modify one of two incompatible polymers by incorporation of a specifically interacting monomer. To understand the properties and performance of polymer blends requires knowledge of the level of intimacy of mixing of the components. Consequently, an NMR study was made on a blend of poly(butylmethacrylate) (PBMA) and a modified polystyrene (PS-OH) where the latter polymer was a styrene copolymer incorporating 1.5 mole % of a styrene monomer having a $-C(CF_3)_2OH$ group attached to the para-position of the ring. The modified styrene units, introduced at random into the PS-OH chains, hydrogen bond to the carbonyl groups of the PBMA to 'compatibilize' two polymers, which, in the absence of the comonomer, are incompatible.

Proton spin diffusion results indicated that the level of mixing was intermediate between the molecular mixing of truly compatible blends and phase separation into pure components.

PBMA-rich and PS-OH-rich domains exist with minimum dimensions in the 6-10 nm range and stoichiometries of the order of 75/25. This minimum dimension is in the same range as the mean separation (6 nm) between decorations in the PS-OH chain, assuming that the chain has unperturbed Gaussian dimensions. The level of mixing in this blend is sufficient to produce intermediate properties which are often the objectives for creating a polymer blend.

Phase Stoichiometries from Spin Diffusion Experiments

The study of phase separation in polymer blends would be enhanced by determinations of both the domain size and the domain stoichiometries. Proton spin diffusion methods can be used to characterize domain dimensions up to about 80 nm; yet, few polymer blends have domains of minimum dimension in this range. More commonly, phase separation yields domains having dimensions of a few micrometers. Therefore, if domain stoichiometries could also be determined by proton spin diffusion methods, then useful information could be obtained from a much larger class of blends.

In general, proton spin diffusion data are insufficient to establish stoichiometries. Only one observable has been identified as sensitive to stoichiometry and it requires identical spin diffusion experiments to be carried out on the blend of interest and a physical mixture of homopolymers having the same overall stoichiometry as the blend. Assuming that the overall blend stoichiometry is known, two observables are needed to determine uniquely both the mass fractions and the stoichiometries of the two types of domains in a bi-phase morphology. Since there is only one NMR observable an assumption must be made about either the mass fractions or the individual stoichiometries of each phase. In some cases, assumptions can be made with confidence. For example, the assumption that the PEI-rich phase of PEI/PBI blends annealed above the T_g of the PEI but below that of the PBI is nearly pure PEI, is supported by DSC studies. With this assumption the stoichiometry of the remaining PBI-rich phase can be determined from spin diffusion data. At annealing temperatures below the T_g of pure PBI (420°C) the composition of the PBI-rich phase might well be determined kinetically instead of thermodynamically, i.e. even if pure PBI and pure PEI are the true thermodynamically stable states, the composition of the PBI-rich phase would approximate that composition of PEI/PBI where the T_g and the annealing temperature roughly coincide. It was found that, using annealing times of 1 h, the composition of the PBI-rich phase corresponded to that having a DSC-determined T_g about 40-50°C higher than the annealing temperature. Most of this disparity probably has to do with the longer timescale for annealing (1 h) versus the DSC measurement using a scan rate of 5-10°C/min.

Search for Multiple Pulse Sequences in Which Polarization can be 'Locked' and its Decay Rate Related to Molecular Motion

As mentioned in the preliminary comments, it is important to find a multiple pulse (MP) sequence which can be applied to protons, and which will yield a decay (or relaxation profile) whose decay rate is determined primarily by molecular motion. The reasons for this follow. First, differences in molecular motion can often be associated with domain structure either because of variations of order or variations in chemical composition. Molecular motion tends to dominate more conventionally measured relaxation rates, e.g. T_1, T_ρ and T_2. Yet, heterogeneity of molecular motion within a sample is not so easy to characterize via the latter kinds of relaxation, especially T_1 and T_ρ, since spin diffusion occurs along with the relaxation, thus scrambling the origin of the motional contrasts. During application of MP sequences each proton relaxes at its own rate since spin diffusion is arrested . Thus, relaxation under MP offers the possibility of producing sharp polarization gradients between those regions having different mobilities. From a spin diffusion point of view, sharp gradients offer the best chance for determining information about domain size. Second, relaxation under MP is expected to be sensitive to molecular motion in the mid-kilohertz range and this is a range of motion which, in a typical polymer, is prevalent enough to offer both efficient relaxation and sufficient contrast in relaxation rates based on differences in mobility. Third, when differences in MP relaxation are truly based on differences in molecular motion, then morphologically meaningful polarization gradients can be established by applying such a MP sequence to obtain a partial decay of the polarization. The ensuing process of spin diffusion would then yield information about the spatial distribution of these morphologically different regions. If these sharp gradients can be produced then spin diffusion experiments can be conducted using only proton observation. However, in principle, this method can be enhanced significantly, by making use of ^{13}C signals which in the presence of magic angle spinning (MAS) offer much more detail for interpretation in morphologically heterogeneous materials. Not only is the resolution in CP-MAS ^{13}C experiments much superior to that of protons under MP and MAS, but the ^{13}C spectra often possess characteristics which directly relate to morphology. For instance, it is not unusual to see a small chemical shift or a substantial linewidth difference associated with crystalline versus non-crystalline regions. Consequently, combining the ^{13}C CP-MAS technique with relaxation under proton MP is highly desired because spin diffusion can be followed as the originally prepared polarization gradient diminishes in a spin diffusion experiment; moreover, the morphological interpretation of the original polarization gradient may be extracted from the ^{13}C spectra at early spin diffusion times.

In anticipation of implementing the experiment just described, various MP sequences were tested for their ability to 'lock' magnetization for extended periods ($\cong$ 100 ms). Molecular samples were selected in which mid-kilohertz motions were sparse and motional contributions to the decay would be weak. It was found that MAS created a very significant pathway for the decay of the locked magnetization. Obviously, if this pathway becomes dominant then the experiments outlined above cannot be performed since contrast in relaxation rates based on internal characteristics of the domains are required rather than external features such as MAS.

That MAS should influence polarization decay rates is not too surprising since most MP sequences are designed to eliminate static proton dipole-dipole interactions. Each so-called cycle of the MP sequence then averages these dipolar interactions to zero. With MAS, the dipole-dipole interaction is not fixed; rather, it becomes periodic with the spinning frequency so the averaging from each MP cycle is compromised. The influence of MAS on the MP relaxation rates could be mitigated by slower spinning (more slowly changing dipolar interaction over the period of each MP cycle). Additionally, the coherent nature of both the spinning and the MP irradiation could combine in such a way that the errors introduced by the spinning might cancel over a rotor period. This is a concept which is best tested experimentally.

The usual practice in designing pulse sequences is to compensate for pulse imperfections with more elaborate sequences. A few successful sequences were reported for solid-state magnetic resonance imaging, an application which usually involves static samples. These sequences had many of the properties desired in the present application several of these sequences were tested. Nevertheless, MAS invariably interfered with the locking and in ways not fully understood.

Therefore, most of our effort was spent exploring the behavior of T_{1xz}, the characteristic relaxation time using a MP sequence in which important parameters for spin locking were better understood. The polarization decay profile for T_{1xz} depended strongly on both the MAS frequency, ν_r, and the offset of the applied rf frequency from MP resonance. Near resonance and for resonance offsets in half-integral multiples of ν_r MAS tended to dominate and shorten the decay rates. However, between these minima, magnetization could be locked quite well; moreover, locking was best at an offset about $\pm\nu_r/4$ from resonance. Combined MP and ^{13}C experiments using differential relaxation based on T_{1xz} differences are planned.

Polymer Characterization by Proton Spin Diffusion Experiments Based on Their Anisotropic Bulk Magnetic Susceptibility

In the course of proton spin diffusion (PSD) work, it was observed that polarization gradients based on small chemical shift dispersions could be stored. One source of such a dispersion is a domain possessing anisotropic bulk magnetic susceptibility (ABMS); a spin will have its resonance shifted according to its position relative to such a domain. These PSD experiments must be done on materials whose chemical homogeneity is high since the initial polarization gradient will be more strongly correlated with actual chemical shift differences between various protons. The latter gradients will disappear quickly (2-5 ms) in a homopolymer, leaving only those gradients associated with ABMS to dissipate over a longer spin diffusion time. Practically speaking, if the first 2-5 ms of spin diffusion is not available, then the accessible spatial range is roughly 5-50 nm in determinations of the minimum domain dimension (MDD) associated with domains of ABMS.

In organic polymers, the most likely source of ABMS are domains containing rather high concentrations of aromatic rings having a sizeable projection of the hexad axes of the aromatic rings in a common direction. Thus, an estimate of crystallite size was obtained in semicrystalline poly(ethyleneterephthalate) or polystyrene using this technique. A more interesting application would be glassy aromatic polymers where MDD's for domains of aromatic orientational correlation could be probed. In the several glassy polymers examined this past year there was no evidence of orientational correlation extended over distances greater than 5 nm. Observation by this method of precrystalline order in quenched poly(ethyleneterephthalate) samples which were subsequently annealed in the vicinity of T_g was also unsuccessful in the sense that no dimensions greater than 5 nm were detected. When MDD's of ABMS were first detected after annealing at slightly higher temperatures, then crystallinity was also detected using a more direct type of NMR analysis (differences in T_{1xz} decay rates in static samples).

The final measurements were made on a polymer-graphite composite. The idea was that the graphite contains crystallites possessing a large ABMS. Therefore, polymer protons at distances from the graphite surface which are comparable to or smaller than the graphite crystallite size will experience ABMS shifts. Then spin diffusion measurements on the matrix polymer protons could, in principle, provide a means of estimating graphite crystal size. Two graphite composites were examined, one had small graphite crystallites (3-5 nm) and the other much larger crystallites (22-32 nm). As expected, the sample with the small crystallites showed no difference in PSD behavior relative to the pure polymer (no ABMS domains exceeding 5 nm). (This result is also to be understood in the context of the small fraction of polymer protons which are within 5 nm of the graphite surface.) The sample with the larger crystallites could not be studied because the conductivity of the large-crystal graphite composite sample caused severe detuning of the NMR coil and raised the question of the uniformity of the radiofrequency field in the vicinity of the graphite. As a possible positive outcome of this experiment, it is suggested that a measurement of rf loss, using a surface rf coil, might be used as a means for non-destructively characterizing the graphite fibers in an unknown specimen.

NIST 10-Meter Digital SAXS Camera

The currently active roster of users includes 7 industrial organizations, 2 government laboratories and 2 universities. The range of problems studied includes industrial fibers, polyelectrolytes for energy storage, block copolymer deformation mechanisms, deformation of polyurethanes, pore structure in microporous filter media, and morphology in films.

An active collaboration to study clustering phenomena in doped membranes for gas separation has been undertaken with the NIST Chemical Science and Technology Laboratory.

In April of 1991 a workshop was organized and attended by almost all of the registered users. Following presentations of work done using the facility, the workshop participants discussed needs for additional software and refurbishment of the facility hardware.

An extensive effort is underway to replace aging computer hardware. New desktop computers with color graphics capabilities have been acquired to replace the data acquisition and display hardware. Specifications are being developed for a combination file server and numeric computing engine to replace the VAX 11/730. Program development has begun on a data acquisition system that will feature a more object-oriented data input scheme coupled with a real-time color display of the SAX data. This will permit increased efficiency in aligning the camera and in exploratory experiments.

Work on interpreting the three dimensional character of SAXS data on oriented specimens exhibiting orthorhombic or monoclinic sample symmetry is continuing. The workshop participants also suggested that there is need for algorithms to treat the scattering from random and oriented assemblages of stacked lamellae (Strobl analysis). This work will be undertaken following completion of a study of resolution smearing in pinhole SAXS cameras.

The effects of smearing have also proven to be important in the development of SAXS intensity standards for absolute intensity measurements. This is one source of potential disagreement in round-robin testing.

Pole Figure Facility

Mathematical techniques for relating the pole distribution and the scattering geometry have been developed and applied to investigations of more efficient data collection schemes involving linear position-sensitive, area, and energy-dispersive detectors.

Development continues on methods for simulating pole figures on the basis of idealized models of crystallite orientation.

MECHANICAL PROPERTIES AND PERFORMANCE

J. M. Crissman, G. B. McKenna, C. L. Jackson, K. M. Flynn, L. J. Zapas, C. G'Sell[1],
S. J. Candau[2], F. Kern[2], J.-C. Willmann[3], A. Thierry[3] and J. M. O'Reilly[4]

[1]Ecole de Mines, Nancy, France
[2]Laboratoire d'Ultrasons et de Dynamique des Fluides Complexes, Université Louis Pasteur, Strasbourg, France
[3]Institut Charles Sadron, Strasbourg, France
[4]Eastman Kodak Company, Rochester, New York

Development of Test Methods to Determine the Compatibility of Liquid Hazardous Materials with Polyethylene Packagings

The U.S. Department of Transportation (DOT) Hazardous Materials Regulations (HMR) specify packaging requirements for plastic packagings used in the transportation of hazardous liquids. The HMR differ from international regulations based on the United Nations Recommendations. The major area of difference is the international use of performance-oriented packaging standards as opposed to the U.S. use of design specifications for packagings. An effort is underway to have the HMR conform to the U.N. standards by the end of 1992. NIST has been asked by the DOT to develop a practical and cost-effective test program based on generic groupings of materials to evaluate the compatibility of liquid hazardous materials with polyethylene packagings. It is anticipated that the results obtained from this project will enable the DOT to amend HMR so that the assessment of chemical compatibility of polyethylene packagings can be improved and at the same time facilitate international trade.

While in many respects the two sets of regulations are similar, they differ significantly in compatibility testing. Current DOT regulations require that polyethylene packagings must be tested with each type of hazardous liquid, whereas European regulations allow for the testing to be done using one or more of six standard liquids, each of which is regarded as being equivalent to a large class of liquid hazardous materials. The central task of this project is to determine the feasibility of using a set of standard liquids for compatibility testing of polyethylene packagings.

In determining the compatibility of hazardous liquids with polyethylene, there are three major areas of concern, permeation and/or swelling, environmental stress cracking, and oxidative degradation. With time, each of the three phenomena can lead to serious deterioration of mechanical properties. If compatibility testing is to be based on the use of standard liquids, then the liquids will have to be chosen to address all three areas of concern. The European test methods involve the use of six standard liquids [wetting solution, acetic acid, normal butyl acetate, mixture of hydrocarbons (mineral spirits), nitric acid, and water]. The particular standard liquid is chosen on the basis of the extent to which a hazardous liquid is expected to attack or swell polyethylene. The tests consist of three laboratory procedures which compare the behavior of a filling substance (proposed lading) to that of one or more of the standard liquids.

The major concern in compatibility testing is permeation and/or swelling which also presents the greatest degree of complexity. No theory exists which can correlate the permeabilities of a large number of liquid hazardous materials through a given barrier. However, an empirical approach was developed in the 1960's whereby it was found possible to determine a relatively simple correlation between measured values of mass loss from standard polyethylene bottles and certain properties of the permeant molecules. This approach is known as the "Permachor" scheme [1].

The rate at which a molecule permeates through polyethylene depends upon various properties of the permeant molecule such as size, shape, polarity and other factors. The Permachor scheme is based on the observation that for the non-polar homologous series of hydrocarbons a plot of the logarithm of the permeation factors versus the number of carbon atoms in the hydrocarbon chain resulted in a straight line having a slope of -0.22. Using a large data base of permeation results, a value was assigned to each permeant species by noting the distance they were shifted from the original hydrocarbon line when plotted against the number of carbon atoms in the permeant molecule. The Permachor number was then derived from the amount of shift from the original line corresponding to the normal hydrocarbons. Once a Permachor value had been established at 21°C data for a permeant it was found that the same value could be used at any other temperature and still yield the same straight line relationship between the permeation factor and the Permachor number.

In choosing a set of candidate materials to be used as standard liquids for permeation and swelling, the following properties must be considered: chemical structure, Permachor number, health factor, permeation factor, flash point and reactivity. Permeation factors were determined for twenty-two different organic liquids, including the normal paraffins, normal butyl acetate, and acetic acid. Permeation measurements were done according to ASTM D - 2684, Standard Test Method for Permeability of Thermoplastic Containers to Packaged Reagents of Proprietary Products, Procedure A. Tests were conducted at the three different temperatures allowed under DOT regulations, 23, 50, and 60°C.

Shown in Table 1 are permeation data collected on the twenty-two organic liquids along with their Permachor numbers as determined using the scheme developed by Salame [1]. For each temperature, the logarithm of the permeation factor was plotted versus the Permachor number and the data fit using linear regression. Qualitatively, the three sets of results obtained in this work show the same behavior as that found by Salame. However, quantitatively there are differences which bear mention. In the earlier work, the magnitude of the slope of the straight line fit was reported independent of the temperature and equal to -0.22 whereas for the present work on polyethylene it was found that the slope varied from -0.192 at 23°C to -0.162 at 60°C.

TABLE 1

PERMEATION FACTORS FOR TWENTY-TWO ORGANIC LIQUIDS

Chemical Compound	Permachor Number	Permeation Factors[1] 23°C	50°C	60°C
n-Hexane	6.0	1.69 (43.0)	12.97 (329.0)	25.39 (644.0)
Toluene	6.4	2.99 (75.8)	20.05 (508.9)	40.56 (1029)
n-Heptane	7.0	1.38 (35.0)	8.72 (221.0)	15.79 (401.0)
Xylenes	7.4	1.83 (46.4)	13.20 (334.0)	21.80 (553.0)
Octane	8.0	1.01 (25.7)	6.30 (160.0)	12.3 (313.0)
Trichlorobenzene	9.0	0.64 (16.1)	7.24 (184.0)	10.96 (278.0)
1,2,3,4-Tetramethylbenzene	9.4	0.30 (7.59)	3.91 (99.3)	6.73 (171.0)
Trimethyl pentane	10.0	0.12 (3.0)	1.81 (46.0)	3.83 (97.4)
n-Decane	10.0	0.46 (11.6)	3.63 (92.1)	6.54 (166.1)
n-Undecane	10.2	0.36 (9.04)	2.65 (67.3)	4.57 (116.0)
n-Dodecane	11.0	0.20 (5.05)	2.20 (55.9)	3.47 (88.1)
n-Tetradecane	13.0	0.14 (3.63)	1.32 (33.5)	2.33 (59.2)
n- Butyl-Acetate	13.0	0.13 (3.21)	1.62 (41.0)	3.52 (89.2)
Acetone	13.8	0.10 (2.53)	0.77 (19.5)	1.81 (45.9)
n-Pentadecane	14.0	0.10 (2.53)	1.08 (27.3)	1.98 (50.2)
n-hexadecane	15.0	0.024(0.61)	0.95 (24.2)	1.69 (42.9)
t-butyl acetate	15.0	0.02 (0.50)	0.44 (11.2)	1.19 (30.2)
Acetic Acid	15.5	0.023(0.58)	0.29 (7.42)	0.61 (15.5)
Methyl Alcohol	17.5	0.043(1.08)	0.33 (8.34)	0.64 (16.3)
n-Butyl Alcohol	18.0	0.0034(0.086)	0.080(2.03)	0.22 (5.49)
Ethyl Alcohol	18.5	0.0183(0.465)	0.142(3.60)	0.32 (3.60)
n-Propyl Alcohol	18.5	0.0092(0.233)	0.103(2.61)	0.21 (5.28)

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[1] g x cm/day x m^2 (g x mil/day x 100 in^2)

One of the six standard liquids used in Europe is specified as a mixture of hydrocarbons (white spirit) and is considered as being equivalent to a very large class of hazardous liquid chemical substances. Mineral spirits are derived from petroleum products and consist of mixtures of both linear and branched paraffinic-like molecules. Three important properties by which they are specified are flash point, initial boiling point, and density. In order to obtain information on the permeability of mineral spirits through polyethylene, permeation measurements were carried out on nine different types of commercial mineral spirits. The results for the various types of mineral spirits suggest serious consequences to their use as a standard liquid. Among the nine different samples tested the permeation factor varies by as much as a factor of eight. Of the nine samples, only one would appear suitable as a standard liquid for testing at all three temperatures allowed. Most of the liquids tested have a permeation factor too small, a flash point too low, or both. The one exception is a product which had a value of Permachor number equivalent to a mixture of normal dodecane and normal tridecane. The wide diversity in the permeation factors of the nine samples means that it will be difficult to compare different sets of test results unless everyone uses very nearly the same formulation. The conclusion to be drawn is that, if one or more types of mineral spirits are to be used as a standard liquid, their composition will have to be carefully controlled.

