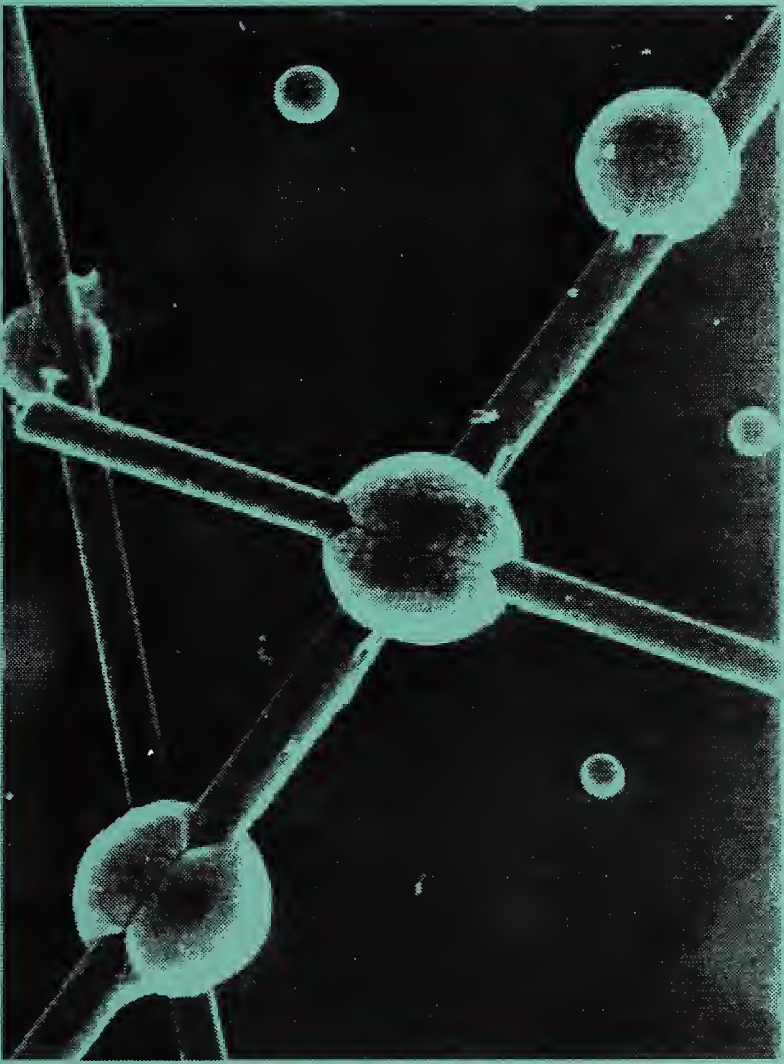
MSEL

Materials Science and Engineering Laboratory

POLYMERS



NISTIR 4396
U.S. Department of Commerce
National Institute of Standards
and Technology

Technical Activities
1990

Melt grown isotactic polystyrene spherulites which have partially engulfed carbon fibers and developed through the narrow interstice between them.

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POLYMERS

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

NAS-NRC
Assessment Panel
January 31-February 1, 1991

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Technical Activities 1990

U.S. DEPARTMENT OF COMMERCE, Robert A. Mosbacher,Secretary
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INTRODUCTION

POLYMERS DIVISION

Leslie E. Smith, Chief
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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.

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 effect of compatibilizing additives, and the morphology of blends. These concepts can be used by polymer scientists and engineers to design new blend materials and processes more efficiently.

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 began work to model the flow of polymers in transfer molding processes. 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 over fifty Research Associates and eighty Guest Scientists who together spent over fifty 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 with the Division staff 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 nine 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. Six Reference Materials were 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.

- A patent was issued to the U.S. Government for a composite material made by dispersing a powdered high T_c superconductor in a polymer. The composite has the processing advantages of a polymer and the levitation properties of a superconductor at temperatures below T_c. Possible applications of the composite include magnetic bearings and transportation systems utilizing levitation to reduce friction.

- In collaboration with Drexel University, we have instrumented an injection molding machine with an optical fiber in order to measure radiation from a fluorescent molecular probe which has been doped into the processed resin. The objective is to monitor fluorescence from a molded part as it cools in the mold. Using a micro-viscosity sensitive fluorescent probe, we are able to observe the onset of the glass transition by noting changes in the fluorescence intensity vs. time curve. This information will be used to examine and control the mold cycle.

- A project to develop a set of reference materials for biodegradable polymers has been initiated. An exposure technique has been developed to test a series of polymer films for their relative biodegradability and potential as reference materials.

- A new solid state NMR technique, based on orientational correlations among aromatic rings in polymers, has been devised for determining the dimensions of heterogeneities in polymers. One application of this new approach is the determination of the uniformity of chain deformation in a deformed aromatic polymer glass.

- Dilatometric measurements of glasses subjected to T-jump thermal histories and simultaneous intermittent torsional deformations show that the underlying thermodynamic state of a glass is unaffected by the mechanical stimulus. The torsional dilatometric results which show that large mechanical stimuli do not alter the volume recovery kinetics in isothermal aging experiments argue strongly against rejuvenation models of glassy behavior.

- Two finite element flow modeling programs were developed to describe resin transfer molding. These "2D" programs can predict filling of shell molds containing anisotropic preforms. One program is computationally faster while the second has added terms which for the first time permit the proper modeling of boundaries such as edges, corners, and joints between preforms of different permeability.

- A new model was developed to describe the flow in resin transfer molding (RTM). By considering the heterogeneous nature of the fiber preform, the model is able to predict a number of previously unexplained features that had been observed in RTM experiments. This new model will significantly improve the ability of future finite element programs to predict RTM mold filling effects.

- Studies with carbon fibers and nylon 66 provide the first strong evidence that transcrystallization at the carbon fiber surfaces is epitaxially specific. This has obvious consequences for the control of interphase morphology during composite processing.

- A patent was obtained for a new thermo-acoustic technique to determine the strength of the interface between fiber and matrix (and between plies) in a composite. This method has the advantage that it can be applied to real parts and prepregs while the other techniques require special test specimens.

- Phase diagrams of bulk polymer blends of deuterated polystyrene/poly(vinylmethylether) and deuterated polystyrene/polybutadiene have been studied by simultaneous SANS and viscosity measurements at various temperatures and shear rates. The suppression of the concentration fluctuation modes has been observed as a function of shear rate. This gives fundamental physical understanding of the mechanism of shear induced miscibility of polymer blends.

- The 10-meter SAXS facility had active outside users which includes: 7 industrial laboratories, 2 academic institutions, and 3 other federal laboratories. Activities of users include: structure/property/processing relationships in blown polyethylene films, microstructure in polypropylene, polyester and nylon fibers, morphology of amorphous/semicrystalline nylon blends and properties of carbon aerogels.

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 polymers 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 measurement 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 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
Coyne, Laurence*	o Molecular deformation mechanics in epoxy networks o Infrared spectroscopy o Neutron scattering of polymers o Polymer gelation

* Research Associate

Crissman, John M.	o Mechanical behavior o Environmental stress-cracking o Failure and fracture of polymers
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
Dickens, Brian	o Polymer oxidation o Monomer design and free radical curing o Automation
Di Marzio, Edmund A.	o Statistical mechanics of polymers o Phase transitions o Glasses o Polymers at interfaces
Douglas, Jack F.	o Theory on polymer solutions o Polymer at interface 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 blends o Polymer blends
Fowler, Bruce O.[*]	o 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
Hair, Dennis	o Dynamic light scattering o Polymer blends o Polymer diffusion
Hampe, Andreas[+]	o Composite mechanical properties o Stress analysis o Acoustic emission

[*] Research Associate
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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
Hailer, Arthur W.[*]	o Chemical reactions, chemical analysis
Herrera-Franco, Pedro[+]	o Composite mechanical properties o Stress analysis o Composite failure behavior
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
Jackson, Catheryn L.	o X-ray diffraction o X-ray line shape analysis o Structure of physical gels o Microcellular foams morphology
Jewett, Kenneth L.	o Redox kinetics of heterogeneous systems o Organometallic speciation o Abiotic transformation of metal species o Analysis of organic mixtures
Johnsonbaugh, David S.	o Atomic absorption spectrophotometry o Microbiology o Bioprocessing
Johnston, Allen D.[*]	o Nuclear magnetic resonance o Mossbauer studies o Chemical adhesion