The standard liquid approach appears to address the three major areas of concern with respect to the compatibility of liquid hazardous materials with polyethylene, permeation and/or swelling, environmental stress cracking, and oxidative degradation. Further, the empirical approach known as the Permachor scheme is useful and sufficiently reliable for estimating the permeation factors of many different liquid hazardous materials based on their chemical structure, and can also be used to rank the severity of individual members within a class of materials. It is also the conclusion of this project that if mineral spirits are to be used as one of the standard liquids, then their composition will have to be carefully controlled.

[1] Salame, M., An Empirical Method for the Prediction of Permeation in Polyethylene and Related Polymers, SPE Transactions, 1, No. 4, 1-11 (1961).

Behavior of Small Molecules and Polymers at Nanometer Size Scales

In previous years, controlled pore glasses were use in our laboratory to study the melting, T_m, and glass transition, T_g, events of small molecule organics at nanometer size scales. In those studies it was found that both the melting transition and the glass transition temperatures decreased as the pore size decreased. ΔT_m and ΔT_g were found to decrease linearly as the reciprocal of the pore diameter in the range 4 to 73 nm. During the past year these studies have been extended to include investigations of the kinetics of the enthalpy recovery using DSC measurements on aged, glassy ortho-terphenyl. In particular, in work carried out in collaboration among workers at NIST, Dupont and Eastman Kodak, the Narayanaswamy-Moynihan-KAHR type models of the kinetics of glassy materials are being used to analyze the results of experiments in which aging time and temperature are varied prior to temperature sweeps in the DSC. From the modeling of the heat capacity vs temperature curves a stretched exponential description of the retardation function $[H(t) \sim \exp(-(t/\tau)^{\beta})]$ allows extraction of the parameters describing the distribution of retardation times. β is a shape parameter describing the breadth of the function and τ is a characteristic time. Preliminary results show that the distribution of retardation times narrows (β gets closer to unity) as the pore size decreases. The characteristic time lengthens with decreasing pore size. These results are consistent with the concept that as the size of the relaxing domain gets smaller, certain mechanisms of relaxation are cut off. (This aspect of the work ties in with different time scales observed in different physical aging processes in epoxy glasses and attributed to different size scales dominating different processes, e.g. yield, viscoelastic response and volume recovery. See Composites Group section of this report.) Work continues to completely reconcile all of the observed results, narrower distribution of retardation times, longer characteristic time, and decreased glass transition temperature as pore size decreases.

Recently, the study has been extended to include poly(tetrahydrofuran) of low molecular weight. Samples have been prepared of 250 and 1000 molecular weight in the controlled pore glasses at diameter ranges from 4 to 730 nm. Work is being carried out to prepare a 2900 molecular weight series and DSC measurements have commenced. This work is important because small molecule glasses exhibit a depression of T_g which is contrary to the prediction from entropy theories of glass formation. Since these theories are strictly valid only for polymeric materials, it is important to extend the studies over a range of molecular weights to determine whether there is a transition to "polymeric" behavior, or if the entropy theories can properly describe the behavior in confined geometries.

Chemical gels

Crosslinked rubber networks form gels upon swelling. Upon freezing from the gel, the subsequent melting transition of the solvent is depressed more than can be accounted for by classical thermodynamics as described by Flory for swollen rubber. The anomalous melting point depression in the natural rubber/benzene system was first observed by Kuhn who speculated that it was due to small crystal size. This speculation was subsequently disputed by Boonstra and co-workers based upon x-ray line broadening studies of benzene frozen in lightly crosslinked natural rubber. Because of the interest in the effects of small crystal size on melting transitions and its possible importance in the gelation of isotactic polystyrene/poor solvent systems, the Kuhn-Boonstra controversy was re-examined with experiments and analysis.

Two important points came out of this study. First, both Kuhn and Boonstra reported large FREEZING point depressions which also were observed in the present studies. Upon MELTING, however, the depression was greatly reduced, which behavior is the reported anomaly in the sense of the Flory theory. The anomalously low melting temperature could be explained by crystallite size effects for the lightly crosslinked rubber and the x-ray line broadening results of Boonstra, et al. which gave crystal sizes of $\approx$ 60-100 nm. For the highly crosslinked system, the ΔT_m anomaly would require a crystallite size of $\approx$10-20 nm to explain. Line broadening results are not available for highly crosslinked systems.

The second point to be made comes from the equation for predicting the crystal size from the observed melting point depression. The Gibbs-Thompson equation provides an estimate that is proportional to γ_{sl}, the solid-liquid interfacial free energy. Both Kuhn and Boonstra reported using an unreferenced value for benzene of 4 10^{-7}J/cm^2. In our measurements on benzene in controlled pore glasses, a value of $\approx$15.7 10^{-7}J/cm^2 was determined, similar to other literature values reported for benzene. This large discrepancy in surface energies also contributed to the erroneous rejection of the Kuhn small crystal size hypothesis for the anomalous melting point depression in swollen gels. It is recommended that the issue be reexamined with x-ray line broadening studies on highly crosslinked gels in order to establish the contribution of the solvent crystal size to the melting point depression in networks. This recommendation is made for two reasons. First, there is an opposing school of thought to that of Boonstra that has accepted the Kuhn hypothesis uncritically and uses the melting point depression as a means of determining the crosslink density of rubber. Second, in stiff rubbers and in highly swollen rubbers, there is a contribution of the gel's elasticity to the thermodynamics of the melting of solvent crystals which is expected to be opposite in sign to that of the crystal size effect. Calculations have been initiated to determine the magnitude of this effect.

Thermoreversible gels

1,3:2,4-Dibenzylidene Sorbitol (DBS), is a very efficient nucleating agent in polyolefins. However, it has only recently come to be understood that the efficacy of this small molecule to nucleate crystallization in polymer molecules is due to its ability to form gels from dilute solutions upon reducing the temperature. The gelling ability is apparently due to the formation of fibrils of DBS that are of virtually infinite length with respect to the diameter of approximately 10 nm. Beyond this little is known of the gelling process and gel structure in this material.

The purpose of this project was to add to the body of knowledge concerning the behavior of the DBS by using rheological measurements to observe the kinetics of gelation and variations of the properties of the gel as functions of solvent type and concentration. It was also hoped that these systems would prove to exhibit some of the properties of giant micellar systems, since their geometry is similar, viz, long filamentous structures with molecular scale diameters(5-10 nm). Of particular interest is the appearance of a rubbery plateau in the micellar systems which was not found in the DBS systems.

Rheological and optical measurements were carried out on gel forming systems from DBS in the organic liquids dimethyl and dibutyl phthalate and dibutyl adipate. DBS is used as a nucleating agent in polypropylenes and has been observed to form a network of fine fibrils having virtually infinite length and diameters of approximately 10 nm. Visual observation of the gel formation indicates a different kinetics and gel structure depending on solvent and concentration. Rheological measurements of G'(1 hz) in a couette geometry verify the different kinetics and show a strong power law dependence of gel time on DBS concentration, viz., $t_{gel} \approx \phi^{-4.5}$. Furthermore, once the gel has formed and stabilized, the storage modulus shows little frequency sensitivity in the range 10^{-3} to 5 hz. Both G' and the 60 s isochronal creep compliance J(60) of the fully gelled systems show strong concentration dependences with $G' \approx \phi^4$ and $J \approx \phi^{-4}$. The absolute values of the stiffness and compliance do not appear to vary significantly with the solvent in spite of the differences in the visual appearances of the gels.

Molecular Rheology of Polymer Melts and Solutions

One of the approaches for assessing the nature of entanglements in polymer solutions and melts is the plateau or rubbery modulus G_N^0 in the limit of small deformations. The distance between entanglements is then estimated by the relationship between G_N^0 and the number of "temporary crosslinks" in a rubber network, viz., $G_N^0 \alpha A_0 \nu kT$, where A_0 is a numerical constant which depends on the molecular model chosen, ν is the number of crosslinks per mole, k is the Boltzmann constant and T is absolute temperature. In this work, the nature of entanglements was examined by measuring the strain energy function at large deformations of concentrated polyisoprene solutions. The data is being analyzed by fitting the experimentally determined Valanis-Landel[1] strain energy function to both the Flory-Erman[2] and Gaylord-Douglas[3] models of rubber elasticity. These two models contain the classical Neo-Hookean term plus a correction. Preliminary results suggest that both models describe the solution behavior at large deformations better than the classical(Neo-Hookean) theories. The molecular interpretation of the nature of entanglements which arises from these models is somewhat different from that normally envisioned based on the classical theories.

[1] K.C. Valanis and R.F. Landel, J. Appl. Phys., 1967, 38, 2997.
[2] P.J. Flory, Polymer J., 1985, 17, 1.
[3] R.J. Gaylord and J.F. Douglas, Polym. Bull., 1987, 18, 347.

POLYMER COMPOSITES

The White House Office of Science and Technology Policy recently issued a report detailing the 22 technologies deemed as critical for America's future. Prominent among these was composite materials. This finding echoes similar conclusions in earlier reports by the Department of Commerce ("Emerging Technologies - A Survey of Technical and Economic Opportunities," 1990), the Department of Defense ("Critical Technology Plan," 1990), the Council on Competitiveness ("Gaining New Ground: Technology Priorities for America's Future," 1990), and industry groups such as the Aerospace Industries Association ("Key Technologies for the 1990's," 1988). All of these reports conclude that the United States must remain a leader in technologies such as composites if we are to maintain and increase our competitive position in the World.

By far the largest category in the composites area is polymer based materials. These composites offer significant advantages in properties relative to conventional materials with the result that advanced polymer composites are growing 16% a year. The continuation of this growth rate, however, requires expansion of their use beyond defense and aerospace vehicles into mass-market, civilian applications. The major barriers to this are the high cost of fabrication and deficiencies in our understanding and predictive capabilities for performance. To address these challenges, the underlying science base, which is currently rather weak, must be strengthened.

The Polymer Composites Program is a response to this need. The objective in this program is to provide industry with generic science and technology: (1) to monitor, understand, model, and ultimately control the chemical and physical changes that occur during processing in order to achieve more rapid and reliable fabrication, and (2) to establish the processing-microstructure-property relationships needed to improve performance and performance prediction.

A two task approach was taken in this program. The first task focuses on Processing Science while the second develops Processing-Microstructure-Property Relationships. The projects generally focus on one of three classes of materials: vinyl esters which are of interest for automotive applications, epoxies which are the basis for printed wire circuit boards, and thermoplastics which were identified by industry workshops at NIST as having great potential for the future. The program has interest in four processing methods: liquid molding, press molding, filament placement, and autoclave molding. Liquid molding (LM) was selected for the primary focus and represents the bulk of the effort in the Processing Science Task. LM is expected to become increasingly important throughout the Composites Program in the future.

To assist with the conduct of this research a number of organizations participated in cooperative programs. In the area of Processing Science assistance was provided by the Automotive Composites Consortium, General Electric, and the University of Delaware, while cooperative programs in task two include Procter & Gamble, duPont, Armstrong World

Industries, Michigan State University, the University of Massachusetts, and Polytechnic University. Another major source of assistance was visiting scientists who spent significant time working at NIST. They include T. Sadiq from Univ. of Delaware, P. Herrera-Franco from Michigan State University, and S. Matsukawa from Nihon University in Japan. W. Orts began a postdoctoral appointment and NIST and will work on polymer structure near interfaces.

FY 91 Significant Accomplishments

- Two computer programs for simulating flow in liquid molding have been developed. The first predicts flow in quasi-2D shell structures, while the second is for arbitrarily complex 3D shapes. The programs can be used to study the effects of a variety of commercially interesting process parameters such as multiple injection gates, anisotropic preforms, regions of variable preform packing, and the influence of gravity on the flow.

- As part of a Cooperative Research and Development Agreement with the Automotive Composites Consortium, a computer simulation was made of flow in liquid molding of the front end structure of a Ford Escort. The initial result shows the ability of the simulation to predict features like venting locations and clamping forces as a function of injection gate positions, resin viscosity, and preform permeability. Such results provide the information necessary for mold design and process optimization.

- The two common methods to measure permeability of fiber preforms, radial flow experiments and unidirectional flow experiments, for the first time have been shown to produce equivalent results. In tests with a number of different preform materials, the radial flow behavior was successfully predicted from measurements in unidirectional flow.

- A unique new tool has been developed to study the physics involved in the adhesion between a polymer and a solid surface like glass. The technique based on neutron reflectivity was shown to provide data on the density of molecular segments near such an interface. The theoretical work to interpret the reflectivity results has also been developed.

- It is generally believed that there is an ultimate glass transition temperature, $T_{g,u}$, which can be achieved by post-curing a sample regardless of the previous cure history. The work here clearly demonstrates that this is not always true. In fact, heating to a temperature above a certain critical value too rapidly was found to reduce $T_{g,u}$ significantly. As industry pushes for greater efficiency with higher speed manufacturing, this result becomes increasingly important.

- A comparison was made of three common tests for measuring fiber-matrix interface strength: a fiber fragmentation test, a microdrop pull-off test, and a microindentation test. The values obtained with the fragmentation and microindentation tests generally agreed, while the microdrop experiment gave results which were usually lower by a small amount.

PROCESSING SCIENCE

D. L. Hunston, F. R. Phelan, R. S. Parnas, W. G. McDonough, S. S. Chang, G. Howard, J. Kasab, and T. Sadiq[1]

[1]University of Delaware, Newark, Delaware

As indicated previously, the majority of work in this task is devoted to liquid molding (LM). This processing method includes both resin transfer molding (RTM) and structural reaction injection molding (SRIM) which is a high speed, process similar to RTM. In addition, a small effort is continuing on process monitoring. The monitoring techniques under study are applicable to all processing methods, but future plans call for increasing coordination with the liquid molding effort.

Liquid Molding

Liquid molding (LM) is viewed with promise by a variety of U.S. industries because it offers the ability to fabricate large composite parts of complex shape (an inherent weakness of other processes) at a fraction of the time and cost. In order for liquid molding to make a greater impact, however, a better understanding of the scientific issues which affect the process must be achieved. The events of importance occur on both a macroscopic scale (i.e. mold filling) and a microscopic scale (i.e. fiber wetting and void formation). To address these problems, the process is being studied in three stages: mold filling without significant chemical reaction, curing of the resin in the filled mold, and finally integration of the filling and curing processes. This separation was made to simplify the analysis problem and to address the most important aspects first. The current program is well on the way to accomplishing the first stage.

During the past year research has been performed in four areas. First, a major effort has developed process simulation models for mold filling. Second, some alternative approaches to predicting flow have been explored. Third, experimental studies of flow have been conducted to characterize the preform material and to provide critical tests for the flow models. Finally, a cooperative program with the Automotive Composites Consortium is permitting a detailed comparison of predictions from the flow models to observations on fabrication of real parts. Each of these four areas is discussed below.

Computer Simulation: Modeling work for LM in the past year has focused on flow simulation using two approaches in an effort to gain understanding of both macroflow and microflow features of the LM process. The first approach uses Darcy's Law to describe the macroscopic mold filling process while the second employs a more general relationship developed by Brinkman.

Prior to last year, Darcy's Law had been used to develop a program for describing the isothermal, free-surface flow of a Newtonian fluid through porous media in 2D geometries. This capability has now been extended with two new programs that can describe more complex situations. First, a simulation was developed for predicting flow in what are commonly referred to as 2.5D geometries. A 2.5D geometry implies some kind of shell structure. It may be quite complex in 3D space, but locally there is a plane which is thin compared to the other direction. This is referred to as the thickness direction. Underlying the analysis with a 2.5D code is the assumption that locally, there is no flow in the thickness direction. This is a good assumption for many of the structures fabricated in commercial applications, and it has the advantage of greatly reducing the computational time necessary to complete the simulation (relative to the fully 3D case) due to the fact that one does not have to discretize through the thickness.

The second new program is for fully 3D flow. In contrast to the 2.5D code, no assumptions regarding local flow characteristics are made. Having a fully 3D code is important for simulating flow in structures with thick sections, or possibly even in shells which have extremely low permeabilities in the thickness direction. In such cases, the assumptions involved in the 2.5D simulation are not valid.

Another new feature added to the Darcy's law simulation is the inclusion of the effect of gravity on the flow. This is accomplished by replacing pressure, P, in the Darcy's Law equation with $\Phi = P + \rho g z$ where ρ is density, g is the gravitational constant, and z is height. The boundary conditions are then specified in terms of Φ. Scaling indicates that the importance of the gravitational term is controlled by the dimensionless group $\Psi = (K_c \rho g \cos\phi / v_c \mu)$, where K_c and v_c are the characteristic permeability and velocity, respectively, and ϕ is the angle between vertical direction and the local plane of flow. When Ψ is much less than unity, gravity has little effect on the flow, at values greater than 10, it dominates the flow.

To simulate mold filling in LM, Darcy's law is first combined with the continuity equation to give a single relationship for P. This equation is then solved by using two numerical techniques. Because the LM operation begins with an empty mold, mold filling involves flow with a free-surface. A technique called FAN (for flow analysis network) is used to predict and track the movement of the free-surface. This is combined with a finite element method (FEM) to solve the governing equations for each successive free-surface. A mold filling calculation, therefore, proceeds as follows. Starting with an empty mold, initial conditions (or multiple initial conditions as the case may be) are given in terms of an inlet velocity, flow rate or pressure. The FAN technique is then used to define a new free-surface location. Boundary conditions on this new free-surface are set, and the FEM technique is used to solve the equation for the pressure. Once this new pressure solution is known, the FAN technique is used again and the process is repeated until the entire mold is filled.

The Darcy's Law programs predict flow front vs. time and the pressure distribution (at each successive free-surface) during mold filling. Some results for flow front vs. time in the filling of a sample geometry are shown in Figure 1. This Figure is a comparison of two 2.5D simulations illustrating the effect of gravity. The mold is a hollow shell structure shaped like a truncated pyramid. It is filled through a rectangular region extending form the base at one side. The figure shows two different views for each of the two simulations. The two upper quadrants are for a case where the dimensionless variable Ψ is 0. In this case, the simulation predicts that the variations in height of the shell geometry have little effect on the flow front patterns so the last region to fill is along the base opposite to the injection position. For the case depicted in the lower two quadrants, Ψ is large (i.e., greater than 10). Under these conditions the fluid fills the lower portion of the mold first and the top last. These different flow front patterns are significant, especially with regard to the different vent locations needed for the two cases. LM molds are normally built with vents to allow air being displaced by the incoming fluid to escape. Improper vent location can lead to trapped air, in which case, the mold will not completely fill and the part may be ruined. For the cases shown in Figure 1, the simulations clearly show that the optimum vent locations are along the base opposite to the injection point when no gravity effects are present and at the top when gravity effects dominate. This illustrates how important gravity effects can be and how useful processing simulations are for mold design.

Work was also begun this year to extend the Darcy's law simulation to cover non-isothermal flow, and this will be extended further in the coming year to include chemical reaction as well.

The second simulation approach that has been developed during the past year for the analysis of flow in LM is based on the Brinkman-volume averaged momentum equation (BVAME), which is given by

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

where

$$\nabla = \frac{\partial}{\partial x} \boldsymbol{i} + \frac{\partial}{\partial y} \boldsymbol{j} + \frac{\partial}{\partial z} \boldsymbol{k}$$

and K is the permeability tensor, μ is viscosity, v is flow velocity, and P is the pressure.

The BVAME differs from Darcy's law by the presence of the second-order derivative terms for the velocity. Examination of this equation reveals that it is simply a superposition of Darcy's law and the Stokes equation. The advantage of this is that it is able to properly describe Darcy flow in regions where velocity gradients are low, but, due to the second order terms, it can also satisfy the proper boundary conditions at solid surfaces and at interfaces between discontinuous media where velocity gradients are high. As a result, it provides more accurate modeling of the details of the velocity field near boundaries.

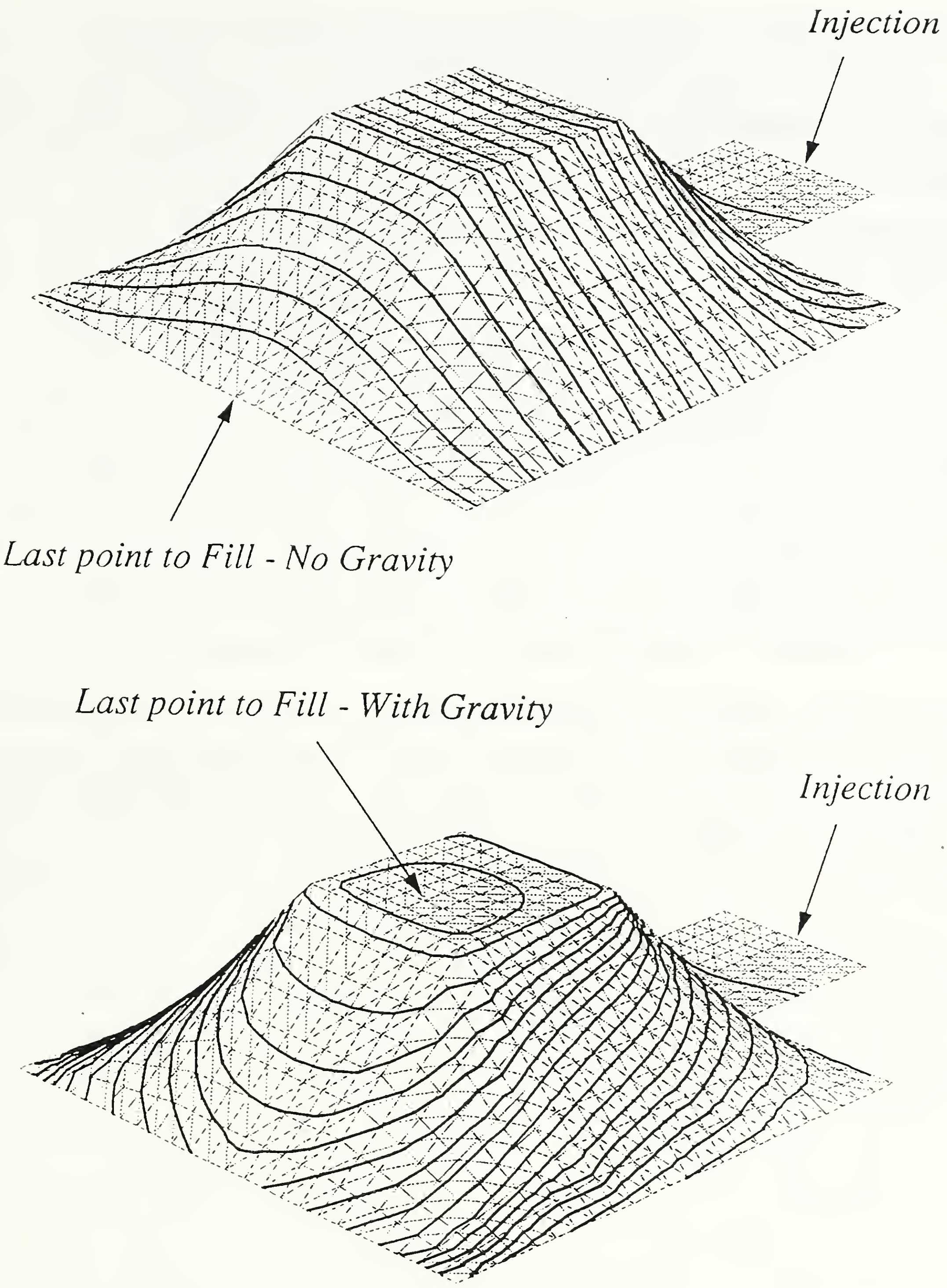

Figure 1. Mold filling for a shell structure shaped like a hollow, truncated pyramid. Two different simulations are shown. The top picture is for a simulation with no gravity effect, while the diagram at the bottom is for the same structure but with a dominate gravity effect. The fine lines are the finite element grid used for the simulation while the heavy lines represent the flow front position as a function of time.

The BVAME approach was used to study the flow in LM performs at the level of the fiber tow. This approach was extremely useful because LM preform materials are heterogeneous in the sense that the network of fiber bundles (tows) which make up the global porous medium are themselves porous. Consequently, the ability to include proper boundary conditions is critical. In order to study the effect of the tow permeability on the overall permeability of a medium, axial and transverse flow through periodic, square arrays of solid and porous cylinders has been modeled. The BVAME was applied to flow inside the fiber tow, and the Stokes equation to flow outside the tow. For both cases (axial and transverse flow), the calculations predict that the flow rate is substantially higher for porous cylinders than for solid cylinders at equal cylinder spacing and the same pressure gradient. This unexpected result implies that the porous cylinders produce less drag on the flow than the solid cylinders. This correlates well with results in the literature in which experimentally determined values of permeability in such model networks are generally higher than their theoretical counterparts which have not taken the tow permeability into account. In addition, preliminary results for the case of transverse flow show that the porosity of the tows can effect the fluid mechanics of the flow around a fiber. Such changes might also account for permeability differences. These results suggest that in order to develop theoretical relationships for permeability as a function of structure in fibrous porous media, it may be necessary to take into account the intra-tow properties of the media.

Theoretical Work on Flow in Arbitrarily Complex Geometries: Although the approaches discussed above show great promise, there are also important limitations. Consequently, alternatives for predicting flow profiles of non-Newtonian fluids in arbitrarily complex geometries are worth exploring. In LM the complex geometry takes the form of a porous medium, for which a number of important results have been obtained using volume averaging techniques, i.e. Darcy's law and Brinkman's equation. There are systems of interest, however, where the porous media possess multiple length scales in which the flows are tightly coupled, and the resultant phenomena cannot be explained using the conventional volume averaging approaches. Moreover, current approaches are not ideal for the analysis of non-Newtonian fluids. The determination of the velocity profile for an incompressible viscous fluid flowing through a pipe of arbitrary cross-section can be reduced to a Dirichlet-type boundary value problem. Exact analytic solutions for the velocity profile of a "Poiseuille" flow can be obtained for a few special boundary shapes (circular, elliptical, triangular, rectangular), but analytic methods rapidly become unmanageable for complicated shaped boundaries and numerical methods must be used to solve for the velocity profile. Thus, a number of investigators are employing large computational resources to directly solve the Navier-Stokes (or Stokes) differential equations by finite difference or finite element techniques in complex geometries. An alternative solution procedure is outlined below.

The velocity profile is a functional of the pipe cross-section shape, and it is convenient to recast the Poiseuille flow problem in terms of functional integration before resorting to numerical solution methods. By recasting the problem, a numerical recipe for calculating the velocity profile for the case of arbitrary boundary shape (even "fractal") can be obtained.

Specifically, it can be shown that the velocity of a Poiseuille flow within a pipe of arbitrary cross-section is equivalent (up to a normalization constant involving viscosity) to the mean first-passage time of a random walk within the cross sectional boundary of the tube. The exact connection holds in the limit that the random walk step size becomes vanishingly small, and the use of finite step size random walks corresponds to a discretization approximation.

Preliminary tests of a prototype serial computer algorithm in simple 2-D geometries (ellipse and triangle), for which analytical solutions of the velocity profiles exist, have yielded good agreement with the analytical solutions. The prototype serial algorithm numerically computes the fluid velocity in an arbitrary geometry by taking a set of random walks within the flow boundary. The fluid velocity at any given point in the domain is proportional to the average number of steps required for a random walk to reach the domain boundary from that point. Additionally, the functional integration formulation of the flow equations is ideally suited to massively parallel computation since the calculation of the mean first-passage time of a random walk at each point within the cross section is 100% independent of the calculations at any other point. In contrast, when conventional numerical solution procedures are used in a parallel computing environment, frequent resynchronization of the calculations among the many processors are required due to the interdependence of the calculations at the node points of the discretization grid. Work is currently underway to implement the functional integration algorithm on a massively parallel computer.

Experimental Studies of Flow Through Porous Media: To complement the research on modeling, an experimental program in flow monitoring is underway. During the past year, this program has focused on the measurement of permeability. Facilities have been developed to measure all three components of permeability (i.e. the two in-plane values and the through thickness component) as a function of fiber volume fraction.

To validate the measurements for the in-plane components, a collaboration with General Electric (GE) Corporate Research and Development allowed independent measurements to be performed on the same materials using different flow geometries. The permeability measurements conducted at NIST used saturated fabrics in a one-dimensional flow geometry designed to minimize edge effects and maximize the accuracy of the flow and pressure measurements. Four experiments were conducted with each material by flowing fluid in four different directions through the fabric and measuring the effective permeabilities. The two-dimensional form of Darcy's law was then used to analyze the data and calculate the principal components K_{xx} and K_{yy} of the permeability tensor, **K**, and the principal angle θ i.e. the orientation of the principal flow axis of the material relative to the tow direction. Thus, a minimum of three one-dimensional experiments are required to characterize the material for in-plane flow. The fourth experiment conducted with each fabric greatly improved the accuracy of the procedure by removing errors due to changes in fiber volume fraction that inevitably occurred during mold repacking.

In the GE experiments, the same fabrics were measured in unsaturated radial flow experiments. Once the tensor **K** was derived from the one-dimensional experiments at NIST, the shape and progress of the elliptical flow fronts in radial flow experiments could be predicted and compared to the elliptical flow fronts observed at GE. The agreement was very good and can be illustrated by comparing values of θ and K_{yy}/K_{xx} obtained in the two experiments. Typical results are given in Table I for an 8-harness satin weave glass fabric.

Table I Comparison of Permeability Data from Different Laboratories

Laboratory	Principle Angle θ	Anisotropy K_{yy}/K_{xx}
GE	73	0.77
NIST	75	0.73

The close agreement between these and several other measurements indicates that the radial and one-dimensional flow experiments are geometrically consistent, and may therefore be combined in characterization studies to maximize efficiency. More importantly, this work confirms the utility of Darcy's law for macroscopic characterization of porous materials.

In conjunction with the permeability measurements, the flow visualization capabilities of the laboratory have been improved by utilizing model porous media constructed with arrays of both solid and porous cylinders. This work, performed in collaboration with the U. of Delaware Center for Composite Materials, allows the careful observation of the flow front within carefully controlled geometries, and thereby improves our ability to make quantitative comparisons to simulations models discussed above. Current work has focused on flow perpendicular to the cylinder axis, and work is planned in which the flow would be parallel. Results obtained to date suggest that models based upon unit cell calculations with periodic boundary conditions may be expected to accurately predict permeability at fiber volume fractions above approximately 60%. At fiber volume fractions below about 40% the permeability is more accurately predicted by single element models. Comparisons of the data with a wide variety of models are currently underway to identify a model that can accurately predict the permeability in the critical fiber volume fraction region between 40 and 60%. More importantly, experiments currently underway have qualitatively demonstrated a previously predicted void formation mechanism in LM preforms which arises from multiple scale induced transient flow phenomena. The optical equipment is currently being upgraded to quantitatively confirm the transient flow phenomena and associated void formation in the fiber tows during mold filling.

Interaction with the Automotive Composites Consortium (ACC): The ACC is a cooperative effort between Ford, Chrysler, and General Motors to conduct precompetitive research in order to promote the use of composites for structural applications in automobiles. The ACC will be demonstrating the results of their work by fabricating a series of parts using the latest technology. The first part chosen was the front end structure of the Ford Escort and the process of choice is liquid molding.

NIST is cooperating with the ACC effort by conducting flow simulations to help optimize the process. The results also serve as a test for the NIST flow models. Use of the models requires the determination of permeabilities for the reinforcement materials, and they are being measured in the NIST permeability facility. To date three materials have been characterized by measuring their properties at several fiber volume fractions. The first two materials were random mat samples and hence the in-plane permeability was isotropic. The third material is uniaxial braid and is highly anisotropic.

Based on these permeabilities, NIST is using the Darcy's Law computer simulation programs described above to model the processing of the ACC part. At the present time, results for the isothermal filling using the 2.5D Darcy's law simulation have been obtained and are shown in Figure 2. These results represent a test case in which it was assumed that the permeability throughout the part was uniform and isotropic. As indicated above, some regions in the part involve preform materials that are not expected to be isotropic. Moreover, packing densities, and hence fiber volume fractions, vary with position in the part so this will cause the permeability to vary significantly from region to region. When the permeability measurements for the remaining preform materials are complete, an extensive series of simulations will be carried out, for different injection points and inlet conditions. Nevertheless, the results shown in Figure 2 demonstrate the current capabilities of the modeling.

Process Monitoring

Over the last five years, the composites program has developed extensive capabilities and expertise in the area of process monitoring. During the past year this capability was utilized to publish a report summarizing the state-of-the-art in composite process monitoring. In addition, a project was initiated to explore the implementation of fiber optic sensors for the press molding process. This is relevant to both liquid molding and electronic applications such as press fabrication of printed wire circuit boards.

Process Monitoring Sensors Report: NIST has published a report entitled "Assessment of the State-of-the-art for Process Monitoring Sensors for Polymer Composites" (NISTIR 4514). It summarizes many of the results from a study that was prepared for the National Center for Manufacturing Sciences (NCMS). The cure monitoring techniques that show the most promise for on-line application, namely: ultrasonic, dielectric, spectroscopic, and optical are discussed and compared in the areas of measurement speed, sampling volume, sensitivity to different resins, effects of fiber type, resistance to the manufacturing environment, interpretation of the data, adaptability for other uses, and temperature capabilities. The most important comparison, however, concerns the research and development work that is needed to achieve the full potential of each technique in applications on the factory floor. Dielectric and ultrasonic methods have an advantage in this connection because commercial equipment

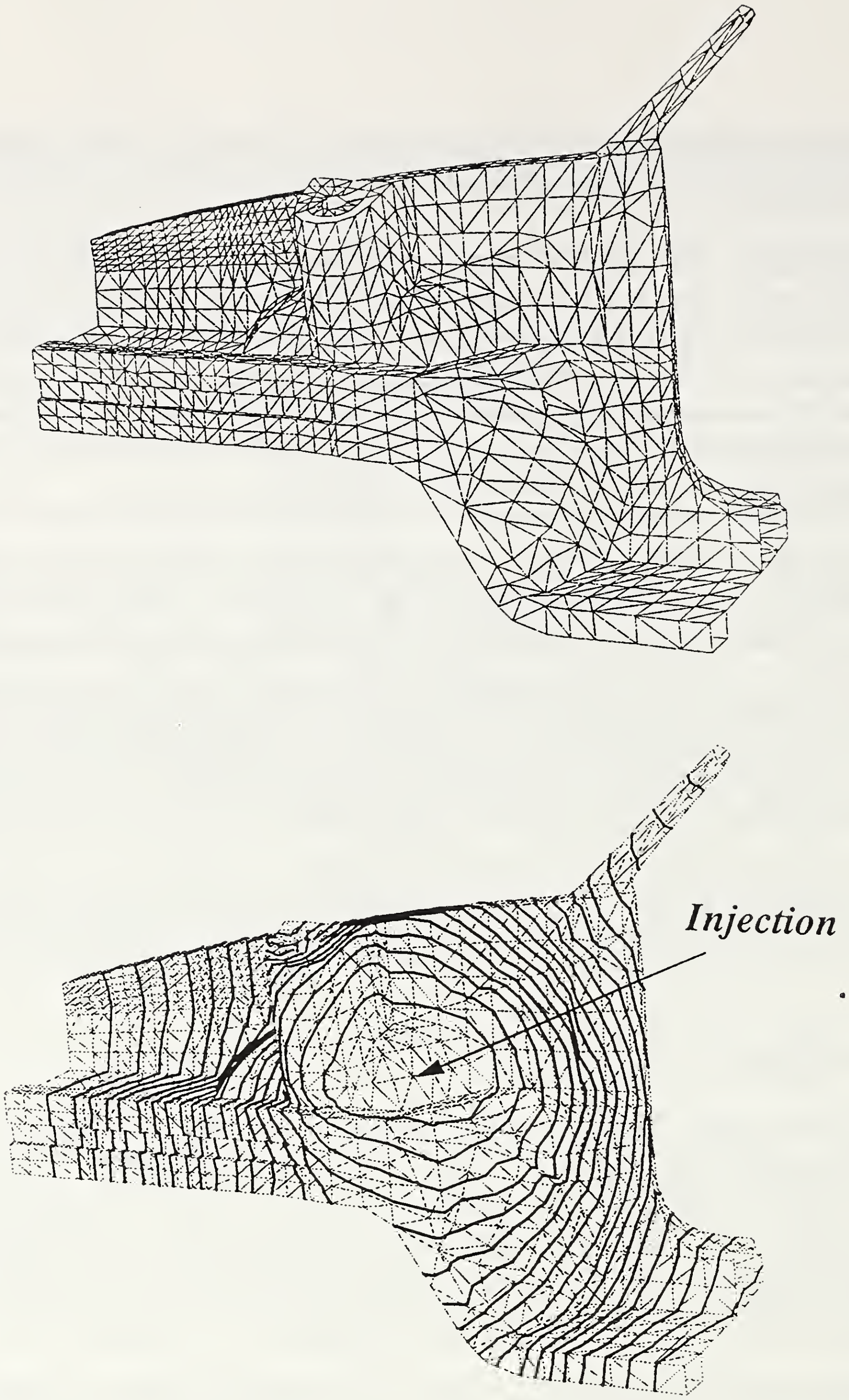

Figure 2. Mold filling simulation for the ACC focal project, the front end struture of a Ford Escort. Shown in the top picture is the finite element grid used as input for the simulation. This part is the structural member on the right side of the automobile. The window pillar is shown at the top right and the shock tower for attachment of the wheel support is in the center. The lower picture gives results for a simulation with the indicated injection point. Bold lines show the flow front position as a function of time.

designed for process monitoring is already available. The various spectroscopic and optical methods are generally at an earlier stage of development. The great potential inherent in these latter methods, however, makes it highly desirable to actively pursue their developments as well. The major short term need in cure monitoring is to build more rugged and reliable equipment that can withstand the harsh manufacturing environment. The major long term issues are the interpretation of the sensor output, and the correlation of the resulting data to process control information through processing models. Despite the critical role that sensors play in process control, the development, interpretation, and implementation of sensors have not received sufficient attention. Research and development on sensors could leverage the work performed in projects addressing other aspects of the process control area and thereby play a vital role. The issues outlined above are particularly appropriate since the results will have maximum impact on the development of on-line monitoring techniques.