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Keeny III, Spurgeon M.	o Gas plasma sterilization o Mechanical testing o Tribiology, dental materials o Polymerization shrinkage
Khoury, Freddy A.	o Crystallization, structure and morphology of polymers (including polymer blends) o Analytical electron microscopy of polymers o Wide angle and small angle x-ray diffraction o Structure and mechanical property relationships
Kim, Hongdoo[+]	o Polymer diffusion o Forced Rayleigh scattering o Polyelectrolyte o Polymer blends
Kikuchi, Hisaji[+]	o Dental composites
Kryder, Samuel J.	o Electronic circuit design and construction o Electronic troubleshooting and repair
Kurakawa, Hidenobu[+]	o Polymer solution thermodynamics o Small angle 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
Manders, William F.	o Solid state NMR of polymers o Structure of asphalt binders
Mao, Yu[+]	o Dental plaque o Microanalytical techniques
Mathew, Mathai[*]	o Crystallography o Calcium phosphate compounds

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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 Nonlinear viscoelasticity o Molecular rheology o Physics of polymer glasses
McKinney, John E.[+]	o Tribiology of dental composites, cements and alloys
Misra, Dwarika N.[*]	o Surface chemistry o Adhesion o Chemisorption
Mizumachi, Hiroshi[+]	o Adhesion science o Fracture mechanics of polymers o Viscoeleasticity of adhesives
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
Nakatani, Alan I.	o Polymer blends and solution properties under shear o Small angle neutron scattering o Phase behavior of polymer blends

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O'Farrell, Thomas J.*	o Mineralization and remineralization
Parnas, Richard	o Flow through porous media with heterogeneous structure o Surface rheology o Polymer dynamics
Phelan, Jr., Frederick R.	o Resin transfer molding: modeling and processing studies o Viscoelastic flow modeling o Engineering rheology
Ratzker, Menahem S.*	o Electrodeposition
Reed, Benjamin B.*	o Synthetic and polymer chemistry o Polymerization expanding monomers
Roth, Steven C.	o Piezoelectric polymer transducers-fabrication and applications o Vacuum deposition of metals o Calibration of polymer transducers o Microcomputer interfacing o Fluorescence measurements
Rupp, Nelson W.*	o Clinical dentistry o Amalgams o Direct golds o 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

*Research Associate
+Guest Scientist

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*	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
Tilstra, Luanne F.	o Polymer biodegradation
	o Time-resolved fluorescence spectroscopy
	o Solution properties of polymers
	o Biotransformation of polymeric materials
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
Tomazic, Branko*	o Atherosclerotic plaque
	o Biological calcium phosphate compounds

*Research Associate

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 on 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
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

*Research Associate

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, 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.

Changes in dielectric spectra at low frequencies (10^4 to 10^{-3} Hz) which are readily accessible in the time domain measurement, have proven especially useful for detecting damage in cable insulation exposed to a combination of heat and gamma radiation such as encountered in nuclear power plants. More subtle changes in cable insulation subjected to ac voltage stresses in a non-nuclear environment 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 which have been modified to reduce the formation of electrical trees is being investigated in an attempt to correlate such measurements with end-use performance. These investigations on electrical insulation have been carried out as part of other-agency contracts or through cooperative research programs with industry and universities.

We are helping the Bureau of Engraving and Printing determine the composition of alkyd resins required to produce intaglio printing inks which have the desired properties of viscosity, water-dispersibility, air-dry curing kinetics, and durability of cured ink. Although alkyd resin chemistry is a well-established field, the requirements for an intaglio printing ink are unique and limited to the specialized area of printing currency and security documents. Considerable progress has been made at NIST in designing and synthesizing resins which in laboratory tests fulfill the requirements for a satisfactory air-dry ink. In a related program, we are designing, synthesizing, and evaluating resins to be used in printing inks which are to be cured in an electron beam. Resins which meet most of the requirements for a satisfactory electron beam ink vehicle have been synthesized from hydroxyethylmethacrylate and acid anhydrides. However, toxicity of such resins, especially skin sensitization is of major concern. Although the resins which we developed were judged to be non-irritants in a Draize test protocol, industrial experience with sensitization from acrylate and methacrylate monomers causes safety officials at BEP to be reluctant to continue development of resins based on these reactive groups. In future evaluations of resins for electron beam curing, the issue of toxicity must be addressed at an early stage of development.

Second-order non-linear optical properties are being imparted to polymers by dissolving 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 and 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 aging conditions. We seek an understanding of the factors which determine the long term stability of dipolar alignment which is very important to the development of NLO polymers.

Polymers with third order NLO properties are being prepared from diacetylene monomers which have been designed to exhibit liquid crystalline phases as well as the usual crystalline phase. The object has been to study the kinetics of polymerization in the ordered and partially disordered states as well as to study the morphology of the resulting polymer. Surprisingly, one finds that the diacetylene monomers with rigid rod mesogens polymerize thermally even in the isotropic molten phase to yield clear, highly colored, amorphous films.

During the past year, most of the effort in pyroelectric and piezoelectric polymers has been directed toward the amorphous vinylidenecyanide/vinylacetate alternating copolymer. Pyroelectric response after poling above the T_g of 175°C is linear with applied field and consistent with a dielectric increment of about 100 at T_g. NLO dye molecules have been incorporated in this copolymer and we are studying the kinetics of reorientation of the polymer dipoles and the dissolved dye molecules. Electrochromic shifts due to internal electric fields have been immeasurably small.

FY 90 Significant Accomplishments

- An alkyd resin designed and synthesized at NIST for use in air-dry intaglio inks performed well in preliminary tests at BEP. A 55-gallon drum of the resin has been synthesized by Superior Varnish and Drier Co. and delivered to BEP for full-scale testing on the intaglio press.

- Criteria were established and a screening method developed to evaluate the conductivity of fire suppression agents proposed as substitutes for Halon. The work was done in cooperation with the Center for Fire Research at the request of the Air Force.

- The thermal pulse apparatus has been improved by adding a solid state Q-switched ruby laser. Pulse durations of 100 ns are possible, pulse energies are more reproducible, and operation is more reliable. These improvements yield information about charge or polarization closer to the pulsed electrode and facilitate signal averaging for low signals.

- A systematic study of the polymerization of diacetylene monomers prepared with varying numbers of methylene units separating the diacetylene core and rigid side chains reveals that the most rigid monomers polymerize readily even within the isotropic melt phase. This alternative to crystal-mediated polymerization leads to new morphologies of polydiacetylenes which are now being investigated.

- A patent was issued to the U.S. Government for a composite material made by dispersing a powdered high T_c super-conductor in a polymer. The composite has the processing advantages of a polymer and the levitation properties of a superconductor at temperatures below T_c. Possible applications of the composite include transportation systems utilizing levitation to reduce friction and magnetic bearings.

AUTOMATED DIELECTRIC MEASUREMENTS

F. I. Mopsik

Instrumentation

Modernization of the computer underlying the Time-Domain Spectrometer has been actively pursued. The data acquisition cards have been installed and tested in order to ensure compatibility with the new PC computer. The tests have shown the validity of original design decisions and that it may be possible to increase the data sampling rate to as high as 1 MHz.

To minimize down-time and redesign of hardware, an interface box has been designed and is currently undergoing testing. This box must make the transition from the Interdata interfaces with 160 bits present, many isolated and numbered in high to low order, to the PC with only 40 TTL bits and numbered in the reverse order. Furthermore, the actual data acquisition will be independent of the computer, as the computer will be used in a multitasking environment in which responses to external signals may be no faster than several tenths of a second. Therefore, the box has been designed to add a level of programmable control so that the computer need not be current with an on-going measurement. This will allow plug-in compatibility of the current measurement circuits.

In addition to the hardware, the programming task involved with the conversion has begun. The graphics programs have been revised and tested to be compatible with existing data file formats. The data reduction routines have also been translated and tested. The new version takes about 0.3 second as opposed to the nearly 3 minutes on the Interdata. As expected, the major problems have been in translating the text handling from Fortran IV and changing the operating system interactions.

Reactor Cable Insulation Testing

This year, there has been an attempt to obtain a more systematic set of samples. A set of cables from EDF in France has been received as well as many from Sandia National Laboratory. The requirement for systematic aging conditions has been emphasized as the Time-Domain Spectrometer has consistently demonstrated changes in the cable insulation upon aging. The samples until now, however, have not covered a large enough range of conditions to satisfactorily investigate effects of both thermal and radiation aging.