Process Monitoring Implementation: During the past year, research on process monitoring was conducted in the area of fluorescence cure monitoring of epoxies, based on success in monitoring the curing of epoxy resins in small batches under bench-top conditions. Work aimed at adapting this technology to on-line curing in a laminating press has been initiated. A small mold capable of having two optical fibers inserted at a 90° angle to each other has been made. Experiments are underway in which a mold is filled with glycerol containing traces of various test dyes such as rhodamine B so the fluorescence signal can be detected and optimized. In this way the best dye can be chosen. Once this has been achieved, an appropriate emission source and suitable detecting device will be selected to give a sufficient level of portability and ruggedness for measurement in the more demanding environment of the press. Equipment has also been obtained to replace the two fibers with a single fiber that can both transmit and detect the signals. Finally, a larger mold is being designed which can be used on the press and accept the single fiber measurement system.

PROCESSING-MICROSTRUCTURE-PROPERTY RELATIONSHIPS

W. L. Wu, H. Chai, F. A. Khoury, W. G. McDonough, M. Y. Chiang, G. B. McKenna, J. M. Crissman, D. L. Hunston, W. J. Orts, C. Ortiz, M. M. Santore, S. Matsukawa,[1] P. Herrera-Franco,[2] C. G'Sell,[3] R. Domszy,[4] S. K. Satija,[5] C. F. Majkrzak,[5] and J. Falco[6]

[1]Nihon University, Matsudo, Japan
[2]Michigan State University, East Lansing, Michigan
[3]Ecole des Mines, Nancy, France
[4]Armstrong World Industries, Lancaster, Pennsylvania
[5]Reactor Division, NIST
[6]Robot Systems Division, NIST

The second task in the Composites Program seeks to establish processing-microstructure-property relationships. There are two areas of focus: first the fiber-matrix interface itself or very thin layers where the interface has a major effect on properties, and second, the resin or resin dominated properties in the composites. These two areas were chosen since they represent the major concern in many applications. The projects in this task address one or more of the following objectives: develop test methods to characterize microstructure and properties, apply these techniques to selected materials with known processing histories, and develop understandings that can generate processing-microstructure-property relationships. The properties of interest include the glass transition temperature, failure behavior, and durability. In addition, based on the conclusions of a NIST sponsored Industry Workshop, durability was selected as an area for expanded emphasis in the future, and plans were formulated during the past year. Environmental attack was chosen as the focus of the work and the approach will be to examine degradation mechanisms. Research in this area will begin next year.

Interface or Thin Layer Behavior

In the area of behavior near interfaces or in thin layers, 6 projects are currently underway. The first two focus on characterization of microstructure using neutron reflectivity and microscopy. The third is studying test methods for determining fiber-matrix interface strength and will be coupling with the work in the first two projects in the coming year. The next two programs are addressing the area of thin layers and both are studying failure behavior. In the first program the focus is on thin resin layers such as those between plies of a composite or in microelectronic structures. The other program addresses a lamination problem of importance to the State Department. Each of these 5 projects is discussed below.

<u>Molecular Basis of Adhesion at Polymer/Solid Interface</u>: The adhesion of polymers at a polymer/substrate interface is an important subject, not only from a theoretical point of view but also for numerous practical applications. Protective coatings of polymers on metals, adhesion of polymer matrices to reinforcing fibers in composites, and the bonding of polymer thin films to various components in electronics packaging are just some examples of great practical importance.

In the past year work has been initiated to develop a test methodology that will characterize the interactions at polymer/solid interfaces down to the molecular level. The technique is based on neutron reflectometry, with emphasis on relating both the specular and the off-specular reflection to polymer density distribution at and near the interface. It is known that the information on the specular reflection does not always provide a unique solution in terms of the polymer density at interfaces. Therefore, it is important to investigate both the theoretical and the experimental aspects the off-specular reflection.

Measurements have been conducted on BT-7 reflectometer at NIST's Reactor Experimental Hall. Silicon single crystal wafers were used as substrates. A semicrystalline polymer, poly(chlorotrifloroethylene) (PCTFE), and an amorphous polymer, polystyrene, have been studied. The polystyrene was synthesized by M. Satkowski and S. D. Smith of Procter & Gamble Co. as part of a cooperative effort. The neutron reflectivity results indicated that the segment density of the polymer at the interface was rather rough. For polystyrene the roughness increased with temperature. For PCTFE the roughness can no longer be characterized with a single length scale even at a temperature 30°C above its melting point. The existence of an absorbed polymer layer and the incipiency of crystallization near the interface make PCTFE an exciting polymer for the reflectivity study.

For the off-specular reflection, the distorted-wave Born approximation has been extended to allow for density fluctuations inside the polymer phase. The off-specular results observed in PCTFE can now be interpreted qualitatively within the theoretical framework developed so far. Such information should make it possible to develop a molecular level understanding of adhesion.

The Nucleating Effect of Carbon Fibers on the Crystallization of Polymers in Composites: The objectives of these studies are: (a) to compare the abilities of various commercial carbon fibers to enhance the nucleation of spherulitic crystallization at the fiber/polymer interface in composites relative to spherulite nucleation in the bulk of the polymer matrix, and (b) to probe the origins of differences among carbon fibers in the nucleation effects. Enhanced nucleation of spherulite growth at the polymer/fiber interface is evidenced by the manifestation of transcrystallization. Differences in the ability of carbon fibers to induce transcrystallization, and the causes of these differences, figure importantly among the factors which must be taken into account in the processing of composites and optimizing the fine structural characteristics of the polymer matrix for the intended uses.

During the past year the investigations have focussed primarily on the Nylon 6,6/carbon fiber system with the specific aim of probing and comparing the ability of various carbon fibers to enhance the nucleation of two different species of spherulites of that polymer, namely positively birefringent spherulites and negatively birefringent spherulites. A second study of transcrystallization is exploring bis-phenol-A polycarbonate as the matrix polymer.

Nylon-6,6, when melted at temperatures well in excess of 265-270°C (e.g. 300°C, to minimize any memory of previous crystallization history) crystallizes upon subsequent cooling in the form of positively birefringent spherulites. The upper temperature limit in which crystallization occurs within a reasonable period of time under these melting conditions is about 255°C. In 'positive' spherulites the a-axis and the hydrogen-bonded planes, i.e. (010) planes, in the constituent radiating lamellae are oriented preferentially parallel to the radial direction. In contrast, when Nylon 6,6 is first crystallized in the form of positively birefringent spherulites at high undercoolings (e.g. at 200°C or lower) and then rapidly heated and held isothermally at a temperature in the range 255-265°C, the polymer melts and recrystallizes at that temperature in the form of negatively birefringent spherulites. Available evidence indicates that such spherulites evolve from persistent submicroscopic crystal nuclei the number of which decreases with increasing temperature within that temperature range. Negative spherulites are characterized by the fact that the (010) planes are preferentially oriented perpendicular to radial direction.

It follows from the foregoing that any transcrystallization of the positively birefringent spherulitic form at the carbon fiber/polymer interface would involve the outward growth of lamellae initiated at the interface and oriented with the hydrogen bonded planes normal to the fiber surface. In the case of transcrystallization of the negatively birefringent spherulitic form however, the hydrogen bonded planes in the outward growing lamellae initiated at the fiber surface would, in contrast, be oriented parallel to the fiber surface.

Eight different carbon fibers were used in the experiments to determine any selectivity in their ability to induce transcrystallization of the two orientationally distinct spherulitic forms described above. Five of the fibers were based on poly(acrylonitrile) (PAN) while the other three were pitch-based. The PAN based fibers (Magnamite) and their respective tensile moduli were AS4 (235 GPa), AU4 (~235 GPa), IM7 (283 GPa), HMS4 (338 GPa), HMU (380 GPa). The pitch based fibers (Thornel) were P75S (517 GPa), P100S (758 GPa), and P120S (820 GPa). With the exception of AU4 and HMU all the fibers had been subjected in manufacture to undisclosed proprietary surface treatments. These treatments are generally presumed to be of an oxidative nature. Except for the HMU fibers none of the other fibers had any sizing. The HMU batch of fibers was supplied with poly(vinyl alcohol) (PVA) sizing. For the experiments described below the PVA was extracted with boiling water, and the fiber dried in vacuum.

With regard to enhancement of nucleation of the positively birefringent spherulitic form in polymer crystallized at low undercoolings (e.g. crystallization at 255°C following melting at 300°C), the fibers fell into two groups. The higher modulus HMS4, HMU, P75S, P100S, and P120S all induced transcrystallization of that spherulitic form at the polymer fiber interface. No transcrystallization occurred with the lower modulus AS4 and AU4, nor with the intermediate modulus IM7 fibers.

No transcrystallization of the negative form was observed under the special conditions described above for the formation of negative spherulites in bulk polymer in the range 255-265°C. None of the fibers enhanced the nucleation of negatively birefringent spherulites. In specially devised experiments, it was possible to demonstrate that the higher modulus HMS4, HMU, P75S, P100S, and P120S fibers, induce transcrystallization of the positively birefringent form at the polymer\fiber interface under conditions in which the crystallization about the polymer matrix occurs in the negatively birefringent spherulitic form. In these circumstances the outward development of the positive transcrystalline sheath occurs at a much slower growth rate than the radial growth rate of the negative spherulites developing in the polymer matrix at the same temperature.

Among the factors which will be investigated in attempts to account for the phenomenological differences in the nucleation influences of the carbon fibers summarized above is whether any epitaxial specificity underlies the propensity of the higher modulus fibers to induce transcrystallization of the positively birefringent spherulitic form. Experiments using highly oriented pyrolytic graphite as a model substrate are planned in this connection.

As mentioned previously, a second system is also being studied, bisphenol-A polycarbonate. It was determined in exploratory experiments with the HMS4 and P120S that these fibers induce transcrystallization in polymer crystallized isothermally at 185-190°C. The rates of development of the transcrystalline sheath and the density of nucleation of spherulites in the polymer matrix were monitored in thin specimens using light optical microscopy. In the coming year an attempt will be made to prepare specimens with controlled transcrystalline sheath development. These samples will then be analyzed with the tests discussed in the next project to determine the effect of transcrystallization on the polymer/fiber interfacial shear strength.

Interface Strength: As the use of composites continues to grow and the variety of fiber-matrix combinations increases, a greater need is developing for reliable, accurate tests that measure the bond strength between the fiber and matrix. Although a number of test methods have been proposed, there are still no well understood and widely accepted methods for measuring the interface strength. Four of these test methods have been evaluated and compared in a joint program with the Center of Composites Materials and Structures at Michigan State University. Two methods are single fiber techniques: a fiber fragmentation method, and a microdrop pull-off technique. The other two methods use composites: a fiber indentation method, and a thermoacoustic technique. NIST has the in-house capability to conduct all of these tests except the fiber indentation method. Carbon fibers having different surface treatments were combined with one resin system to systematically vary the fiber matrix interface strength.

The single fiber fragmentation technique involves casting a dog bone specimen around a single fiber, applying a tensile load to the specimen, and relying upon the interfacial shear transfer mechanism to bring 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 microdrop pull-off technique consists of embedding a fiber through a droplet of resin, and placing a load at a free end of the fiber until it is pulled out of the resin droplet. The average strength of the interface is determined by dividing the measured pull-out force by the area of the fiber-matrix interface. The microindentation technique involves cutting and polishing a small section of a composite so that the fiber direction is perpendicular to the prepared surface. Individual fibers are loaded in compression until debonding occurs, and the interfacial shear stress is calculated from the maximum load. In the thermoacoustic technique, intense heat is applied to a small area on the surface of the composite, and the difference in thermal expansion between the resin and the fiber produces interface debonding. The amount of acoustic signal is inversely related to the interface strength, but the relationship is only qualitative.

The results of experiments with five samples with different strengths show that all four test methods give the same ranking, i.e. higher values for stronger interfaces. The three quantitative methods display similar sensitivities, the fragmentation and indentation tests were generally in agreement while the microdrop pull-off test was consistently lower by a small amount.

A basic understanding of the forces transmitted at the fiber-matrix interface is of paramount importance for the correct evaluation and interpretation of the events that occur in each of the interface testing techniques. Finite element analyses have been performed for the single fiber fragmentation test and the microdrop pull-off method. The fiber-matrix system in the fragmentation test was modeled as a concentric cylinder with a penny shaped crack (broken fiber) embedded in it. All of the results have been obtained with axisymmetric 8-node isoparametric elements. The microdrop test was modeled as a fiber embedded through a resin droplet. The presence of a meniscus formed by the matrix at the surface of the fiber was also considered. A 3-D finite element analysis was adopted, and the stress results were compared with the stress predictions of the 2-D and the axisymmetric models. Different boundary conditions, which are inherent to these tests, were examined. A cylinder surrounding the fiber was used to mimic an "interphase" for both tests. Moreover, the residual stresses resulting from curing were also studied.

Upon fiber fracture in the fragmentation test, the matrix stress and the interfacial shear stress become very large due to the singularity at the crack tip in the fiber. Depending on the fiber and matrix mechanical properties and the amount of energy released, the crack may or may not propagate into the matrix or along the interphase. Thus, the distribution of stress and strain depend on the mechanical properties of the fiber, the matrix, and the extent of damage in the neighborhood of the fiber break. All of these factors can affect the values calculated for the interface shear strength. In the microdrop test, the points of application for the loading can vary from one test to another and this can cause variations in the measured values that do not reflect the differences in the interface strength. These and other similar results show potential complications in the interpretation of the tests and are therefore very useful in identifying problems and limitations in the various test methods.

Characterization of behavior for Thin Film Samples: Experiments have shown that certain mechanical properties can change significantly when a material is stressed while under tight spatial constraint. In this work, the yield and post-yield behavior of brittle and ductile epoxy adhesives were determined as a function of film thickness using the "napkin ring" shear test. Real time observations of the deformation process in the bond as well as SEM post-failure analysis were employed to gain information on the failure sequence.

The complete stress-strain histories of the adhesives were established over bond thicknesses ranging from the micron level and up to values large enough to expose the bulk properties. In general, the ultimate shear strain, γ_f, was found to decrease with decreasing thickness, and this was attributed to premature bond failure caused by tensile microcracks or voids that are formed in the interlayer during loading. The specific γ_f vs. thickness interrelationship is felt to be a mere reflection of the variations in the degree of stress concentration at the tip of the flaws. The most dramatic variations occurred for the ultimate shear strain, γ_f, of the brittle adhesive. The latter was found to increase by over thirty fold relative to the bulk material when the bond thickness was decreased to a few microns. These astonishingly large values of γ_f (i.e. 2.8-3.4) in the micro thickness range are believed to represent an intrinsic material property which is unaffected by the presence of flaws.

Testing of Thin Laminate Structures: The State Department is interested in the use of laminated plastic coatings to protect important data on passport pages. A critical factor for the optimum performance of such a laminated system is the adhesion of the coating to the page. As a result, a test procedure was developed using peel experiments. The samples were prepared by placing a polytetrafluoroethylene insert between the coating and the page along the edge. The system was then laminated following the standard procedure. The insert provided an unbonded area where the coating and page could be separated and gripped in a tensile test machine. The load required to peel the coating from the page was measured, and this provided a measure of adhesion strength.

During the past year, this test was used to examine a variety of new laminate materials made with the latest technology. Such experiments help optimize the evaluation tests for comparing new materials and provide data for the formulation of improved laminates.

Resin and Resin Dominated Properties

In the area of resin properties and resin dominated behavior of composites, 5 projects are currently underway. The first addresses the characterization of microstructure in two component polymeric systems. The second and third focus on determining properties as a function of processing history. In one case, the glass transition temperature of the cured resin is studied as a function of the cure cycle, while the second investigates the properties of composites prepared by filament placement using different processing conditions. The fourth project studies physical aging as a potentially important aspect of durability. Each of these projects will be discussed below. In addition, a new program has been initiated with duPont to study the microstructure of polyetherketoneketone (PEKK), but no results are yet available.

Crosslink Induced Phase Segregation and Change in The Conformation of Embedded Linear Chains: To enhance the toughness of thermoset resins used for composites, one route is to blend linear polymers with the base resin. Upon curing, it is possible to form regions rich in the linear chains. The physical properties of the cured system depend strongly on the morphology resulting from demixing and any phase separation that occurs. Hence, it is highly desirable to control the phase morphology in order to optimize the resin properties. Toward this goal a sound understanding of both the thermodynamics and the kinetics of phase segregation is a must. With regard to the thermodynamics, there are at least two pressing questions that remained to be answered. The first concerns the effects of elastic energy on the phase equilibrium. Theories based on the mean field approach predicted that the elastic energy from the crosslinked matrix tend to favor mixing. This is because any demixing of linear chains will perturb the surrounding matrix, hence causing a increase in elastic energy. The other question concerns with the conformation of the linear chains dissolved in the crosslinked matrix. Theoretical consideration based on impenetrable random obstacles suggests that the presence of crosslinks can result in the collapse of the linear chains.

In order to shed light on the above questions, experiments are conducted in cooperation with the University of Massachusetts and Polytechnic University. During the past year, small angle neutron scattering measurements have been made using poly(tetrahydrofuran) (PTHF) as the model system. Linear PTHF chains with capped end groups were dissolved in PTHF chains containing reactive ends, both species have monodisperse molecular weight. All materials were synthesized by L. Jong of Polytechnic University. The molecular weight of the linear PTHF was chosen to be 15,000. End crosslinkable PTHF with molecular weight from 700 to 15,000 were included in this study. By selecting the same polymer for both components, the experiments can concentrate on the contributions from the elastic energy alone. The concentration of the linear unreactive chains was in the dilute region.

The phase behavior as well as the single chain conformation of the unreactive chains were investigated after the reactive chains were crosslinked, and the results depend strongly on the molecular weight of reacting polymer before crosslink. At all the levels studied, crosslinking induced demixing. Concurrently, it also causes the embedded linear chain to collapse. The extent of demixing increased as the molecular weight of the crosslinkable PTHF decreased. As the molecular weight reached 700, phase segregation occurred and the conformation of the linear chain return to the uncollapsed state. This is because most linear chains are now situated amidst similar molecules instead of being surrounding by crosslinked PTHF.

__Processing-Microstructure-Relationships in Samples Made by Filament Placement__: A cooperative program is underway with the Robot Systems Division of NIST in which they are preparing samples using an advanced manufacturing workstation based on filament placement technology. The samples are made with continuous carbon fiber tows pre-impregnated with thermoplastic, polyetheretherketone (PEEK). The fabrication uses *in-situ* consolidation and tow placement techniques by means of two cooperating robot manipulators. The Polymers Division is evaluating the composites for microstructure and properties. The initial measurements are void content by density measurements and interlaminar shear strength using ASTM D 2344 "Apparent Interlaminar Shear Strength of Parallel Fiber Composites by Short-Beam Method."

The bonding mechanism during processing of thermoplastics is autohesion. Autohesion is initiated when the oncoming ply surface and the substrate surface achieve close contact. During autohesion, segments of the long chain molecules making up the thermoplastic diffuse across the ply boundary. Maximizing molecular diffusion insures a strong bond at ply interfaces. The compaction mechanism is assisted by pressure at the ply interface since it helps bring the individual layers of prepreg into intimate contact. Improper consolidation of the thermoplastic prepreg may lead to defects at the ply interface and result in poor mechanical performance. Such defects may include voids, resin rich areas, resin starved areas, and delaminations.

Density was determined by weighing the samples in water and air. The mechanical tests were carried out using ASTM D 2344 as noted above. A specimen in the shape of a short circular arc is subjected to force on its top surface. As the load is applied, the top surface is stressed in compression while the bottom surface is stressed in tension. Due to the tension and compression in adjacent surfaces near the mid-plane, a strong shear stress occurs between the center plies. The specimen dimensions are designed so that failure is most probable at the mid-plane interface rather than at the surface fibers. The "apparent shear strength (S_H)" is determined from the relationship $S_H = 0.75P_B/bd$ (N/m^2), where P_B is the load at break, b is the specimen width, and d is the specimen thickness.

Table II shows the results for apparent shear strength and density for samples from 8 different batches. The average value for five specimens was used for each shear strength measurement while two samples were used for each density determination.

Table II: Comparison of Samples

Batch Number	$<S_H>$ ($X10^{-7}$ N/m^2)	Density (g/cm^3)
28	2.47	1.438
11	2.49	1.512
28	2.63	1.452
26	3.30	1.482
26	3.58	1.502
22	3.69	1.526
23	3.70	1.524
21	4.90	1.558

With the exception of batch 11, which was made with a different head on the filament placement apparatus, a consistent trend is found with increasing shear strength for lower void content (higher density). A variety of placement rates, consolidation temperatures and consolidation pressures were used to make these samples, and the limited data now available do not provide sufficient information to formulate a clear correlation. Nevertheless, there is a general trend in which slower placement rates produce better consolidation (higher density), and higher shear strength values. Additional data are now being gathered so the effects of the various parameters can be defined.

Glass Transition Temperature and Processing History: The glass transition temperature of a cured resin is commonly used to indicate the degree of cure. For a partially cured resin, the glass transition temperature is generally about 20°C higher than the isothermal curing temperature. The glass transition temperature and other properties of the resin may remain unchanged, as long as the temperature of the resin is not raised again near or above the highest temperature the resin had experienced during cure. In order to fully develop the cure, the resin is often post-cured at much higher temperatures. For a fully cured resin, there exists an ultimate glass transition temperature. The ultimate glass transition temperature remains unchanged, even if the resin is further post-cured at temperatures beyond the ultimate glass transition temperature.

The experiments in this study show, however, that ultimate glass transition temperature, and hence the associated ultimate properties of the resin are dependent on the curing history. For a catalytically cured homopolymer of diglycidyl ether of bisphenol-A the influence of the heating rate was found to be relatively minor if the ceiling temperature was below the ultimate glass temperature. When the ceiling temperature was near or above the maximum ultimate glass transition temperature, however, high heating rates were found to decrease the ultimate glass transition temperature by more than 50°C. Although industry is interested in high speed processes to increase the throughput, there are limits in the processing cycles that can be used. Beyond a certain point, a degradation in the performance of the finished product may occur. It is important to study the mechanisms and the kinetics of each system, to map out the regions of curing history that yield best performing materials. Cure monitoring techniques can play a critical role in this regard.

Physical Aging and the Performance of Polymer Glasses: It is well known that the volume recovery which is observed in glasses subjected to a quench from above the glass transition to below it is accompanied by changes in the viscoelastic properties of the glass. Furthermore it has been observed that the magnitude of the effect on the viscoelastic properties decreases as the magnitude of the stress or deformation increases. Thus, if the glass "physically ages" during the volume recovery, application of large mechanical stimuli causes an apparent "erasure" of the prior aging or a "rejuvenation" of the glass. The causes of the erasure or rejuvenation are a subject of controversy.

The samples examined here are made with diglycidyl ether of bisphenol-A reacted with amine terminated poly(propylene oxide) (PPO). Two different types of experiments were performed to explore the interpretation of the effects of large mechanical stimuli on the aging of the glass. First, aging experiments were carried out in these epoxy glasses near the glass transition temperature so that a state of volumetric equilibrium could be attained in several days of aging. In these experiments the time required to reach equilibrium, t^*, was unaffected by the magnitude of the applied stress. This is in spite of the fact that at the largest stresses the apparent aging is greatly reduced. The second experiment was torsional dilatometry on samples subjected to intermittent large deformations after a thermal quench from above the glass transition temperature to below it. In this instance, although the volume of the glass increased during the deformation, returning the mechanical deformation to zero caused the volume of the glass to relax rapidly back to the same volume as that which would have been observed if no mechanical deformation had been applied.

The results of these two types of experiments make a strong argument that the large deformation response of the glass is impacted differently by volume recovery than is the small deformation response. Furthermore, the underlying thermodynamic state of the glass is essentially unchanged by large mechanical stimuli.

The effects of physical aging on the yield behavior of model epoxy glasses has also been studied. These glasses are the same as those discussed above. Specifically, the yield behavior for samples made with PPOs having molecular weights of 230 and 400. The resulting samples are designated D230 epoxy and D400 epoxy respectively.

Cylindrical specimens were prepared from each of the two epoxies and subjected to quenching and isothermal aging treatments at different temperatures and aging times in the range from 0.1 to 1000 h. The influence of the evolution of the non-equilibrium glass towards equilibrium was assessed by measurement of the yield stress in uniaxial compression at the aging temperature. It was found that for both resins the yield stress after aging increases by as much as 1.8 times the original yield stress after aging for 0.1 h. It was also found, upon aging at temperatures near to the conventionally measured glass transition, that the evolution of the yield stress with aging time virtually ceases at a characteristic time, t^*, which increases as temperature decreases. From the influence of temperature and strain rate on the above phenomena, the kinetics of the physical aging process were examined quantitatively in terms of a time-aging time-temperature correspondence principle. The results suggest that the increase in yield stress on aging is correlated to the decrease in volume after the quench and to the corresponding increase in the viscoelastic modulus.

Two new results have come out of this study. First, although the yield stress increases with aging time in a manner similar to the changes in viscoelastic modulus, it is found that the value of t^* relevant to the yield stress is approximately an order of magnitude greater than that found for the cessation of the evolution of the relaxation modulus. This suggests that, even though the yield phenomenon is related to the viscoelastic response, the exact mechanisms responsible are not the same.

In addition, it is found that the time for the volume itself to recover into equilibrium is longer than the t^*'s for either the viscoelastic or the yield processes. In order to explain this, the existence of hierarchical responses in glassy materials under isothermal conditions is postulated. Moreover, these responses must occur at different size scales in the order viscoelastic $<$ yield $<$ volume recovery.

POLYMER BLENDS AND SOLUTIONS

The goals of the Polymer Blends and Solutions Group are 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 world wide 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%.

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.

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 improvement of properties by an order of magnitude 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, mixing and demixing kinetics of polymer blends especially in the non-linear (late stage) region, and shear effects on the phase separation of polymer blends.

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), small angle x-ray scattering (SAXS) 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 91 Significant Accomplishments

- A combined light scattering photometer and rheometer has been constructed to examine phase separation behavior of polymer blends and solutions under the influence of a simple shear field. This device utilizes a cone and plate geometry to generate the shear gradient for torque and normal force measurement and utilizes a special lens system, a charge coupled array detector and an optical multichannel analyzer for steady shear as well as time resolved 2-d light scattering detection. Steady shear as well as kinetics of mixing/demixing after starting and cessation of shear can be studied.

- Shear induced mixing of a polystyrene/polybutadiene blend in dioctyl phthalate has been studied with the newly constructed shear light scattering instrument. The anisotropic deformation of phase separated droplets, the gradual loss of phase boundary and the eventual homogenization to a one phase mixture can be observed through scattering patterns as a function of shear rate. The de-mixing process has also been observed after cessation of flow by the time resolved capability of this instrument. An anisotropic spinodal decomposition process has been observed for the first time in phase separation kinetics study.

- SANS has been used to measure the Flory-Huggins interaction parameter in a ternary polymer blend system consisting of deuterated polystyrene (PSD), poly(vinylmethylether) (PVME), and protonated polystyrene (PSH) using the random phase approximation theory for three components. By solving the equations describing the scattering for the three interaction parameters, the thermodynamics of the protonated components, PSH and PVME can be studied. A quantitative measurement of χ-parameter between two protonated components using this technique has been demonstrated.

- Two polyurethane (PU) SRM's are being certified with weight-average molecular weights determined by light scattering and the limiting viscosity numbers determined under the conditions commonly used for the estimation of MWD by gel permeation chromatography. The weight average molecular weight of the low molecular weight PU has been found to be 5×10^4 g/mol. This material will be certified as SRM 1480.

- The apparent "shift" in polymer blend phase separation temperature, T_c, under shear flow has been interpreted in terms of the mode-coupling theory for mean-field polymer blend systems. This theory indicates that there is no true shift of T_c and explains the apparent shift of T_c along the flow direction as arising from suppression of fluctuations along the direction of flow. Upon dilution of the polymer blend, fluctuation effects become important and mean-field theory no longer applies. The shift in T_c in diluted blends is consistent with a crossover from mean-field to Ising critical behavior upon dilution. The combination of detailed scattering data and the hydrodynamic theory allows for a rational interpretation of polymer blend phase separation subject to deformation.

EXPERIMENTAL

C. C. Han, R. M. Briber, C. M. Guttman, J. R. Maurey, A. I. Nakatani, P. H. Verdier, D. A. Waldow, D. Hair, E. Hobbie, B. J. Bauer, M. M. Santore, G. B. McKenna, K. J. Jewett, B. Hammouda[1], S. Sakurai[2], H. Hasegawa[3], T. Hashimoto[3], H. Tanaka[3], H. Jinnai[3], M. Motowoka[3], and Y. Feng[4]

[1]Reactor Radiation Division
[2]Kyoto Institute of Technology, Kyoto, Japan,
[3]Kyoto University, Kyoto, Japan,
[4]East China University of Chemical Technology, Shanghai, China

A Shear Light Scattering/Rheometer Instrument for Both Steady Shear and Time Resolved Kinetics Studies of Polymer Phase Behavior

A combined light scattering photometer and rheometer has been constructed to examine phase separation behavior of polymer blends and solutions under the influence of a simple shear field. The device utilizes a special lens system and a two-dimensional charge-coupled device

(CCD) array detector to quantitatively measure the scattering intensity as a function of shear rate. A cone and plate geometry is used for the rheometer to generate the shear gradient for torque and normal force measurements. Time resolved measurement of mixing/de-mixing behavior are achieved with the CCD detector and a optical multichannel analyzer.

Phase Behavior of Polystyrene/Polybutadiene Blend in Dioctyl Phthalate

The shear induced mixing phenomena of a 8% solution of a 50:50 blend of deuterated polystyrene (PSD) ($M_w=8.5x10^4$, $M_w/M_n=1$) and polybutadiene (PB) ($M_w=2.2x10^4$, $M_w/M_n=1.1$) in dioctyl phthalate has been studied in the shear light scattering/rheometer. The initial quiescent condition of the system is established in the two phase region. The anisotropic deformation of phase separated droplets, the gradual loss of the phase boundary and the eventual homogenization into a one phase mixture can be observed through scattering patterns as a function of shear rate.

The de-mixing process has also been observed after cessation of flow using the time resolved capability of this instrument. An anisotropic spinodal decomposition process has been observed for the first time in phase separation kinetics study.

Shear Induced Phase Separation of Polystyrene in Dioctyl Phthalate Solution Studied by SANS and Time Resolved Light Scattering

Small angle neutron scattering measurements were taken of a high molecular weight ($M_w = 1.9x10^6$) deuterated polystyrene in diocytl phthalate solution at a low concentration (3% weight fraction) under steady shear with rates ranging from the quiescent condition (0 s^{-1}) to 1100 s^{-1}. Above a characteristic shear rate $\gamma_c=57$ s^{-1}) the scattering intensity increased dramatically in a manner similar to the increase seen following a temperature drop from the one-phase region (ambient temperature) to the two-phase region in this upper critical solution temperature system. The cloud point is estimated to be a few degrees lower than the cloud point for protonated polystyrene in dioctyl phthalate at this molecular weight and concentration. Based on this analogy, the mean field random phase approximation (RPA) approach (the Zimm inverse scattering formula) was used along with a swollen radius of gyration in the Debye function to analyze the data and extract a statistical segment length b and a polymer-solvent interaction parameter χ_{ps}. The segment length was seen to increase slightly indicating a slight increase in chain dimension beyond γ_c while the interaction parameter showed a dramatic increase up to its "spinodal" value at $\gamma_s=280$ s^{-1} where the RPA breaks down therefore giving unreliable values.

This shear induced phase separation has also been studied by light scattering which provides measurements at low q (longer dimensional scale). The mixing kinetics after cessation of shear flow is being studied by the time resolved light scattering measurements as well.

Microstructure Effect on the LCST Phase Behavior of Deuterated Polybutadiene and Protonated Polyisoprene Blends

The miscibility of the blend of protonated polyisoprene (HPI) with the content of 3,4-linkage in the range of 7 to 15% and deuterated polybutadiene (DPB) with the content of 1,2-linkage in the range of 12 to 28% was studied by small-angle neutron scattering (SANS). It was found that all blends studied here show the lower critical solution temperature (LCST) type phase behavior, i.e., the phase-separation may occur above the spinodal temperature. It was also found that the miscibility is quite sensitive to the microstructure of the polydienes used. The effective thermodynamic interaction parameter χ_{eff} per segment between two polymers can be determined by fitting the SANS data with the theoretical scattering curve obtained on the basis of random phase approximation. The χ_{eff} values decreased, and therefore the blends became more miscible, with an increase in the content of 1,2-unit in DPB and/or a decrease in the content of 3,4-unit in HPI. Furthermore, the temperature dependence of χ_{eff} shows a systematic change with the microstructure. In order to understand the microstructure effects on χ_{eff}, an attempt was made to separate the effective interaction parameter χ_{eff} into the fundamental segmental interaction parameter χ's between every pair of 1,2- and 1,4-unit in DPB and 3,4- and 1,4-unit in HPI, based on a treatment for the random copolymer blends. As a consequence of such analyses, all fundamental χ's were found to have the temperature dependences of the upper critical solution temperature (UCST) type, which is opposite to the LCST-type of χ_{eff}. An alternative explanation for the LCST phase behavior was proposed, that is, the LCST-type phase behavior of a given HPI/DPB blend may originate from a subtle balance of the temperature coefficients of all the UCST-type fundamental χ's.

Small Angle Neutron Scattering and Light Scattering Study on the Miscibility of SBR/PB Blends

Miscibility of binary blends of polybutadiene (PB) and poly(styrene-r-butadiene) (SBR) was studied on the basis of fundamental segmental interaction parameters. In this analysis PB was assumed to be a copolymer comprising 1,2-linkage (V) and 1,4-linkage (B) and SBR to be the one comprising styrene (S) and butadiene with V and B. The fundamental segmental interaction parameters between V and S (χ_{VS}), B and S (χ_{BS}), and V and B (χ_{VB}) were determined on the basis of the copolymer blend theory from the effective interaction parameters (χ_{eff}'s) for the blends of PB and SBR, and those for poly(styrene-b-butadiene-b-styrene) triblock copolymer (SBS), with different copolymer compositions and microstructures of polybutadienes. The values χ_{eff} were determined from either the small-angle neutron or x-ray scattering of the mixtures in the single-phase state. Using these interaction parameters, χ_{VS}, χ_{BS}, and χ_{VB}, the miscibility of the SBR/PB blends was predicted for a given set of V, B, and S contents in PB and SBR, again on the basis of the copolymer effect. The predictions of the miscibility for several SBR/PB blends agreed very well with their results of the light scattering experiments.

SANS and SAXS Study of Block Copolymer/Homopolymer Mixtures

The lateral and vertical components of the radius of gyration for a single block copolymer chain and those of a single homopolymer chain in the lamellar microdomain formed by a mixture of diblock copolymers and homopolymers were investigated by means of small-angle neutron scattering (SANS), and the microdomain structures by small-angle x-ray scattering (SAXS). Homopolymers were used whose molecular weights are much smaller than those of the corresponding chains of the block copolymers so that the homopolymers are uniformly dissolved in the corresponding microdomains. The SANS result suggests that the homopolymer chains in the microdomain as well as the block copolymer chains are more compressed in the direction parallel to the interface and more stretched in the direction perpendicular to the interface than the corresponding unperturbed polymer chains with the same molecular weight. With increasing the volume fraction of the homopolymers the thickness of the lamellar microdomains increases. The block copolymer chains were found to undergo an isochoric affine deformation on addition of the homopolymers or with the change of the thickness of the lamellar microdomains.