Although samples in hand do not cover the full range of conditions, the data from them show that dielectric measurements can be used to monitor cable aging. The EDF samples, from a prototype experimental cable, were subjected to rather severe thermal as well as radiation exposure. For the EDF samples received to date, clear differences are seen between the thermal and radiation exposures.

Guest-Host Polymer Systems

As part of a program to study the suitability of guest-host systems for optical second harmonic generation, PMMA with added active dyes was studied from near room temperature to the glass transition temperature, T_g. Data from the polymer, molecular weight 3400, with different dyes were compared to those for the polymer alone. For this polymer, the addition of about 1% azo dye was found to greatly affect the relaxation behavior of the host polymer. The secondary glass relaxation was changed both in magnitude and frequency. The apparent DC conductivity was greatly reduced, which is opposite from the expected change for an added component. There were also indications of changes in the glass relaxation, but the high conductivity of the base polymer made this change unambiguous. All these effects where not as striking with the addition of a stilbene dye.

These changes in the loss spectrum suggest that a small amount of dye can lead to large complexes in the PMMA. These complexes then change the relaxation behavior of the polymer matrix. Some additional data are necessary to clarify a few experimental questions before the results can be published.

HALON SUBSTITUTES

As part of an Air Force contract with NIST, work was undertaken to establish a screening method for evaluating the conductivity of Halon substitutes used as fire suppression agents. This evaluation is important as the Halons are currently the agent of choice where either large electrical equipment, such as for power distribution or sensitive equipment such as computers, are present.

There are currently no objective criteria used to specify the Halons. They are presumed adequate as manufactured. This presumption, in fact, is quite valid as the Halons are non-polar liquids with very low conductivity. Since replacements possibly will have quite different chemical structures, they may have proven insulation properties. Both a test method and criteria were needed to estimate reliably the conductivity of liquid substitutes and exclude those clearly not suitable.

A test method using a 1000 Hz measuring frequency and a three-terminal cell was proposed. A cut-off of $10^{-11}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ was chosen as being easily met by good insulating fluids and assuring compatibility with the known electrical requirements of different types of electrical equipment. Measurements were made on several liquids, including Halon 1211, to show the feasibility of the method and criterion. A report was written documenting the proposal.

LASER THERMAL PULSE MEASUREMENTS OF POLARIZATION AND CHARGE DISTRIBUTIONS

A. S. DeReggi and B. Dickens

During the past several years, we have used the laser-induced thermal pulse method to measure the polarization, space-charge or electric field distribution across the thickness of planar dielectrics. The heat produced by Laser pulses applied to the electroded surface of a sample diffuses into the sample and produces a time-dependent, inhomogeneous thermal deformation inducing an electrical response signal that is measured. One of the salient results of this program is that polymer insulators under an applied voltage acquire and store for extended periods of time a considerable amount of space charge of low mobility. This space charge does not show up in usual conductivity measurements but it produces potentially large internal electric fields in dielectrics. The space-charge fields may be comparable to the applied fields which gave rise to the space charge in the first place. More recently, it has become apparent that the charging behavior carries new diagnostic information about the state of an insulator.

In a collaborative research effort with the University of Connecticut, Detroit Edison and CREIPI (of Japan), we showed that the length of AC (aging) service of cross-linked linear polyethylene, XLPE, samples can be deduced from the charging behavior. Specifically, we found that the total charge that is injected by a moderate applied voltage in the charging steady state, is proportional to the service time, while the polarization distribution is independent of the service time and is homopolar (charge density is of one sign, positive, across the entire thickness). We found also that oxidized XLPE has a markedly different charge distribution when charged by similar applied voltages. The sign of the charge in that case is still positive in the greater part of the dielectric thickness but is negative near the negative electrode. These findings were presented at the Conference on Electrical Insulation and Dielectric Phenomena in Vienna, VA in November 1989 and at the IEEE Insulation Society Meeting in Toronto in June 1990.

In a research program sponsored by the Union Carbide Corporation and carried out jointly with a UCC consultant at NIST, we studied the charging behavior of thermoplastic PE, XLPE, water-tree-retardant XLPE and an EPDM-based formulation sold commercially. The charging behavior of each material is different and the particular behavior of the water-tree-retardant material provides clues as to the microscopic function of the water-tree retarding additives. We also found unexpectedly that the EPDM formulation is pyroelectric and traced the pyroelectricity to a clay filler material. The pyroelectricity is indicative of the presence of a polarization associated with the alignment of electric dipoles. This polarization is not desirable as it may be a source of dielectric loss. The results of these findings were presented at the IEEE Insulation Society Meeting in Toronto already cited in the previous paragraph.

During the course of the year, the range of experiments that can be performed has been increased by evolutionary improvements to the thermal pulse method. Laser pulses now can be obtained routinely from either of the two lasers, a flashlamp-fired dye laser (generating 1 μs pulses) or a Q-switched ruby laser (generating 100 ns pulses), A beam-splitter arrangement coupled to two light pipes has been incorporated into the system. This arrangement provides improved precision monitoring of the energy delivered to the sample from either laser. A double diffuser suitable for use with high power lasers that have been installed in the ruby target area provides continuous adjustment of the ruby laser energy delivered to the sample. Additional improvements were implemented via software to speed up data transfer from the signal-averaging transient digitizer to the computer and to facilitate file handling and management as well as numerical analysis of the data. The improved precision of the system has allowed new measurements to be made that could not previously be made.

In the area of NLO, we have succeeded in measuring the distribution of polarization in a 20 μm thick film of vinylidene cyanide/vinyl acetate copolymer containing dissolved dimethylaminonitrostilbene (DANS/P(VDCN-VAc) adhered to the conducting indium tin oxide surface of 1mm thick glass. This achievement was presented at the Specialty Polymers Conference at Johns Hopkins University in August 1990.

In a collaborative experiment with a guest scientist from the Kyoto Institute of Technology, we showed that soaking the P(VDCN-VAc) copolymer in amyl alcohol used as a NLO-dye transport solvent has quasi-irreversible effects on material properties governing the temperature coefficient of the capacitance, $\alpha_c = 1/C\ dC/dT$. The effects are manifested as an increase in the pyroelectric response coefficient without an increase in polarization. These results indicate that future measurements in this NLO guest-host system need to take account of the changes of the thermal properties.

Additional measurements in the DANS/P(VDCN-VAc) system, and in another NLO guest-host system DANS/PMMA (covered in detail in the NLO materials paragraph) have shown that the normal thermopoling process results in a highly inhomogeneous polarization characterized by a peak near the negative poling electrode and a polarization depletion near the positive poling electrode. These results have been presented also at the already cited Specialty Polymers Conference.

In collaborative work with the Ecole Superieure de Physique et de Chimie in Paris where the acoustic pulse analog of the thermal pulse method is practiced, the thermal pulse method and the acoustical pulse method (called the pressure wave propagation method by the ESPCI team) have been compared using samples accessible by both methods. The methods are sufficiently different in practice that the comparison is not straightforward. In particular the time scales of the two measurements are typically in a ratio of 10^3 to 10^4 depending on the sample thickness and this brings into play very high frequency acoustical properties against much lower frequency thermal properties. For 2 mm thick samples of lead zirconate titanate ceramic, the two methods were found to be complementary.

The collaboration with the ESPCI team is continuing and currently has shifted to the study of samples with axial symmetry. Preliminary results have been obtained on the distribution of charge injected by the point of a voltage-biased needle embedded in polyethylene. These measurements show that the injected charge is homocharge which remains near the point where it has the effect of reducing the local electric field controlling the charge injection and cutting off the injection. Preliminary results have been obtained also on the measurement of charge adhered to the inside wall of a polyethylene pipe by means of an acoustic pulse applied to the outside wall. These results show that the measured signals, as expected, are directly proportional to the charge on the inside wall.

DESIGN AND SYNTHESIS OF INTAGLIO INK RESINS

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

NIST is developing prototype ink vehicles for intaglio printing at the Bureau of Engraving and Printing. 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. The objective of this project is to provide information on the design and synthesis of resins suitable for intaglio inks that crosslink on exposure to air or during exposure to an electron beam. The air-dry systems are based on drying oil technology and the electron beam systems use a free radical mechanism.

The properties required of an intaglio resin for adequate performance on the printing presses are: resin viscosity in the region of 30 to 300 poises; 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; ink ingredients, including resins, are to be of acceptably low toxicity. In addition, the formulated ink must transfer acceptably from the engraved cylinder to the paper substrate.

Two series of air-dry intaglio inks have 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 are like extra large drying oil molecules. They were synthesized by esterifying high polyhydric alcohols 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 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.

The resins which cure in electron beams are based on groups which crosslink readily when initiated by the free radicals formed in the resin on exposure to the electron beam. The work has concentrated on using methacrylates because they are less injurious to personnel than the faster curing acrylates. Several candidates were provided which cured rapidly enough, gave satisfactory inks, and performed well in laboratory tests. The resins contain polymerizable groups and acid groups. They were synthesized by reacting methacrylate-containing and acrylate-containing alcohols with various acid anhydrides to give esters with one free acid group for each ester group. Di-anhydrides give more than one isomer, which inhibits crystallization of the individual isomers and thus tends to make the resultant resin liquid.

These electron-beam materials easily disperse the pigments and other solids in the ink. They cure well and disperse well in the alkaline washing medium. Because the degree of crosslinking is high, the cured film is very resistant to solvents. However, several of the resins are so viscous that they must be diluted before they can be used as intaglio ink resins. Water-dispersible, low viscosity, electron beam-active monomers are commercially available for use as reactive diluents.

Macromonomers were used as components in radiation cured ink resins. The approach was to modify the viscosity and glass transition temperature of existing radiation-curable resins. Thermal and neutron scattering studies showed that polymerization of monomers containing macromonomers gave much more homogeneous structures than did samples containing equivalent polymers without the macromonomer functionality. Macromonomers with different polymerizable groups gave samples with very different uniformities. Therefore very slight differences in the copolymerization kinetics lead to very different properties. Electron beam curing studies of inks made from macromonomers and conventional radiation curable resins showed that the functionality of the macromonomer greatly affects the dose required for full cure. Many macromonomers seemed to inhibit the cure. Acrylate functionality and high molecular weight macromonomers improved the cure rate, but the macromonomers studied need improvement. New macromonomers with a variety of structures are being produced in collaboration with du Pont.

CHROMATOGRAPHIC EXAMINATION OF INTAGLIO INKS AND VARNISHES

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

Size exclusion chromatography (SEC), also known as Gel Permeation Chromatography, has been used to examine inks and ink components supplied by the Bureau of Engraving and Printing (BEP). Currently, the BEP purchases fully formulated inks for printing security documents such as currency and stamps. While there is a series of quality control tests to insure that the printed documents are acceptable, many of the tests have to be run on printed matter that is produced by a full production run. Failure to pass tests at this stage means destruction of the full press run at considerable expense.

No chromatographic techniques are presently used to characterize soluble ink components. We have proposed the use of SEC as a way to examine the inks upon delivery to estimate batch-to-batch variations in compositions before printing. SEC separates molecules by molecular size, components with the largest hydrodynamic volume eluting first followed by increasingly smaller components. Since ink resins contain a variety of polymeric and low molecular weight components, SEC should be a good method of characterizing these resins.

The first series of experiments involved optimising chromatographic parameters for best separation and detection of components present in typical inks. Three SEC columns of different pore size were used on a variety of ink types supplied by BEP. A mixed bed column was most efficient at separating the largest components, while a column with a 500 Angstrom pore size proved more efficient at separating small components. To best identify the full range of components, runs with each type of column are necessary. Tetrahydrofuran extracted the most material from the inks supplied and allowed for best characterization of the largest components. 1-2,dichloroethane extracted less of the largest components, but allowed for better UV characterization due to its transparency, and is better for detection of the smaller components than tetrahydrofuran because it does not contain interfering inhibitors which are necessary for stabilizing THF.

A variety of detectors was used, and each was useful in a different molecular weight range. The mass evaporative detector can detect larger components with roughly equal efficiency, but is not linear with concentration and does not sense volatile components such as solvents. The refractive index detector can see all components regardless of molecular weight, but some combinations of resins and solvents do not have sufficiently different refractive indices to give measurable signals. UV detectors are very sensitive to components with strong UV absorption and a detector with multiple wavelength detection can provide compositional information for each eluted species.

The first series of samples studied contained many individual inks in several different general categories. Each class of ink had a distinct SEC signature. Air-dry currency inks, heat set inks, prewipe inks, and custom formulated inks could easily be distinguished. Within each class, more subtle differences could reproducibly identify each individual sample.

Another series of samples contained inks that had been used to print large amounts of currency. Two samples labeled "good" and "poor" were supplied as identical inks by the manufacturer, but had very different durability in tests on the currency. These two inks were extracted with tetrahydrofuran and run in the mixed bed column. Repeat runs of either type of ink matched extremely well, while the cross matching of the two types showed distinct differences. There were very different UV responses for the larger components of the pair.

Recently, a new UV detector has been purchased and software has been written. It is now possible to take UV spectra of each component as it elutes. In this way one can tell if the different size polymeric components differ in chemical composition. This will add a new dimension not only in ink characterization, but as a research tool for general polymers.

NONLINEAR OPTICAL MATERIALS

M. A. Schen, A. S. DeReggi

Nonlinear optical, NLO, materials research inside and outside of NIST continue to focus on both third order, χ^3, and second order, χ^2, active polymer systems. For χ^3 applications, polymeric structures containing highly delocalized charge correlated pi-electrons along the polymer backbone are needed. Reports characterizing optical responses of well-known electro-active and ladder-like polymers such as polyacetylene, polydiacetylenes, polyphenylene sulfide, poly(benzo-bis thiozole), and poly(benzo-bis-oxazole) continue in the literature, as well as reports involving macro-cyclic organo-metallic containing polymers. For χ^2 applications, investigations continue on functionalized copolymers containing intramolecular conjugated donor/acceptor molecules that act as the χ^2-active species. NLO activity derived from alignment of the non-centrosymmetric dye is imparted to the structure by parallel plate or corona poling of the dye. To combat reorientation of dye molecules after poling, highly cross-linked networks have been reported in the literature which show much improved stability in comparison to uncross-linked acrylate type polymers.

Ongoing efforts in χ^3 materials comprising rod-like diacetylene monomers and polymers, some of which exhibit monomer phase liquid crystallinity were reported previously. The monomers discussed are symmetrically disubstituted diacetylene molecules incorporating oxybenzylidene-n-octylaniline substituents and designated nOBOA. In this nomenclature, n refers to the number of methylene carbons bridging the diacetylene core to the mesogenic substituents. Three members of a homologous series where n=1, 3, and 4 have been synthesized.

X-ray diffraction studies have been completed on all three materials. All three show a room-temperature paraffin-like structure in that distinct small angle diffraction peaks due to a layered crystal morphology is observed. With increasing molecular length, lamellar spacings concurrently increase. All molecules appear to be tilted within the layer plane. This characteristic makes these materials likely candidates for preparing polymerizable mono and multilayer assemblies.

High temperature diffraction experiments conducted in cooperation with Dr. James Cline of Ceramics Division showed that in the n=1 homolog, polymorphic crystal phases exist before the material enters the first liquid crystalline phase. Combined optical dark-field microscopic texture and elevated temperature x-ray scattering results confirm the presence of a smectic G or H phase upon first becoming liquid crystalline followed by a smectic C microstructure. The n=4 homolog does not show monomer liquid crystallinity. No elevated temperature scattering studies have been completed on the n=3 monomer. Based on optical textures and the observed narrow temperature range within which the material is liquid crystalline, a disordered smectic of either the C or A type is envisioned.

It was previously believed that the spontaneous and rapid thermally induced polymerization of the n=1 homolog in the liquid crystalline and isotropic phases was due to the liquid crystalline behavior of the monomer. Yet polymerization of 3OBOA at 171°C and in the liquid crystalline region shows only a 17% conversion to polymer after four hours in contrast to 100% conversion of 1OBOA, also at 171°C and in the lc region, after two hours. Isothermal polymerization of all three monomers at 190°C and in the isotropic monomer melts shows: 99% conversion within forty minutes for 1OBOA; 42% conversion after eight hours for 3OBOA; and 17% conversion after eight hours for 4OBOA. Poly(1OBOA) prepared in the isotropic monomer melt appears to be an amorphous glass from x-ray and differential scanning calorimetry. Therefore, relative to the n=1 homolog, 3OBOA is roughly ninety times less reactive and 4OBOA is over two-hundred times less reactive to non-crystal phase thermal polymerization. These results appear to reflect increased monomer flexibility in the higher series members which diminishes polymerizability. From this, rod-like monomer architectures are viewed to be a prerequisite for melt phase polymerization yielding amorphous polymer.