Time-Resolved Small-Angle Neutron Scattering in Intermediate and Late-Stage Spinodal Decomposition of DPB/HPI Blends

Time-resolved small-angle neutron scattering (SANS) experiments were performed to study the later stage (i.e., the intermediate stage and the late stage) of spinodal decomposition (SD) of a critical mixture of perdeuterated polybutadiene (DPB) and protonated polyisoprene (HPI) with an LCST-type phase diagram and a critical temperature $T_c=36.1°C$. Time-sliced SANS intensity, $S(q,t)$, is generally composed of the scattering due to growing domains, $I_d(q,t)$, and that due to the thermally induced local composition fluctuations inside the domain $I_T(q,t)$ where q and t are the scattering vector and time, respectively. $S(q,t)$ as a function of q shows the "spatial crossover". At q much below and above a time-dependent wave-number, $q_s(t)$, $S(q,t)$ depends only on $I_d(q,t)$ and $I_T(q,t)$, respectively. The time evolution of the composition difference between the two coexisting domains, $\Delta\phi(t)$, was determined from $I_T(q,t)$, which was found to be consistent with the prediction of the scattering theory based upon the random-phase approximation. $\Delta\phi(t)$ was found to increase with t and reach a constant equilibrium value $\Delta\phi_e$ at $t>t_{cr}$, where t_{cr} is the crossover time from the intermediate to the late-stage SD. The crossover wavenumber, $q_s(t)$, also underwent a characteristic change at t_{cr}.

Phase Separation in Deuterated Poly(carbonate)/Protonated Poly(methylmethacrylate) Blends Near Glass Transition Temperature

Time resolved small angle neutron scattering technique has been used in the study of phase separation kinetics of deuterated poly(carbonate)/protonated poly(methylmethacrylate) (DPC/PMMA) blends near their glass transition temperature. It has been found that the LCST of this blend is below the glass transition temperature. A miscible configuration can be frozen into a specimen prepared by fast solvent casting. The very early stage of spinodal decomposition kinetics has been studied by SANS at temperatures slightly above the glass transition temperature. Quantitative features predicted by the Cahn-Hilliard-Cook spinodal decomposition theory and the polymer specific q-dependent rate of growth (or decay) can be studied due to the slowing down of kinetics by glass transition. The virtual structure factor, $S_x(q)$, can be obtained and the effective interaction parameter, χ_{eff}, in the two phase region which is normally inaccessible by experimental measurement, has been obtained through time extrapolation.

Molecular Weight Dependence of the Mobility in Polymer Blends

The molecular weight dependence of the mobility in polystyrene/poly(vinylmethylether) blends (PS/PVME), in polybutadiene/styrene-butadiene random copolymer (PB/SBR) blends and in polyisoprene/styrene-butadiene random copolymer (PI/SBR) blends have been studied by the time resolved light scattering technique. In the PS/PVME case, blends samples were quenched from an initial equilibrium temperature which is close to the critical temperature to a final temperature which is deeper in the miscible region. The decay of concentration fluctuations were measured, the interdiffusion coefficient was deduced and then the mobilities were calculated. In the PB/SBR and PI/SBR cases, samples were homogenized by uniaxial compression. Interdiffusion coefficients were obtained through the time resolved light scattering measurement of the spinodal decomposition in the early stage. The mobility was related to the ratio of the interdiffusion coefficient and $q_m^2(0)$ where $q_m(0)$ is the initial peak position during the spinodal decomposition. It is clear from the results that the mobility can be represented by the vacancy model at lower molecular weights but shows deviation towards the incompressible model at higher molecular weights. The overall molecular weight dependence of the mobility can be well represented by the Akcasu-Naegele-Klein equation.

Small Angle Neutron Scattering Studies of Blends Containing Linear and Crosslinked Polymers

Work continues on blends containing crosslinked and linear materials. Small angle neutron scattering measurements are currently being conducted to measure the chain conformation (radius of gyration) of linear chains trapped in a network . This work is seeking to establish whether linear chains in a network are collapsed or expanded (or remain the same) with respect to bulk mixtures without the presence of the network. Most of this work has concentrated on the protonated polystyrene/deuterated polystyrene system with the network formed by a free radical polymerization of styrene with a small amount of divinyl benzene. Recently, work was initiated to examine the same questions using model networks made from siloxanes. This work is in collaboration with Professor Claude Cohen in Chemical Engineering Department at Cornell University. Model networks can be synthesized from narrow distribution functionalized oligomers of siloxane using a multifunctional coupling agent. This leads to systems which have a well defined molecular weight and molecular weight distribution between crosslinks. This will allow a more detailed analysis of the data to examine the effects of network homogeneity.

Small Angle Neutron Scattering Studies of Ternary Polymer Blends

Small angle neutron scattering has been used to obtain the Flory-Huggins interaction parameter in the ternary polymer blend system consisting of deuterated polystyrene (PSD), poly(vinylmethylether) (PVME), and protonated polystyrene (PSH) using the random phase approximation theory for three components. By solving the equations describing the scattering for the three interaction parameters, $\chi_{PSH/PSD}$, $\chi_{PSD/PVME}$, $\chi_{PSH/PVME}$ and the thermodynamics of the protonated components, PSH and PVME can be studied. In the past it has been difficult to quantitatively measure the interaction parameter in protonated blends as a function of temperature and composition. The results indicate that the temperature dependence of $\chi_{PSH/PVME}$ (at fixed composition) can be described with the form $A+B/T$. The PSH/PVME data (plotted as χ versus T^{-1}) exhibits a parallel shift relative to PSD/PVME (to larger values of χ at a given temperature) indicating that the enthalpic portion of χ (B) is approximately equivalent while the entropic portion (A) differs. This helps to explain the origin of the lower cloud points observed in PSH/PVME blends relative to PSD/PVME blends.

Thermodynamic Stability and Phase Separation Kinetics of Polymer Blends Containing Cyclic Chains

The LCST phase envelopes of two PS/PVME blends were examined: one blend consisted exclusively of linear components and a second blend contained cyclic PS. Each blend component had a molecular weight greater than the entanglement molecular weight of the pure component. The blend containing the cyclic PS yielded a cloud-point curve that was elevated 7-8°C above that for the exclusively linear blend, at compositions from 10% to 65% PS. Furthermore, cyclization does not appear to shift the critical composition significantly, though more tests are needed to establish this with certainty.

Time resolved light scattering studies of the phase separation kinetics yield mutual diffusion coefficients when data analysis is based on Cahn-Hilliard-Cook theory for the early stage of spinodal decomposition. The mutual diffusion coefficients near the critical composition (20% PS / 80% PVME) of the two systems are nearly identical when comparisons are made at the same temperature increments above the respective spinodal temperatures. An estimate of the second derivative of the free energy makes possible the calculation of the mobilities at various temperatures. Here it is apparent that molecules within the cycle-containing blend are significantly less mobile than those in the exclusively linear blend. This is true even though the cycle-containing blend was measured 7°C higher above its T_g compared to the exclusively linear blend.

Direct comparison with literature on cycles is not possible; however, our static and dynamic results are consistent with prior work. For example, the stability enhancement of a few degrees by the cyclization of one blend component complements the observation of a depressed θ-temperature for solutions of cycles with respect to their linear analogs. The stabilizing effect is also consistent with ring threading and the expansion of rings in linear melts predicted by computer simulations. The link between ring expansion and enhanced stability can be rationalized in terms of the negative chi parameter for blends of rings and linear chains of the same chemical makeup, and by an increased energy of the pure cyclic melt.

Our mobility results are consistent with the data of Mills *et al.*[1] for diffusion of cycles through chemically identical linear matrices. More important, though, is that our observation of slower cyclic mobility relative to linear chains in linear matrices concurs with the observation that linear contaminants drastically increase the viscosity of cyclic melts.[2,3]

1. Mills, P.J., Mayer, J.W., Kramer, E.J., Hadziiaonnou, G., Lutz, P., Strazielle, C., Rempp, P., and Kovacs, A.J., Macromolecules **20**, 513 (1987).

2. McKenna, G.B., Hotstetter, B.J., Hadjichristidis, M., Fetters, L.J., and Plazek, D., Macromolecules **22**, 1834 (1989).

3. McKenna, G.B., and Plazek, D., Polym. Commun. **27**, 304 (1986).

Image Processing Studies of Late Stage Phase Separation In Polymer Blends

Real time video microscopy is used to study the late stage domain growth in phase separating polymer blends. Current studies are on the polystyrene/poly(vinylmethylether) system, which is a model system with well characterized thermodynamics and phase diagram. Thin films of the polymer are cast from solution, the film is subjected to a temperature jump into the two phase region, and the growth of the domains is followed as a function of time. Two regimes are observed. The first is when the wavelength of the phase separation (q_m) is less than the film thickness ($d \sim 10 \mu m$). In this regime the structure exhibits the classical interconnected "network" structure characteristic of spinodal decomposition. The second regime is when q_m is greater than the film thickness. In this case distinct droplets are observed, which increase in size with time. From two dimensional Fourier transforms of the images the size scale of the droplets can be measured. It is found that the growth of the domains exhibits a classical power law behavior of the form $q_m \sim t^n$ with $n = 1/3$. From the images the area fraction of the domains and domain interface can be followed as a function of time. It is found that the area fraction does not reach the equilibrium values, as determined by the phase diagram, until very late in the phase separation process.

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 two areas: (1) the study of shielding mechanisms of containers commonly used in protecting archival materials from pollutants such as sulfur dioxide, and (2) selection of storage modes with respect to the degradation of SO_2 acting on various types of paper and the mechanisms of those degradations.

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

Accelerated aging tests have been performed to study the degradation of newsprint and rag paper in the presence and absence of sulfur dioxide. Samples were maintained in an enclosed environment with a relative humidity of 50% and a temperature of 60°C. Such conditions lead to the detection of low molecular weight acid after 4 to 6 months of reaction time. Further work on detecting these and other species is continuing.

Failure of Latex Barrier Films

The failure of latex barrier films is of commercial and medical interest. Regions with low local cross-link density may be expected to fail before the rest of the film fails under certain loading conditions. The change in the cross-linked density across the film is measured through the change in local swelling as determined by fluorescence and FTIR microscopy.

THEORY

E. A. Di Marzio, J. F. Douglas, and P. H. Verdier

The Viscosity of Glass Forming Systems

The Gibbs-Di Marzio theory of glass formation postulates that the glass temperature occurs when the configurational entropy reaches a critically small value. The usefulness of this concept lies in the ability of the entropy theory to predict from first principles the glass temperature of all varieties of polymer systems. The theory has been very successful in predicting the glass temperature which is an important processing variable. The entropy postulate also gives an insight into why viscosity increases so dramatically as the system approaches the glass transition. Fewer configurations at low temperature means that it is more difficult to jump from one configuration to another thereby giving a high viscosity. Adam and Gibbs had used this idea to obtain an expression for the viscosity but their derivation is heuristic. An expression has been derived that is algebraic in the entropy and not of the Vogel-Fulcher form. The frequency dependent viscosity is also being investigated.

Mixing Strong and Weak Bonds in a Polymer Blend

Hydrogen bonds provide a means for compatibilizing polymer blends. This suggests that a polymer molecule that is connected to its environment via hydrogen bonds should be studied as a fundamental problem in hydrogen bonded polymer systems. The problem of a polymer molecule being pulled off of a plane surface (or off of a line) to which it is attached with hydrogen bonds has been solved. The existence of a critical force was observed. This raised the question as to whether a critical force causes real systems to behave as gels below the transition and as ordinary liquid above the transition. A hydrogen bonded polymer system mimics a cross-linked system but the cross-links, being hydrogen bonds, can break and reform. This is different from the case where the cross-links are covalent bonds. Does such a system show a yield point, or will it flow no matter how small the value of the applied force? The answer to this question, which is being pursued, determines whether the compatibilized polymer system is viewed as a gel or as a liquid.

Also of interest is the question of how a mix of strong bonds and weak bonds affects polymer behavior, as in the case of 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? This problem is addressed by modeling the adsorption of a polymer that has many weak and few strong bonds onto a surface. The adsorption is very different from that of a homopolymer with the average value of attractive energy.

Thermodynamic Phase Transitions in Polymers as Models for Self-Assembling Systems

Self-Assembly exists and is widespread in polymeric systems because there are many different kinds of phase transitions in polymers. It occurs whenever a collection of molecules undergoes a structure inducing thermodynamic phase transition.

The phase transitions occurring in isolated polymer molecules are: (1) Helix to random-coil transition which can be first-order, second-order or diffuse. (2) Adsorption onto a surface which is second-order. (3) Collapse transition which is second-order. (4) Polymerization, or one-dimensional crystallization which is first-order. (5) The coil-stretch transition in a shear field.

The five classes of many molecule transitions in polymers are (1) Crystallization which is first order. (2) Liquid crystals and plastic crystals which are weakly first order and second order. (3) liquid-liquid transitions which are first order. (4) Glass transition which is second order. (5) Soaps-Membranes-Micelles-Vesicles-Block Copolymers which can be first or second-order transitions.

Two areas of study, outlined below, have been identified which have relevance to polymeric materials.

In a given material these various transitions can couple to form a symphony of structure. Two examples of this are (1) A bicontinuous material which is cooled below the glass transition temperature of one of the phases. The other phase is then leached out resulting in a porus material with no dead end pores. (2) Multilayer Langmuir-Blodgett films in which a given layer is doped in some given way. An investigation into pairs of coupled transitions is being made to see if interesting new materials can be fabricated.

A self healing material is characterized by a structure which if destroyed or damaged can reconstitute itself by incubation at a fixed temperature. At most an annealing cycle is required. Self-healing materials seem to be self-assembling structures whose structure represents a stable thermodynamic phase. In order to understand self-healing polymer structures knowledge is needed of various thermodynamic phase transitions that can occur in polymers and how they interrelate. A list of self-healing materials is being compiled and the principles behind the concept of self-healing are being studied with the ultimate goal of understanding self-healing systems as a subcase of self-assembling systems.

Relaxation in Disordered Materials with Applications to Polymer Dynamics

Classical models of viscoelastic materials neglect memory effects arising from material inhomogeneity and cooperative molecular motion. Relaxation with memory is treated by starting from an exact integral equation for the relaxation function and a model form of the memory kernel which is deduced from exactly solvable dynamical models exhibiting memory. The relaxation model is applied to polymer melt dynamics to deduce the temperature and molecular weight dependence of the zero shear viscosity and the diffusion coefficient.

Rubber Elasticity

Work on molecular models of polymeric network elasticity has concentrated on certain minimal aspects of the rubber networks. The classical theories of Wall and Flory, James and Guth, and others focused primarily on the property of network connectivity. Non-classical theories, such as that of Edwards and coworkers have emphasized the "topological interaction" associated with the uncrossability of network chains. Di Marzio and Jackson et al. attempted to derive more realistic models by including the physical constraint of finite network chain volume, i.e., packing effects. Gaylord and Douglas incorporate these minimal features of a crosslinked network (network connectivity, entanglement interaction, finite chain volume) into a simple theory of rubber elasticity which they call the "localization model".

Comparison of the localization model with torsion data for dicumyl peroxide cross-linked natural rubber by McKenna et al. indicates good agreement where molecular parameters vary in a sensible fashion. Generalization of the localization model to describe the elasticity of swollen rubbers by Douglas and McKenna indicates that the change of the elastic contribution to the free energy of a network with swelling differs substantially in highly cross-linked and lightly cross-linked rubbers. Comparison of the localization model to experimental data for highly cross-linked and relatively lightly cross-linked rubbers yields good qualitative agreement. Generalization of the localization model to describe network swelling is in progress. This generalization will require a 1/d expansion generalization of the Flory-Huggins mean-field theory to take into account the cross-link dependence of the χ mixing interaction parameter.

"Shift" in Polymer Blend Phase Separation Temperature in Shear Flow

Recent scattering studies of high molecular weight blends subject to simple shear flow have been interpreted to show large shifts of the apparent phase separation temperature, T_c. The nature of the shift seems to depend on polymer concentration. In a blend melt a large "shift" of T_c is observed along the flow direction while no detectable shift is observed in the normal to flow direction. Upon dilution of the blend to semi-dilute concentrations in a low molecular weight solvent a large shift in T_c in the normal to flow direction is found. These experimental studies raise a number of theoretical questions. Most importantly how is it possible for the critical temperature to differ along the flow and normal to flow direction? Why does dilution have such a strong effect on the phase stability of blends under shear?

The "mode-coupling" theory of phase separation under shear has been modified to describe high molecular weight melt blends. This hydrodynamic theory indicates that there is no shift in T_c for these melts. Rather the inverse scattering function has an additional shear rate dependent term which can be interpreted as an apparent shift of the T_c along the direction of flow.

Upon dilution of the polymer blend with solvents, fluctuation effects become important and mean-field mode coupling theory no longer applies. The shift in T_c, as these blends are diluted, is consistent with a crossover from mean-field to Ising critical behavior.

The hydrodynamic theory provides important insight into the origin of the "apparent" shift of T_c which differs along the applied field and normal to applied field directions in other physical situations. For example, such apparent "shifts" have also been observed in the critical scattering of stretched cross-linked blends. Using classical equilibrium theory of phase separation to interpret the scattering data can lead to the fundamentally mistaken impression of a critical temperature which depends on the field direction.

The combination of detailed scattering data and the hydrodynamic theory allows for a rational interpretation of polymer blend phase separation subject to perturbation.

Dynamics of Polymer Chains and Blends

Better understanding of chain dynamics is important to improving both the characterization and the processing 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.

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.

Present efforts in this project are in four areas. First is a study, now completed, of the effects of changing chain move rules upon relaxation behavior, to resolve discrepancies between results obtained by different groups using different models. Second is a study of the effects of chain "architecture"-- ring closure, branching, knotting, etc.-- upon chain dimensions and dynamics. The results of this work will help to explain anomalies found in experimental data on such systems. Third is a study of the effects of the "bulkiness" of chain monomers upon equilibrium and relaxation behavior. The results of this work will provide a critical test of some of the theoretical treatments currently in use. These three projects are all essentially studies of the behavior of isolated chains (dilute solution limit). As such, the first and third are necessary preliminaries to the fourth project, a study of phase separation in polymer blends, and are expected to be the major continuing emphasis in this area. Computer programs for blends simulations have been written for the new Cray computing system at NIST, and are presently being tested.

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 commercial polyurethanes used in medical devices. Because of wide variations in compositions of these block copolymer systems, 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, a program was initiated to produce polyurethane Standard Reference Materials (SRM's) and to develop improved methods for characterizing these and other block copolymer systems.

Two polyurethane SRM's are being produced whose weight-average molecular weights will be determined by light scattering and the limiting viscosity numbers determined under the conditions commonly used for the estimation of MWD by gel permeation chromatography. The 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 was used to measure the weight average molecular weight 5×10^4 g/mol of the low molecular weight PU. The intrinsic viscosity of this material in THF also was measured.

Polyolefin Melt Flow Rate Standards

Melt flow rate and melt index measurements are used in the 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 standard.

A branched polyethylene, SRM-1476a, with a melt flow rate of about 2.0 g/10 min was recertified and a report is to be issued. 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 under way 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 Standard

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 Assessment Panels, 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 calibration standards for aqueous size exclusion chromatography (SEC). For this purpose, samples of narrow molecular weight distribution polyethylene oxides have been chosen as proposed standards. The polyethylene oxide SRM's should be usable on most aqueous SEC columns without special column conditioning.