Linear optical spectroscopy experiments have been completed on thermally polymerized 1OBOA. These spectra are being compared to spectra of crystal-phase-polymerized n=1, 3, and 4 polymer obtained by gamma irradiation. Spectra of poly(1OBOA) show a marked dependence on the microstructure within which polymerization takes place. Surprisingly, and yet unexplainably, the optical band edge is seen to move to lower energies as the temperature at which polymerization occurs increases. Also, the total integrated absorption intensities due to the polymer backbone are seen to increase with increasing temperature. Resonance Raman scattering experiments are planned to better understand the microstructure of these polymers. Nonlinear optical measurements are anticipated in the next year.

In the area of second order NLO polymers, studies have been initiated in the system 4-(N-dimethylamino)-4'-nitrostilbene, DANS, incorporated in poly(methyl methacrylate), PMMA films; a system well-studied by many workers using second harmonic generation techniques. Fundamental to measurement on all χ^2 polymer materials is the need to introduce dipolar orientation of the NLO unit by electric field poling. As important as this is for the successful fabrication of NLO devices, little is known of the cross-sectional orientational uniformity obtained from poling. Our work has the goal of measuring the polarization distribution of poled DANS/PMMA and PMMA-only films using the thermal pulse technique in conjunction with pyroelectric measurements and optical spectroscopy.

Samples containing only 0.5% and 1.0% by weight dye have been examined to date. Above this dye loading level, phase separated polycrystalline films result. Pyroelectric coefficient, P_y, aging curves for 0.5% and 1.0% samples poled for thirty minutes above T_g show only a small decrease in P_y over the first seven hours after poling. In contrast, a 1% sample poled for only five minutes above T_g shows a P_y coefficient that is similar to the longer poled samples but decays very rapidly to ca. 28% of its original value within one hour. P_y values for polymer alone are of similar magnitude to those of dye-containing films. At such low dye concentrations, the dipolar contribution of the dye is lost relative to the dipolar contribution of the PMMA host. Consequently, P_y measurements made to date reflect properties of the total sample, weighted most heavily in favor of the host itself.

Thermal pulse measurements of ca. 30 µm thickness DANS/PMMA films and pure PMMA films poled for five and thirty minutes reveal signatures of strong polarization inhomogeneities across sample thickness. In all samples, both dyed and undyed, a region of enhanced polarization relative to the mean is seen within the film adjacent to the negative electrode. Concurrently, an area of diminished polarization, in some cases of opposite sign, is seen in the film adjacent to the positive electrode. In experiments in which the time of poling was varied, signatures within the thermal pulse data indicate enhanced polarization inhomogeneity at thirty minutes compared to five minute poling time. The region of "depleted" polarization adjacent to the positive electrode is interpreted to extend deeper into the sample after longer poling periods. It is viewed that polarization inhomogeneities arise due to charge injection near the positive electrode which then acts to decrease the electric field within that region. Since dipolar orientation being viewed by the thermal pulse technique is that of the total sample, guest and host, these results reflect most strongly the properties of the host itself. However, it is viewed that the orientational homogeneity of the dye can not be any better than what is being measured for the total film and so this data reflects the limit of dye homogeneity.

FERROELECTRIC POLYMERS

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Last year's report described the use of spectral changes in electrochromic dyes dissolved in vinylidenefluoride/ trifluoroethylene copolymers to assess internal electric fields. The internal fields created by the aligned polar crystals impose a preferred alignment on the dissolved molecules, which if they have NLO properties, can impart second harmonic generating capability to the film.

This type of investigation has been extended to the alternating copolymer of vinylidene cyanide (VDCN) and vinylacetate (VAc). The VDCN/VAc copolymer is not ferroelectric but very large polarizations can be induced in this amorphous material by applying high electric fields at temperatures above its T_g of about 170°C. Dielectric measurements reveal a change in dielectric constant ($\Delta\epsilon$) of about 100 upon going through the glass transition. Pyroelectric coefficient at room temperature is linear with the electric field applied above T_g and the slope is consistent with the $\Delta\epsilon$ value of 100. The polarization of the copolymer as revealed by pyroelectric measurements is very stable at temperatures up to 150°C. Of interest is measurement of the rate of decay of the preferred orientation of dissolved NLO molecules compared with that of the copolymer dipole orientation. Preliminary measurements of polarization distribution after poling above T_g using evaporated aluminum electrodes indicates polarization above the average near the positive electrode and below the average near the negative electrode. The effect of poling time has not yet been investigated.

CHEMICAL PERFORMANCE

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

Investigations in the bioprocessing program involve the use of microorganisms and their metabolic products for upgrading, synthesis, recovery and degradation of materials, and the development of methods for monitoring biotic transformations of a variety of substrates. A project, sponsored by EPRI, on biodesulfurization of coals and an inter-laboratory comparison, sponsored by OSRM, of bioleaching rates from a Pyrite Ore Reference Material were successfully completed. Procedures were developed for evaluating the appropriateness of certain polymers as standards for biodegradable plastics.

The need for improved monitoring of polymer processing has escalated in recent years because of the large demand and market for advanced polymeric products which require tight controls in processing conditions over a broad range of variables. To satisfy these new requirements, sensors based on fluorescence spectroscopy are developed to monitor process conditions at the molecular and microscopic level. The objective of the polymer processing program is to utilize these new measurement techniques in conjunction with processing models to predict and control the materials properties and performance of the final product.

FY 90 Significant Accomplishments

- The onset of the glass transition during injection molding of a resin has been monitored through the use of a micro-viscosity sensitive fluorescent probe. The collaborative project with Drexel University involved instrumentation of an injection molding machine with an optic fiber in order to measure radiation from a viscosity-sensitive fluorescent probe which is added to the resin.

- Shear-induced orientation functions for an anthracene-labeled polybutadiene were determined by fluorescence anisotropy measurements conducted as a function of shear stress. Under shear, the orientation of the polymeric probe can be described as perturbed random orientation. The slope of the anisotropy vs shear stress curve yields an anisotropy/stress coefficient characteristic of the material's response to shear stress.

- An inter-laboratory comparison of bioleaching rates from the Pyrite Ore Reference Material has been completed and the report has been prepared for distribution with the Reference Material.

- It has been demonstrated that the mechanism of desulfurization of coal by Pyrococcus is initiated by an abiotic reaction that results in soluble polysulfides.

This desulfurization does not require direct contact between the cell and the sulfur in the coal.

- An exposure technique has been developed to test a series of polymer films for their relative biodegradability and potential as reference materials for biodegradable polymers.

POLYMER PROCESSING

A. J. Bur, F. W. Wang, R. E. Lowry, S. C. Roth, C. L. Thomas, F. M. Gallant[1], and J. L. Rose[2]

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In this program, fluorescence spectroscopy is being employed as a tool to monitor polymer processing parameters which are important for understanding process behavior. The measurements involve the detection of fluorescence spectra from fluorescent dyes which have been doped into the processed polymer material. The character of the fluorescence, i.e. intensity, polarization, and wavelength distribution, yields information about the state of the polymer matrix. The work focuses on developing concepts and methods to measure molecular orientation, shear stress, shear rate, non-Newtonian viscosity, velocity, flow instabilities, quality-of-mix of ingredients, glass transition temperature, and intersegmental mixing. Work on each of these measurement problems is ongoing and in various stages of development. During the past year significant achievements have been attained in application of these measurements to polymer extrusion processing at NSWC and injection molding at Drexel University. In addition, an extensive laboratory study of the effect of shear stress on fluorescence anisotropy of polybutadiene doped with a fluorescent probe has been carried out.

Residence Time Distribution and Quality-of-Mix

In collaboration with NSWC, on-line measurements have been made of quality-of-mix and residence time distribution of twin screw processing of polybutadiene mixed with $CaCO_3$ particulate. For these experiments an optical fiber probe was installed at the exit die of the extruder and used to monitor the fluorescence intensity from a dopant dye. By applying the results of previous work, the fluorescence was interpreted in terms of the concentration of $CaCO_3$ in the mix. Figure 1 shows fluorescence intensity vs time for time after a step function change has been made in the operating set points of the process. At time $t = 0$, the feed ratio of $CaCO_3$ to polybutadiene was changed from 63/37 to 60/40 by weight and the subsequent change in the product was monitored via the fluorescence. The sensitivity of this measurement is approximately a 1% change in composition. In this case, the smooth transition from one state to the other took approximately 7 minutes. The flat regions at either end of the curve are typical of the response from a well-mixed product which does not change in composition more than 1%. On-line measurements of transition time and quality-of-mix are important for maintaining the quality of the product. By continuously monitoring the output, constant surveillance was maintained on product quality and on changes in the operating conditions.