Light scattering experiments have been started to obtain the weight average molecular weight of polyethylene oxides.

This work is supported, in part, by SRMP.

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.

Materials research efforts are pursued for reducing the marginal leakage of tooth restorations and for the development of materials and techniques for promoting adhesion to dentin, enamel, bone, and soft tissues. Durable space occupying materials are investigated for use in cavity preparations. New composite resin formulations with reduced polymerization shrinkage and more resistance to attack by oral fluids are explored. Strong, more durable, versatile dental cement formulations are developed. The durability of dental materials is investigated by pin-on-disc wear studies and by characterization of aged materials by the application of the Weibull method of statistical analysis. Studies of calcium phosphate compounds for endodontic sealants, bone augmentation or caries-reducing agents are being investigated. The basic chemistry of precipitation of calcium phosphates is explored as it relates to formation of mineral deposits such as bone, teeth, and atherosclerotic plaque.

Theoretical and experimental studies of stresses within bonded dental systems are explored with the objectives of defining the most compatible material-property and geometrical design combinations for porcelain-to-metal, tooth-to-resin, resin-to-filler bonding and so forth. Characterization by Weibull statistics is employed, with a view toward incorporation of finite element stress analysis, for evaluation of the reliability of dental systems.

The partnership between the Federal Government and the American Dental Association, which extends back to 1928, was further strengthened by the inclusion of a Center of Excellence for Materials Science Research in 1989, one of three such research entities currently funded by the National Institute of Dental Research. The Center for Excellence 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.

FY 91 Significant Accomplishments

- Novel, siloxane-containing difunctional and multifunctional vinyl monomers were prepared based on a modification of the method used for the synthesis of analogous hydrocarbon and fluorocarbon cyclopolymerizable monomers.

- Spiro orthocarbonate monomers with 1,3-diene functionality were synthesized. This provides highly reactive monomers which undergo double ring-opening polymerization with expansion.

- Promising dentinal bonding systems based on the mono- functional methacrylate, mono-2-(methacryloyloxy)ethyl phthalate, were developed.

- The technology surrounding glass ceramic compositions with intrinsic tooth-like colors was transferred from laboratory to dental manufacturing.

- A viscoelastic model of stresses in porcelain-metal strips has shown a relationship between the temperature at which stress first develops in porcelain and the differences in thermal expansion between porcelain and metal.

- Liposome studies show that of the lipid constituents making up the membranes of matrix vesicles, the nidi for initial calcification in cartilage, phosphatidylserine and sphingomyelin may have the greatest influence in controlling biomineralization in this tissue by delaying the expansion of intravesicular crystals into the surrounding tissue matrix.

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

J. M. Antonucci, S. M. Keeny III, 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[1], Y. Matsuya[4], and S. Matsuya[4]

[1]Guest Scientist
[2]ADAHF/PRC
[3]Fukuoka Dental College, Fukuoka, Japan
[4]Kyushi University, Fukuoka, Japan

A new pin-on-disk wear machine has been used to evaluate the wear rates of several commercial and experimental resin-based composite systems. The high run-to-run variability indicated that not all the variables were well controlled in the tests and attempts have been made to improve the consistency of the results. Recirculating water jets to flush the wear debris off of the samples were added as was a sub-micron filter to remove the wear debris. After these modifications were implemented the testing variability was reduced and the results were similar to those obtained from the original wear machine.

The original wear machine was utilized in an ADA sponsored round- robin test comparing several different types of wear apparatuses from different laboratories using identical commercial composites.

Clinical trials of ADA Health Foundation dental enamel bonding systems were completed. The technology was transferred to a third patents licensee in 1990, and products based on the system command a market share greater than 11%. Total sales of products based on the system have exceeded $10 million since the technology was first transferred in 1986.

Clinical research continues on the optimum concentrations of system components and component analogs.

A patent application has been filed on the development of radiation shielding materials for protecting soft tissues from radiation damage during head and neck tumor therapy. Protocols for the fabrication of the materials and shields have been completed, and the materials and techniques are currently in clinical trials at various military facilities in the Washington, D.C. area.

Improved setting (hardening) time of calcium phosphate cement (CPC), a DMMG-developed material, would make it more feasible for use as (1) a root canal sealer-filler, (2) an implant material for periodontal bone defects, (3) a binder for other nonsetting calcium phosphate implant materials, (4) a remineralizer for incipient root caries and a desensitizing agent for hypersensitive dentin, and (5) an implant material in the reconstruction of calvarial defects. The reaction of tetracalcium phosphate (TTCP) and dicalcium phosphate (DCPA) anhydrous has been shown to be responsible for the hardening of CPC, and recent studies investigated the effects of the TTCP/DCPA ratio and pH on reaction time. Other studies examined the effects of TTCP and DCPA particle sizes on the pH of the CPC slurry and on the compressive strength of set cement specimens. Particle size was found to have a strong effect on pH by controlling the rates of dissolution of DCPA and TTCP. Highest compressive strengths were obtained from mixtures containing large TTCP and small DCPA particles.

A genetically engineered protein bioadhesive (PBA) based on a bioadhesive naturally produced by mussels has been shown to be adhesive in moist conditions. In a study with Genex Corp. (Gaithersburg, MD) scientists, the properties of composites of PBA and calcium phosphate cement were investigated. PBA was found to greatly reduce setting times and increased the cohesiveness of the cement paste. Importantly, PBA did not interfere with hydroxyapatite formation.

In collaborative research with A. Sugawara of Nihon University School of Dentistry (Tokyo), the *in vivo* aspects of calcium phosphate cement (CPC) were evaluated using a dog model. The results showed that CPC is highly compatible to periapical tissues in comparison to Grossmen's cement and a commercial calcium hydroxide-iodine paste, and point to the possibility that CPC may be used in endodontic procedures.

Efforts continued in the Center of Excellence project to develop and test "synthetic dentin" materials that consist of a self-setting calcium phosphate cement (CPC) and hydrophilic resins that have acidic calcium-binding groups. Incorporation of 13 to 15 wt% of an experimental resin, PMGDM/B4400-HEM5, significantly improved the properties of CPC by increasing the strength and decreasing the setting time. Water sorption caused a significant reduction in the strength of CPC-resin composites, however, and ongoing studies will seek to minimize this effect.

A new polymeric calcium phosphate cement was developed based on the reaction of CPC powders and other TTCP mixtures with aqueous solutions of poly(methylvinylether-maleic acid). These cements combined excellent strength properties with a degree of toughness not found in the previous polymeric calcium phosphate cements.

MEDICAL MATERIALS INSTRUMENTS AND DEVICES

J. A. Tesk, S. M. Keeny, III, J. M. Antonucci, M. Anderson[1], B. Moore[1], C. Goodman[2], B. O. Fowler, and M. Tung

[1]U.S. Navy, Dental School, Bethesda, MD
[2]Air Techniques, Hicksville, NY

Research on the use of microwave generated gas plasmas has been brought to a close. The results showed that one could achieve sterility in short times (several minutes) under prescribed conditions. However, the recent introduction of efficacious, short time, conventional sterilization units to the marketplace severely limits the commercial utility of gas plasma sterilization. It was concluded that only small, specialty niche applications might be available and that the expenses involved could render the use of gas plasmas as virtually noncompetitive.

DENTAL POLYMER, COMPOSITE, CEMENT SEALANT AND ADHESION CHEMISTRY

J. M. Antonucci, J. W. Stansbury, R. L. Bowen[1], F. C. Eichmiller[1], M. Farahani[1], A. D. Johnston[1], N. W. Rupp[1], S. Venz[1], and J. Rusz[2]

[1]ADAHF/PRC
[2]U.S. Navy, Dental School, Bethesda, MD

The formaldehyde insertion/condensation reaction was applied to 2-hydroxyethyl acrylate in an attempt to prepare a symmetrical, crosslinkable HEMA-like monomer. The presence of the hydroxyl group in the starting acrylate led to difficulties in the reaction. When a hydroxyl protecting group was utilized, the reaction proceeded as intended. After product isolation, the protecting group was removed to give the oxybismethacrylate monomer with 1,6-diene and diol functionalities. Like HEMA, the monomer is water soluble. Bulk polymerization yields a crosslinked, hydrophilic polymer potentially suitable for a number of biomedical material applications.

The formaldehyde acrylate insertion reaction also has been extended to the synthesis of novel, difunctional and multifunctional siloxane acrylate monomers and oligomers. As was the case in the synthesis of highly fluorinated di- and multifunctional monomers, the use of aprotic solvents such as dimethyl sulfoxide appears to be essential for the successful insertion/condensation reaction of siloxane mono- and diacrylates with paraformaldehyde.

Spiro orthocarbonate monomers with exocyclic double bonds have been utilized to obtain free radical ring-opening polymerization with expansion. Various curing conditions were studied using dental composite materials based on spiro monomers. The dual-cure and chemical-cure techniques provided the most effective polymerizations as monitored by diametral tensile strength results. The photo-cure procedure produced significantly weaker composites.

New spiro orthocarbonate monomers with 1,3-diene functionality were prepared. Important characteristics of the new monomers include their excellent free radical reactivity and the ability to form rigid, crosslinked, ring-opened polymers.

A related Center of Excellence project is seeking to enhance the durability and marginal adaptability of dental composites and related materials through the use of monomers that undergo minimal, zero or even positive volume changes on polymerization (hardening). Several classes of novel monomers were synthesized, characterized and evaluated in this effort. Significant progress has been made in this regard with free radical single- and multiple-single-ring-opening model monomers, as well as monomers that undergo ring opening through hydrogen abstraction.

A Center of Excellence research team is preparing and evaluating a range of organophilic and hydrophilic (water-soluble) surface-interactive coating monomers that can lead to a decrease in caries on crown and root dentin surface. With the ability to bind and bond to both enamel and dentin, these materials can be used as shields against attack by microorganisms. More than a dozen monomers have been synthesized, characterized and studied in this effort, and substantial progress has been made in defining the parameters of likely monomer candidates.

The technology surrounding a liquid analog (PM-GDM) of the surface-active monomer PMDM (the diaduct of pyromellitic dianhydride and 2-hydroxyethyl methacrylate) derived from this dianhydride and glycerol dimethacrylate, which was shown to be highly effective in several dentin bonding systems, was transferred to industry.

A simple liquid analog of PMDM, mono-2-(methacryloyloxy)ethyl phthalate (MMEP), was shown to be an effective surface active monofunctional monomer in several dentin bonding systems. In the presence of certain types of amines, especially tertiary aryl amines, MMEP, PMDM and similar carboxylic acid vinyl monomers were shown to undergo self-initiated free radical polymerization under ambient and near ambient conditions. A mechanism involving complexation of the acid and amine moieties followed by a single electron transfer from the amine to the carboxylated monomer (similar to the electron transfer mechanism for the decomposition of benzoyl peroxide by aryl amines) is believed to be involved in these "nonperoxide" polymerizations. This spontaneous polymerization also is thought to be a significant factor in achieving bonding to dentin.

The properties of composite restorations have been shown to be improved by incorporating large glass-ceramic inserts into composite resins to increase the inorganic component of the restoration and displace a major proportion of the resin. One patent has issued from a Center of Excellence research and a second patent application was filed. The ADA Health Foundation negotiated a license on the patents with a dental manufacturer, and inserts kits are expected to be available to dentists before the end of calendar year 1991. Clinical trials are being organized in the U.S. and abroad. Additional research remains to be done to complete the quantification of the physical characteristics of the inserts, to optimize insert shapes and sizes, and to optimize heat treatments for achieving a variety of dental shades.

ADA Health Foundation research begun in the late 1970s on metal-reinforced polymers was resumed in a Center of Excellence pilot project. The project is currently in the information-gathering phase: promising functional monomers, alloy powders and coupling agents were selected and coinvestigators were identified.

CALCIUM PHOSPHATE CHEMISTRY, BIOCHEMISTRY, STRUCTURE AND CLINICAL IMPLICATIONS

W. E. Brown[1], C. M. Carey[1], L. C. Chow[1], N. Eidelman[1], E. D. Eanes[2], B. O. Fowler[2], D. Skrtic[3], A. W. Hailer[2], M. Mathew[1], D. N. Misra[1], B. A. Sieck[1], S. Takagi[1], B. Tomazic[1], M. S. Tung[1], and G. L. Vogel[1], and K. Ishikawa[4]

[1]ADAHF/PRC
[2]National Institute of Dental Research (NIDR) at NIST
[3]Ruder Boskovic Institute, Yugoslavia
[4]School of Dentistry, Tokushima University, Japan

Work was continued on testing the hypothesis that the structure of stoichiometric hydroxyapatite contains about one water molecule per unit cell and that the cell is distorted from hexagonal symmetry to provide an additional lattice site to spatially fit this water. Further experiments are in progress but results are currently incomplete.

Results from model liposome studies of proteoglycan(PG) control of cartilage mineralization show that when glycosaminoglycan (GAG) chains, the components principally responsible for the mineral growth inhibition properties of the intact PG, are enzymatically removed, other regions of PG become inhibitory. This latent activity appears to be associated with the core protein of PG and/or oligosaccharides o-linked to it. N-linked oligosaccharide regions appear to be inactive. Also non-inhibitory is hyaluronic acid. The level of inhibition of PG and its constituent parts correlate with the capacity to bind Ca^{2+} ions. This latter finding suggests inhibition results from Ca-linked PG functional groups blocking apatite growth by binding to growth sites on the crystal surfaces. Other liposome studies show that of the lipid constituents making up the membranes of matrix vesicles, the nidi for initial calcification in cartilage, phosphatidylserine and sphingomyelin may have the greatest influence in controlling biomineralization in this tissue by delaying the expansion of intravesicular crystals into the surrounding tissue matrix.

A study was initiated to explore the relationships between the various solution parameters governing apatite nucleation and growth kinetics and the textural properties (e.g., size and shape) of the apatite crystals precipitated. The hydrolytic conversion of anhydrous dicalcium phosphate to apatite was used as a precipitation reaction model for studying these relationships under a variety of controlled solution conditions. Findings to date suggest that the Gibbs free energy of precipitation (i.e., solution supersaturation) appears to be an important factor in determining the final size attained by the apatite crystals.

Under physiological conditions octacalcium phosphate (OCP) is a precursor that hydrolyses to a more apatitic phase. Hydroxyapatite (OHAp) does not form under these conditions, apparently because of natural inhibitors in blood. Since pyrophosphate ($P_2O_7^{-4}$) is an important inhibitor of OHAp growth in blood, its effect on the relative growth rates of OCP and OHAp were studied. Results suggest that OCP precipitated on both OCP and OHAp seeds followed by its hydrolysis to a more apatitic phase.

Investigations of OCP and its role in biomineralization continue. Double salts of OCP and dicarboxylates were studied and the crystal structure of a calcium adipate salt was determined. The structure was not compatible with the proposed model for OCP-succinate double salt, indicating that there could be different models of these double salts. Attempts to grow single crystals of these double salts for structural studies are continuing.

The calcium phosphate cement (CPC) based on the self-setting reaction of tetracalcium phosphate and dicalcium phosphate was shown to have better biocompatibility and osteoconductivity than several commercial endodontic materials. An *in vivo* collaborative study with Northwestern and Yale Universities indicated that CPC may be useful in the reconstruction of skeletal tissues that do not bear significant stresses. The postulated mechanism is thought to involve a combination of implant resorption and osteoconduction.

Work on identification and semi-quantitation of phases and structural states of calcium phosphates and other substances formed upon coating biological implant surfaces by a plasma technique from hydroxyapatite sources was expanded to include additional phases expected to arise from different calcium phosphates used for plasma deposition. Knowledge of the chemical and physical composition of these implant coatings is essential for evaluating and controlling *in vivo* bonding with the contiguous tissue when the implants are used for bone and tooth restorations.

The tooth-bound fluoride (F) content of enamel or root dentin can be increased significantly by pretreatment with a viscous acidic (pH 2) gel containing monocalcium phosphate monohydrate (MCPM), followed by exposure to saliva-like solution containing 1 ppm of F.

With increased F content, the average rate of demineralization for the controls was about twice that of the MCPM-treated samples, and there exists a significant correlation between tooth-bound F content and resistance to lesion formation.

DENTAL ALLOYS, CERAMICS, METROLOGY, AND ANALYSIS

J. A. Tesk, M. Y. Chiang, S. M. Keeny, III, J. E. McKinney[1], K. Asaoka[2], R. L. Bowen[3], F. C. Eichmiller[3], A. A. Giuseppetti[3], T. Matthews[5], Y. Sato[4], and R. M. Waterstrat[3], L. A. Winnert[3], and H. Kikuchi[6]

[1]Guest Scientist
[2]Tokushima University School of Dentistry, Tokushima, Japan
[3]ADAHF/PRC
[4]Hiroshima Dental School, Hiroshima, Japan
[5]Howard University, Washington, D.C.
[6]Nihon University, Tokyo, Japan

Computer simulations and analytic investigations of the development/relaxation of stress in dental porcelains and porcelain-metal systems showed good agreement between predicted and experimental load bearing temperatures. Also, a theoretical relationship between the applied stress σ_o at the deformation temperature, and retained stress, σ, for any heating rate, in a porcelain-metal strip with coefficient of thermal expansion α (metal) and $\Delta\alpha$ (porcelain-metal) was found: $\sigma_o/\sigma = \alpha/\Delta\alpha$.

Studies have continued on new alloys that are expected to produce mechanically reliable prosthetic devices having excellent biocompatibility. Mechanical tests of a metallic compound (zirconium, ruthenium, and palladium) have produced evidence that microscopic crack propagation is inhibited in this alloy by the occurrence of stress-induced atomic shear transformations. Cracks that normally lead to fracture are apparently being stabilized by the formation of small plates near the tip of each growing crack (a region of high stress). Transformation toughening behavior has been observed previously in certain ceramic materials, but never in a metal. Transformation toughening is associated with enhanced ductility, greater strength and improved reliability. A patent application has been filed on this development.

The intrinsic colorations of several experimental glass ceramics were shown to be controllable by both heat treatment and composition to yield typical dental shades. Castability of these glass ceramics has been demonstrated. Potential applications for these new glass ceramics include, megafillers ("inserts") for composites, crowns and CAD/CAM restorations.

The effect of post cure storage time (5-1440 mins) on the diametral tensile strength of an experimental composite was evaluated at two storage temperatures (22°C and 37°C) using the characteristic strength (S_o) and the Weibull modulus (m). It was found that m shows some fluctuation while S_o increases significantly with storage time.

A study of the uniaxial tensile strength (UTS) and the diametral tensile strength (DTS) of resin based dental composites revealed that for macrofilled composites UTS > DTS while for microfilled composites UTS $\approx$ DTS. UTS also was shown to be a more sensitive indicator of interfacial bonding between polymeric matrices and particulate glass fillers than DTS.