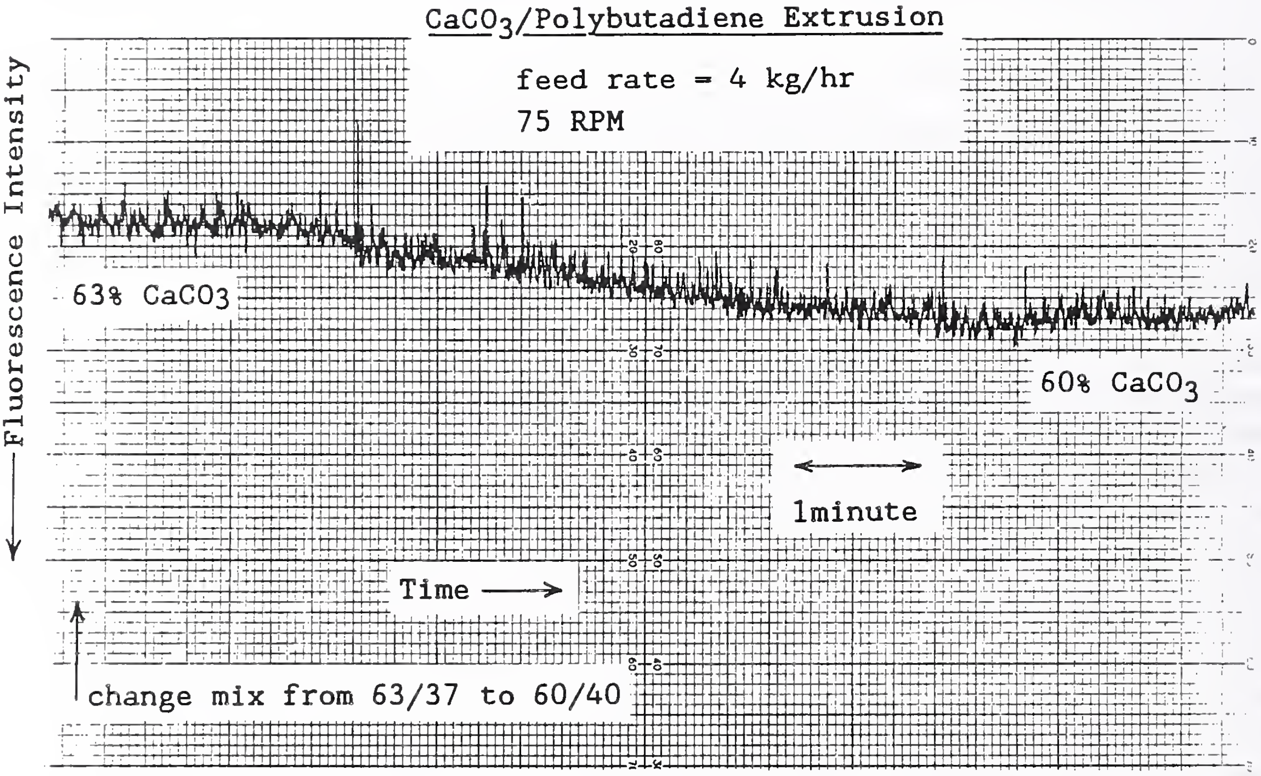

Figure 1 Fluorescence intensity vs time is shown after extruder feed rate ratio was changed from 63/37 to 60/40 $CaCO_3$/polybutadiene ratio. The fluorescence was detected at the exit die of the extruder.

The fluorescence probe was also used to observe residence time distribution. In these experiments, a fluorescent dye was "instantaneously" injected into the extruder at a point which was 62 cm upstream from the exit die. The dispersion of the dye in the mixture was measured at the exit die of the extruder. The delta function distribution at the time of dye injection was observed to transform into a dispersion which extended over several minutes, indicating the extent of spatial mixing and residence time of dye in the extruder. A series of residence time experiments, carried out for different operating conditions, demonstrated the applicability of this technique to monitor the transit time of the ingredients through the machine. This information is being used by NSWC to optimize productivity and product quality.

Shear Stress and Non-Newtonian Viscosity

Our working hypothesis for the fluorescence anisotropy experiments is that, for a non-Newtonian fluid, viscosity decreases with increasing shear rate, and that the underlying cause of this effect is molecular orientation. The fluorescence anisotropy experiment is designed to measure this molecular orientation, and to monitor shear stress and non-Newtonian viscosity. The fluorescent probe for these measurements is polybutadiene tagged with fluorescently active anthracene which is situated at a central position of the polybutadiene backbone. The tagged polybutadiene has a molecular weight of 30,000, i.e. larger than its entanglement molecular weight of 6,000.

The apparatus to measure both fluorescence anisotropy and rheological parameters is a cone and plate rheometer which has been instrumented with optical components. With this equipment, anisotropy and rheological parameters can be measured simultaneously. The measurement involves the use of polarized light to determine anisotropy and orientation of the fluorescent probe which was doped into a polybutadiene matrix. The anisotropy, measured as a function of the applied shear stress and shear rate, decreased as a function of the applied shear stress for the neat polybutadiene and for a polybutadiene plasticized with 5% cetane. For polybutadiene plasticized with 50% cetane, anisotropy was nearly independent of the applied shear stress. These data, shown in Figure 2, were interpreted in terms of a molecular model which depicts the polymeric probe participating in the orientation of both the neat and 5% plasticized polymer matrix, but not participating at 50% plasticization. This is because

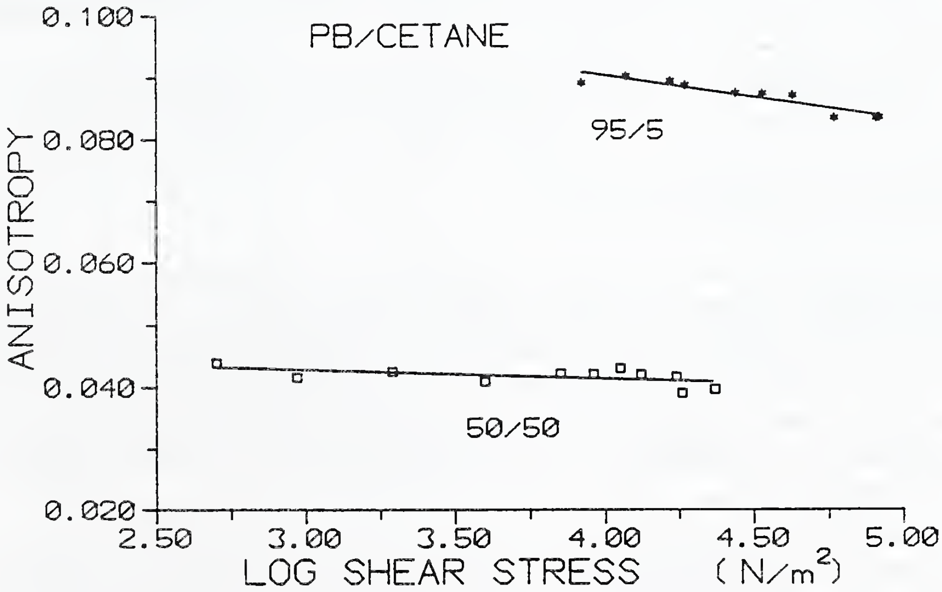

Figure 2 Fluorescence anisotropy is plotted vs shear stress for 5 and 50% cetane plasticized polybutadiene specimens, designated 95/5 and 50/50 respectively. Each specimen was doped with an anthracene tagged polybutadiene probe molecule at 0.1% concentration by weight.

ne probe molecule, having a molecular weight of 30,000, is not as strongly entangled in the 0% plasticized matrix as in the neat matrix. The model also yielded molecular orientation unctions which showed that, upon application of shear stress, orientation of the probe nolecule in the neat and 5% plasticized specimens is small and can be described as a slightly erturbed random orientation.

he ultimate goal is to apply this measurement technology to monitor molecular orientation nd rheological parameters during polymer processing. To do this a fiber optic probe has een designed which contains polarizing optics.