Work continued during FY91 on developing superstrong alloys for dental prostheses. Conductive epoxies have been found to be useful die materials because they are easy to handle, nonhazardous, and preliminary studies indicate that their accuracy is better than conventional die materials. An electroplated alloy has been prepared, and a study of the alloy's corrosion resistance and mechanical strength is underway. Specimens of other candidate alloys are nearly complete and their properties will also be studied in the immediate future.

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Industrial and Academic Interaction

Industrial

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.

A program of technology transfer with **E.I. duPont de Nemours Co.** to study copolymerization of macromonomers has been renewed. The macromonomers have been incorporated in cross-linked interpenetrating networks where phase separation has been studied by neutron diffraction. Copolymerization with methacrylate resins for possible application in polymerization initiated by electron beams has also been explored.

A collaborative research with Procter & Gamble has been initiated to study the nature of bonding between bulk polymers and solids. Neutron reflectivity measurements are being made using deuterated polystyrene and polymethyl methacrylate with narrow molecular weight distribution. All the deuterated materials are synthesized by Procter & Gamble while the neutron measurements are being conducted by scientists from both Procter & Gamble and the Polymers Division at NIST.

A workshop on New Measurement Technology for Polymer processing held at NIST was attended by 19 scientists and engineers representing the polymer processing and instrument manufacturing industries. The discussions focused on the need for new in-line, real-time measurement capabilities for polymer processing. As a result of this workshop a NIST/industry consortium is being formulated for the purpose of developing new measurement technology based on fluorescence and optical methods.

Union Carbide Corporation has sponsored a joint program with NIST to study charge distribution in polymers designed for high voltage cable insulation. A paper describing results from the project was presented at the IEEE meeting in Toronto in June 1990.

Research personnel from **Westinghouse Central Research Laboratory** have been to NIST to use the thermal pulse apparatus to attempt to measure charge distribution in polymer films subjected to ion implantation.

Under a Research Associate Program with **Enimont America** an evaluation of fluorescence techniques for cure monitoring of crosslinkable polycarbonate polymers has been carried out.

The **Strategic Highway Research Program** and Montana State University collaborated on measurements of the structure of asphaltic cements and concretes of the sort used in road pavements. Our work in association with this program involved application of solid state nuclear magnetic resonance techniques to characterize heterogeneities in asphalt cements.

Industrial visits were made to **Kodak, General Electric, IBM, Xerox, Ford, GM and Dow Chemical** to elicit industrial support for programs in physical aging and mechanical performance in solid polymers. As a result, a collaborative effort was initiated with Kodak in mechanical behavior of glassy polymers.

A Research Associate agreement with **Rheology Research** investigates the mechanical behavior of polymers.

The **Forest Products Laboratory**, Madison WI collaborates on measurements of the chemical and physical structure of cellulosic materials by solid state nuclear magnetic resonance spectroscopy.

Cooperative programs have been initiated with the **Automotive Composites Consortium** (ACC) formed by **Ford, Chrysler, and General Motors**. Polymers Division staff are formulating flow models to assist the ACC in fabricating a polymer composite structural element that demonstrates the technology developed by the ACC. Other projects are analyzing fabrication problems in the preparation of test specimens for crash worthiness and developing test methods for automotive composites.

A collaborative program with the Central Research and Development of **duPont** to investigate the morphology of poly(aryl ether ketone) (PEKK) has been initiated as a means to improve it performance properties. The first phase of study consists of using a combination of neutron and x-ray scattering to determine the lattice dimensions.

A joint program with **General Electric** investigates resin transfer molding of composite materials. The initial studies compare measurements of permeability made by different methods at the two laboratories. These will be followed by studies of preform anisotropy to verify the applicability of the usual two parameter model to off-axis flows.

Polymer Division scientists are participating with **Southwest Research Institute** in a program sponsored by the **National Center for Manufacturing Science**, a consortium of more than 80 companies. The goal of this effort is to develop and demonstrate the use of on-line process control in polymer composites fabrication.

In an ongoing activity, **Mobil Chemical** R&D laboratories makes proprietary use of the Division's x-ray facilities to characterize the effect of process conditions and molecular variables on polyethylene materials produced in blown film manufacturing processes. Films of high molecular weight high density polyethylene produced by two stage deformation in a "high stalk" bubble have been shown to result in films that exhibit orientation distributions that are well balanced in the machine and transverse directions.

In an ongoing activity, **General Motors** Research Laboratories uses the Polymers Division's x-ray facilities to characterize the thickness of the boundary between crystalline and amorphous regions in Nylon 6 and Nylon 66 plastics that are blended with an amorphous nylon.

Firestone Tire and Rubber Co. makes proprietary use of the Polymers Division x-ray facilities to provide morphological data on polyester fibers as a function of spinning conditions.

A new effort has been initiated with **duPont Plastics Department** for use the small angle x-ray scattering facility to make proprietary measurements on the microstructure of poly(ethylene terephthalate) films used in electronic and mass storage applications.

duPont Fibers Department uses the small angle x-ray facility to make proprietary measurements on the microstructure of nylon fibers.

A new agreement with **Amoco** will involve using the small angle x-ray scattering facility to make proprietary measurements of the microstructure of polypropylene fibers and engineering plastics.

Industrial funding through **ASTM-D20** subcommittee on thermal methods resulted in the production of a polypropylene SRM certified for melt flow rate. This standard reference material facilitates calibration of melt flow apparatus described in the voluntary standard method ASTM D-1238.

Ford Motor Company has an interest in polymers at interfaces and phase changes in thin films. The Polymers Division has expertise in this area and as a result a staff member has been invited to spend time at Ford Motor Company.

Hercules uses the small angle x-ray scattering facility to characterize the microstructure of polypropylene fibers.

Projects on polymer blends are planned with **Exxon, IBM, Eastman Kodak, Hercules, Mobile Chemical** and **General Motors.** The work will focus on equilibrium phase behavior and phase stabilization problems for specific polymer blends with Exxon, IBM and Eastman Kodak, and on the domain orientation, fiber structure and blends morphology with Mobil Chemical, Hercules and General Motors.

Industrial/Academic

Specimens of polymer insulation subjected to electrical stress at **Detroit Edison** were examined for charge injection and decay characteristics in a joint effort with University of Connecticut and NIST personnel.

Academic

A joint program with the University of Massachusetts and Polytechnic University analyzes the interaction between polymer networks and linear chains. The Universities are to prepare samples based on special networks that form a monodisperse distribution of molecular weights between crosslinks. The samples are then analyzed for microstructure by Polymer Division staff.

Mr. Zicai Liang of Chengdu University of Science and Technology, Peoples Republic of China has been a foreign guest scientist in the Specialty Polymers Group during the past year. He has been investigating the pyroelectric properties of vinylidene cyanide/vinylacetate copolymer and the effects of incorporating NLO dye molecules.

A joint program with the University of Massachusetts analyzes the molecular network structure of thermoset resins. The University of Massachusetts works with networks that form a bimodal distribution of molecular weights between crosslinks. The samples are analyzed by Polymers Division staff.

A collaborative arrangement has been made with Prof. H. Marand of the Chemistry Department, Virginia Polytechnic Institute, for research on the morphology of crystallizable polymer blends.

Professors Ray Chen and Gary Carter at the University of Maryland, Baltimore County have continued to cooperate in experiments for NLO measurements on polymers synthesized at NIST.

Dr. Aime S. DeReggi was again invited as visiting Professor at the Ecole Superieure de Physique et de Chemie Industrielles in Paris, France during April and May 1990. He performed experiments using a pressure pulse to detect electrical charges deposited on the interior of a section of polyethylene pipe and did preliminary experiments on detection of charges injected from a metal point imbedded in a polymer dielectric.

A cooperative program with Dr. Stansilaw Slomkowski of Polish Academy of Sciences explores by fluorescence spectroscopy the interactions of proteins with polymeric microspheres.

A cooperative program with Professor I. K. Varma of Indian Institute of Technology, Dehli explores the role of interface in the mechanical performance and chemical durability of fiber-reinforced composites.

A collaborative program has been established with Professor Joseph Rose at Drexel University to instrument a polymer injection molding machine to use fluorescence spectroscopy to monitor the mold cycle.

An experimental program using fluorescence spectroscopy to monitor the quality-of-mix of the product output from a twin screw extruder has been carried out in cooperation with the Naval Surface Warfare Center.

A cooperative program with Professor Jim Wu of the University of Maryland, Baltimore County, uses the technique of fluorescence recovery after photobleaching to measure the self-diffusion of poly(ethylene oxide) (PEO) in NaI-PEO electrolytes.

Under the sponsorship of the U.S. Yugoslav Fund for Scientific and Technological Cooperation, David L. VanderHart has been collaborating with Dr. G. LLahajnar, Dr. Zupancic and Prof. Blinc of the Josef Stefan Institute in Ljubljana, Yugoslavia. Work involves measuring diffusion of solvent in polymer gels and describing NMR relaxation properties in systems like gels using ideas of fractal geometries. Work on NMR imaging in polymers is also being explored.

A joint program with Michigan State University investigated test methods for fiber-matrix interface strength in composites. A variety of currently available test methods were evaluated using model materials carefully prepared to have different interface strengths. The results as well as the advantages and disadvantages of each method were compared to determine the current state-of-art in this field.

A collaboration with Prof. Suresh Advani of the University of Delaware Center for Composite Materials has been established to measure the flow properties of fluids in model porous media. These measurements are designed to explore the disagreements between theory and experiment that are prevalent in the field of flow through porous media.

The Dental and Medical Materials Group participated in collaborative research 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, Memphis University, Catholic University, University of the District of Columbia, Loyola University, Northwestern University, the University of Maryland, the University of Florida, the Oregon Health Sciences University, The University of Texas (San Antonio), Taiwan University, Howard University, the University of Strasbourg (France), and the West China University of Medical Sciences. Research projects included 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. Dr. John Tesk was invited to conduct collaborative research for three weeks at Tokushima University in Japan.

Associated Activities

Invited Talks

Division personnel presented a total of 107 invited talks on research activities at the following types of organizations and symposia: industrial laboratories, 23; international symposia, 18; universities, 16; topical symposia, 10; national and government laboratories, 13; professional society meetings, 20; and Gordon Conferences, 7.

SRMS and Patents

Dr. Charles M. Guttman and Dr. John R. Maurey: SRM 1473, Low Density Polyethylene Resin.

W.L. Wu: Thermal Technique for Determining Interface and/or Interply Strength in Composites. U.S. Patent 4,972,720, November 27, 1990.

Air Drying Resins and Processes for Preparing Same. B. Dickens and B.J. Bauer. (Pending)

Radiation Curable Resins Based on Hydroxy Acrylates and Acid Dianhydrides. B. Dickens and B.J. Bauer. (Pending)

Radiation Curable Resins Based on Polyethylene Glycol Acrylates and Poly Isocyanates. B. Dickens and B.J. Bauer. (Pending)

An Optical Sensor for the Measurement of Molecular Orientation and Viscosity of Polymeric Materials Based on Fluorescence Radiation. A.J. Bur, S.C. Roth, R.E. Lowry, C.L. Thomas and F.W. Wang. (Pending)

Dental Monomer/Resin Systems Based on Vinyl Metallocarboxylates. J.M. Antonucci, J.W. Stansbury, and B.O. Fowler. Applied for 8/10/90.

Novel Fluorinated and Siloxane Multifunctional Acrylates and the Synthesis Thereof. J.M. Antonucci, J.W. Stansbury, and Guo Wei Cheng. Applied for 8/10/90.

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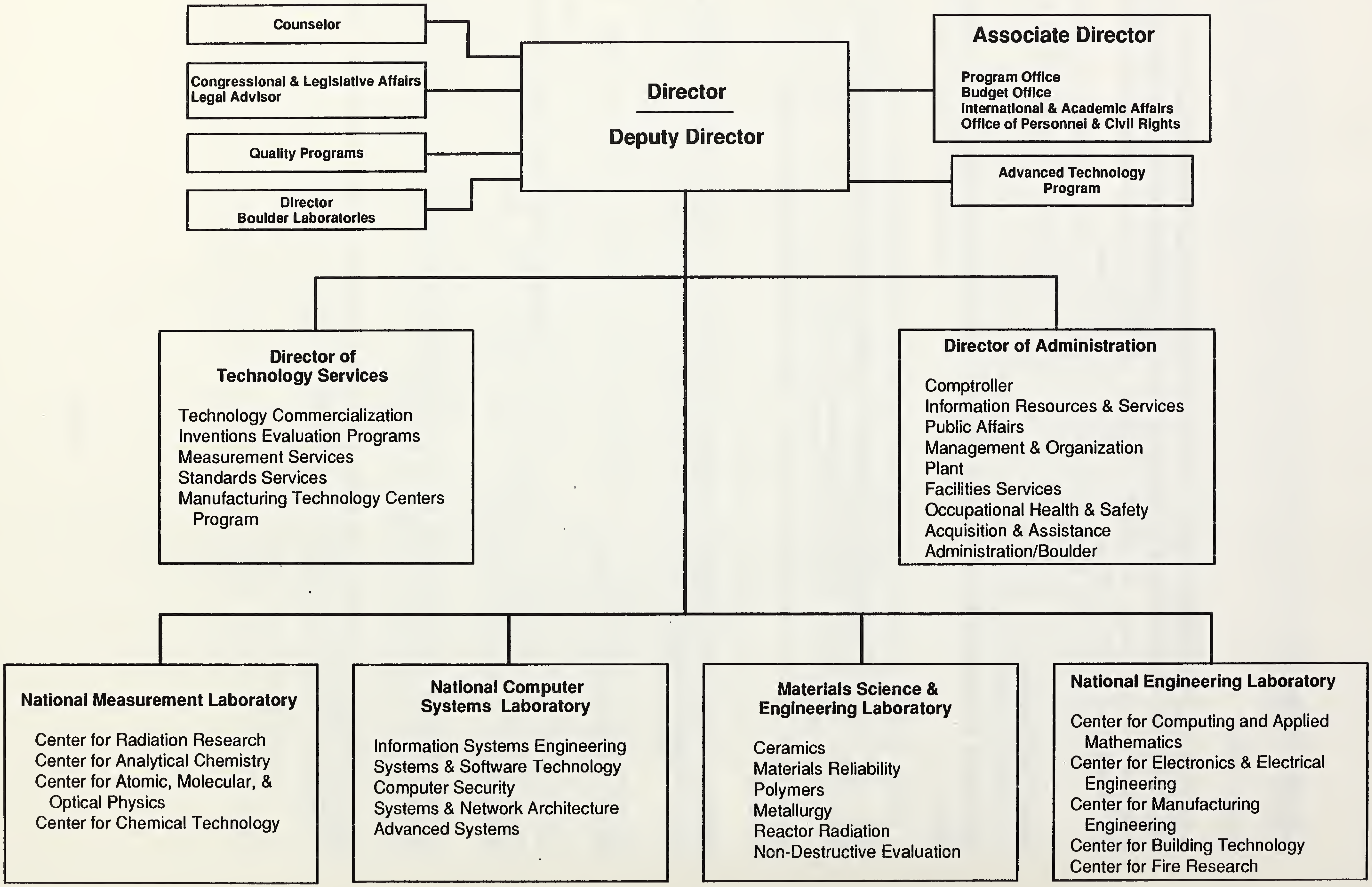

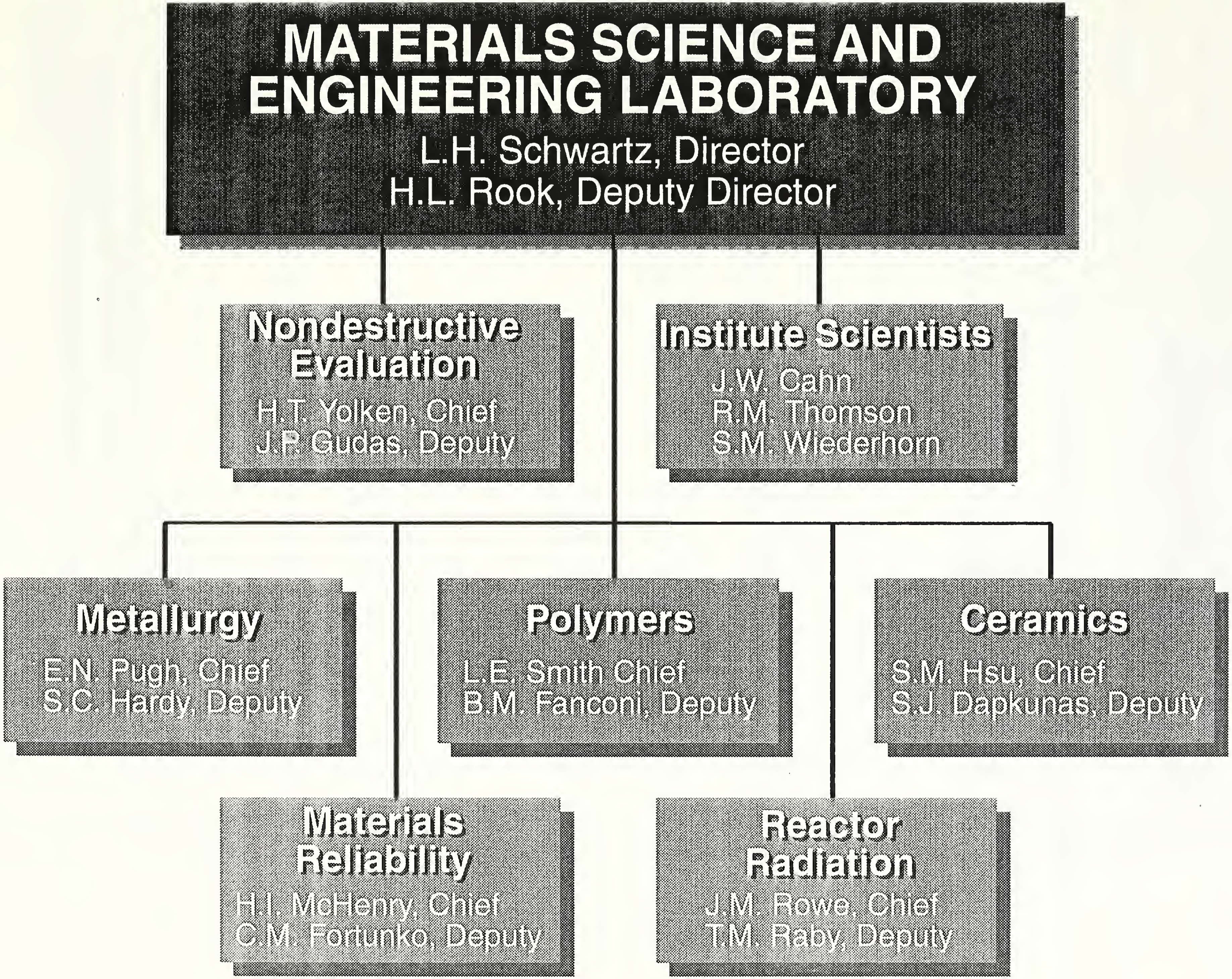

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Technical Activities of the Polymers Division for FY91 are reviewed. Included are descriptions of the 6 Tasks of the Division, project reports, publications, and other technical activities.

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