ntersegmental Mixing

he phenomenon of intersegmental mixing occurs in a two component material which ndergoes a transition from phase separated to homogeneous at a critical shear stress. etection of this transition has application to the processing of block copolymers and polymer lends. Of specific interest to us is the block copolymer styrene-butadiene-styrene (SBS). In rder to detect intersegmental mixing via fluorescence observations fluorescent dye will be sed which has a thermodynamic preference to reside in one of the phases and whose pectrum is sensitive to the polarity of its molecular neighborhood. For SBS we have ynthesized a polystyrene which is tagged with pyrene at 1% monomer mole concentration. n the phase separated state, the tagged polystyrene is assumed to reside in the polystyrene hase. Polarity sensitivity was tested by measuring spectra from a doped SBS copolymer and rom model solvents. Polarity sensitivity of this probe was expressed in the relative ntensities of fluorescence bands from the pyrene. By comparing the intensity of fluorescence ands at 380 and 400 nm, it is possible to distinguish the presence of the probe in the olystyrene phase or the polybutadiene phase. Future experiments will be carried out as a unction of applied shear stress at elevated temperatures using a cone and plate rheometer.

luorescence Monitoring of the Glass Transition

his work uses 1,3-bis-(pyrene)propane, a fluorescent probe molecule which has been used in ne past to monitor the curing of epoxies. The fluorescence radiation from this probe occurs n two prominent bands which change in relative intensity in response to changes in viscosity f the probe neighborhood. The relative fluorescence intensity of this probe doped into olystyrene was monitored as the temperature was lowered from above the glass transition 105°C) to room temperature. At the onset of the glass transition temperature, the relative luorescence intensity displays a distinct change in slope on the intensity vs temperature urve. Application of this phenomenon is being carried out at Drexel University where an njection molding machine has been instrumented with an optical fiber cable for the purpose f measuring fluorescence from polystyrene as it resides in the mold. As the molded part is ooled in the mold, fluorescence measurements will indicate the onset of the glass transition nd will permit control of the mold opening time. The fluorescent probe can also be used to nonitor the temperature of polystyrene as it is injected into the mold.

BIOPROCESSING

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

Bioprocessing of Coal

Improved methods for control of SO_2 emissions from coal combustion are sought in order to reduce the harmful effects of acid rain in the environment. Sulfur in the form of pyrite can be removed by physical coal cleaning processes. However, organic sulfur, which often comprises a significant percentage of sulfur in coal, is removed only with great difficulty and expense. Research on new methods for removing organic sulfur from coal is complicated by uncertainty over the exact forms of organic sulfur in coal.

Biotechnical processes for removal of sulfur from coal are under study world-wide. Microorganisms are capable of removing significant amounts of inorganic sulfur from coal (i.e., pyrite), and some recent research suggests microbial removal of organic sulfur from coal. Our EPRI-supported research is focused on using microorganisms 1) as probes for the forms of organic sulfur in coal and 2) as agents for removal of organic sulfur from coal. Elemental sulfur-reducing, extremely thermophilic bacteria (Pyrodictium and Pyrococcus) from marine hydrothermal vents were used to resolve conflicting reports over the occurrence of elemental sulfur in coal. Only highly weathered, pyrite-rich coals contained significant elemental sulfur according to these bioassays. It was also determined that certain di- and trisulfides are reduced to hydrogen sulfide by Pyrococcus. However, several coals tested with this organism did not give evidence of metabolic activity, suggesting these forms of sulfur did not occur in the coals.

Because simple di- and trisulfides may not be adequate representations of the forms of sulfur in coal, especially with regard to steric factors related to organism/enzyme accessibility, model compounds were synthesized with bulky alkyl and aryl groups surrounding sequences of two, three, and four sulfur atoms. A linear polymer with chains of four sulfur atoms in its backbone was also synthesized. Pyrococcus is able to reduce the sulfur from dinaphthyl tri- and tetrasulfide, di-tert-nonyl polysulfide ($[C_9H_{19}]_2S_n$, n=3-5), and di-tert-dodecyl polysulfide

($[C_{12}H_{25}]_2S_n$, n=4,5) as well as from polyethylene tetrasulfide, suggesting that steric hindrance to accessibility does not prevent sulfur reduction by Pyrococcus. Experiments in which model compounds are separated from the microorganism by dialysis tubing also demonstrate that direct access by the microorganism is not essential for sulfur reduction. Results indicate that the mechanism involved in sulfur reduction includes 1) a chemical reaction to form a soluble polysulfide, and 2) reduction of the sulfur in the soluble polysulfide to hydrogen sulfide. Pyrococcus did not reduce sulfur from the coal samples of this study, therefore we conclude that the organic sulfur in the coal is either 1) not of a form that can solubilize, or 2) not accessible to the metabolites that would initiate the formation of soluble polysulfides.

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. 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 Office of Standard Reference Materials (OSRM), is investigating the appropriateness of certain materials as standards for biodegradable plastics. In the process, we are testing procedures developed in other labs as well as developing additional procedures in our labs.

During the past year, many plastic film samples were obtained for study: 1) polyethylene with 0, 6, and 12% starch from Tredegar, 2) polyethylene with 0, 7, and 12% starch from St. Lawrence Starch, 3) polyhydroxyalkanoate from ICI, 4) polycaprolactone/ polyethylene blends with 0, 10, 30, 80, and 100% polycaprolactone from Union Carbide, 5) an uncoated cellophane film from du Pont, and 6) a film that is 80% starch and 20% 'other' from Novamont. With the exception of samples number 2) and 6), these were exposed to a five-species population of mixed fungi for varying lengths of time. A short-term, ten day, exposure was monitored for oxygen consumption. Comparison of fungal oxygen consumption in polymer-containing flasks in excess of oxygen consumption in flasks containing no polymer indicates use of the polymer as a food source. During this short period of time, only cellulose results in greater oxygen consumption by the fungal mix, an expected result because the fungi used are primarily cellulase producers. Studies are underway to develop an inoculum that includes equally ubiquitous fungi that produce enzymes more likely to degrade the types of polymers being produced as biodegradable polymers.

Also underway are long-term tests, one to six months, employing the same exposure conditions as the short term tests. Samples from these longer exposures will be 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. In addition, a procedure is being developed which will allow long-term monitoring of CO_2 production as well as cycling of the media. CO_2 production is a measure of metabolic rate and may parallel polymer metabolization. Media recycling minimizes the build-up of metabolic waste thereby helping to maintain fungal growth. In addition, periodic media collection will allow the identification of predominant organisms and any soluble degradation products.

Pyrite Ore Reference Material for Bioleaching

Industrial applications of bioprocessing of coal and metal ores are hampered by the lack of standards. Standard ore substrates and testing procedures are needed for testing the growth of the processing bacteria, identifying superior strains and determining reaction mechanisms. OSRM has supported our production of a pyrite ore reference material. Twenty kg of a New Mexico pyrite was washed, ground sieved, bottled, sterilized, and packaged under nitrogen with OSRM assistance. The material has been characterized 1) chemically, by x-ray diffraction, x-ray fluorescence and other techniques and 2) microbiologically, by bioleaching rate. The bioleaching rate determination follows a technique developed in our laboratory and submitted recently to ASTM E-48 for approval as a voluntary standard procedure. An inter-laboratory comparison of bioleaching rates has been done and the report has been filed with OSRM for distribution with the reference material.

Quantitative Microbial Biosensor System for Evaluating Bioactive Compounds

In collaboration with Research Associates from Technical Assessment Systems, Inc. (TAS), FDA, and USDA, a laser-monitored bioassay system has been established which measures the effects of toxicants or nutrients on bacterial growth. This is measured as the angular dependence of scattered light from media containing cultures of genetically engineered Bacillus subtilis strains or on a Lactobacillus plantarum auxotroph that has specific requirements for niacin and other water soluble vitamins. This collaboration involving TAS and NIST with the USDA Nutrient Composition Laboratory, Food and Drug Administration's Center for Food Safety and Applied Nutrition (Nutrient Surveillance Branch) has expanded the capabilities of the system. Federal Agencies supporting the technology transfer which is now entering the third year at NIST Polymers Division, include NIST/Polymers, NIST/OSRM, USDA, FDA, DOD/ARMY, AND USEPA/EMSL; in addition a project sponsored by du Pont de Nemours & Co., Agriculture Products Department was conducted and some pesticide products provided by Florida Dept. of Agriculture and Consumer Services and California Dept. of Food and Agriculture were also evaluated using the laser-microbial bioassay system.

We have found that the bioassay system can detect and quantitate several important toxic chemicals in soil or water matrices which are of high priority at toxic waste sites or might be released into the environment as an industrial waste; these include benzo(a)pyrene, pentachlorophenol, and N-nitrosodiphenylamine. For the successful application of the technology, a new approach and procedure for determining bioavailability in a soil matrix was developed; this procedure was also modified to determine bioavailability of various pesticide products in soil or vegetation (i.e., rice stalk and citrus leaf) matrices without having to form chemical analytes.

The current microbial procedures accepted as standards by the Association of Official Analytical Chemists (AOAC) for assaying water soluble vitamins in food, e.g., egg powder, whole milk, or cereal, were developed more than 40 years ago and have undergone few changes during the interim period. We have proven the feasibility to assay for these vitamins with Lactobacillus plantarum in a system utilizing differential light scattering of a laser beam with photodetectors integrated with a microcomputer system to collect and analyze the data. The approach is based on the differential growth rate, rather than total growth, in response to the total amount of vitamin available. This technological improvement reduces the detection and quantitation time to conduct the assay to approximately 1/5th that of the standard AOAC method and increases the sensitivity by more than an order of magnitude.

In summary, the laser-microbe bioassay's technical applications have been significantly expanded and improved for monitoring a wide variety of toxicants or nutrients in the environment. Furthermore, a recent survey of eleven rapid bioassays conducted by the Army (M.S. Thesis Reported at Hood College, Frederick, MD) showed that for 11 toxic compounds of interest to the Army, the laser-microbe bioassay was several orders of magnitude more sensitive than all other surveyed assays (including five standard EPA bioassays--Margaret Toussaint, August 1990). The laser-microbe scored a Mann-Whitney mean rank of 1.1 where 1.0 is the highest score possible; whereas the next highest mean rank was 3.6 and was achieved by one of the standard EPA assays. The author concluded that the laser-microbe assay was "consistently several orders of magnitude more sensitive than the other assays". From our progress on this technology, it appears that transfer of the technology for application by the Federal Government and private industry is forthcoming in the near future.

MECHANICAL PERFORMANCE

The Mechanical Performance Group provides U. S. polymer industry with data, standards and concepts of mechanical properties of polymeric materials, long term performance, and of the relationships among solid state structure, mechanical properties, performance and processing. Activities are concerned with characterization of mechanical properties and performance, the development of continuum and molecular models to describe mechanical response and the elucidation of solid state structure by microscopic and spectroscopic techniques. Work is conducted on materials ranging from elastomers to polymer glasses, and consists also of studies on materials used as either reinforcements or matrix materials in polymer composites. The development, refinement and utilization of continuum theories which describe mechanical properties are integral aspects of mechanical characterization. Solid state structure characterization uses optical and electron microscopy, x-ray diffraction and infrared spectroscopy and solid state nuclear magnetic resonance (NMR). Parallel studies of the mechanical response and structure are conducted to better understand structure-properties relationships.

Cooperative work is carried out for other federal agencies on polymeric materials specific to their mission. A project with the Department of Transportation develops improved test procedures to assess the compatibility of liquid peroxide ladings with polyethylene packages. Solid state NMR is used in a study funded by the Strategic Highway Research Program to characterize the molecular organization of asphaltic cements and determine how the structure is affected by temperature, oxidation, aging and the presence of mineral additives.

FY 90 Significant Accomplishments

- A new solid state NMR technique, based on orientational correlations among aromatic rings in polymers, has been devised for determining the dimensions of heterogeneities in polymers. One application of this new approach is the determination of the uniformity of chain deformation in a deformed aromatic polymer glass.

- A method has been formulated for predicting under uniaxial loading conditions the time of the onset of inhomogeneous deformation in polyethylenes of the sort used in natural gas transmission systems. The creep behavior of these materials cannot be described by the procedures which apply to other polyethylenes and therefore the new method may be relevant to predicting the useful service lifetime.

- Measurements of the thermodynamic behavior of samples having small dimensions show that the glass transition temperatures decrease with respect to bulk values, rather than increase as predicted by entropy or free volume considerations. The discrepancy may be explained by a decrease in the density caused by confinement in small pores.

- Dilatometric measurements of glasses subjected to T-jump thermal histories and simultaneous intermittent torsional deformations show that the underlying thermodynamic state of a glass is unaffected by the mechanical stimulus. The torsional dilatometric results which show that large mechanical stimuli do not alter the volume recovery kinetics in isothermal aging experiments argue strongly against rejuvenation models of glassy behavior.

- Viscoelastic and yield experiments on systems for which dilatometric results are available show that the evolution of the glass towards equilibrium exhibits different characteristic time scales. The viscoelastic properties change their rate of evolution prior to the yield properties which, in turn, change their rate of evolution prior to the volume itself. This suggests that the microscopic mechanics governing the viscoelastic, yield and volumetric responses are different.

CHARACTERIZATION OF SOLID STATE STRUCTURE AND MORPHOLOGY

F. A. Khoury, D. L. VanderHart, G. C. Campbell, Jr., W. F. Manders, G. B. McKenna and C. L. Jackson

Projects concerned with characterization of the solid state structure and morphology of polymeric materials focus on crystallizable polymers, polymer blends, asphaltic materials and polymers at surfaces of graphite fibers. In addition, studies are conducted on the structure of low molecular weight substances confined in porous media such as polymer gels, polymer networks and controlled pore glasses.

Solid state NMR techniques were designed to probe different types of heterogeneities in solids via proton spin diffusion and were applied to polymer morphology, mainly in polymer blends, and to the structure of asphaltic cements in work supported by the Strategic Highway Research Program. Given the recognized advantages of proton observation in this regard, initial efforts were directed at spectrometer modification and setup for operation in the multiple pulse (MP) mode. These experiments, although technically very demanding, average homonuclear dipolar couplings to the extent that they can provide sufficient resolution for direct observation of chemically-shifted proton resonances in solid-state NMR spectra. Also, in the absence of proton dipolar couplings under MP, sharp polarization gradients (based on structural or dynamic contrast) may be generated for use in spin diffusion experiments. In the case of polymer morphology, these studies led to the development of a new experimental approach for probing heterogeneous structure, particularly in polymers having aromatic chemical content. The importance and generality of this approach, which is based on chemical shifts associated with magnetic susceptibility anisotropy, is currently under evaluation. Most of the asphalt work also required proton observation because of quantitative considerations. MP techniques were also employed in these experiments.

The effect of confined geometry on liquid-solid phase transitions of non-polar organic molecules was studied to elucidate the swollen polymer network state. The work relates to the structure of solvents in thermoreverisble polymer gels and crosslinked networks as well as effects of small system size on glass transition temperatures.

Morphological Investigation of Blends of PEI/PBI and the Effect of Annealing Temperature on Phase Separation

The phase separation behavior of a 50/50 by weight blend of PEI, polyetherimide (Ultem 1000 from GE), and PBI, polybenzimidazole (Celanese), was studied. The glass transition temperatures of these materials are quite disparate: 220°C for PEI and 420°C for PBI. Moreover, blend films, which are solvent cast from DMAc solutions, seem compatible since the T_g of the blends is a single-valued smooth function of composition.

The objective was to examine phase separation, estimate domain size and, if possible, deduce domain compositions in the morphologies which result from high-temperature annealing. This system is interesting since when the annealing temperature lies between the T_g of the blend and that of PBI phase separation is expected to result in domains whose dimensions are rather small. This follows from the condition that the initially produced PBI-rich phase generally has a T_g which is above the annealing temperature. Therefore, molecular mobility is greatly diminished in one of the phases, thus limiting the evolution of the morphology.

The experimental challenge was to optimize a spin diffusion experiment so that it could be sensitive enough to monitor phase separation. [The proton spin diffusion experiment for determining domain size is based on producing proton polarization gradients, monitoring them as they subsequently disappear via spin diffusion, and interpreting the time taken for this process in terms of characteristic dimensions.] The PEI/PBI system is not a simple case for study by proton NMR because the spectra of both PEI and PBI polymers are dominated by resonances from aromatic protons. In the observed MP spectrum resolution is such that chemical shift differences between aliphatic and aromatic protons are resolved, but differences within these categories are not resolved. Thus, in order to perform optimum spin diffusion experiments, the gradient preparation was tailored to the minor differences which the spectra of PEI and PBI offered. Furthermore, the data interpretation had to deal with instrumental drift, a consequence of the stringent conditions placed on instrumental stability in these experiments. Model calculations were used to define the polarization gradient for optimizing lineshape sensitivity to phase separation. Experimental data were also taken and analyzed on samples annealed for one hour at various temperatures. Findings are summarized as follows: Average domain sizes, R, which are to be understood as the minimum dimensions for non-spherical domain shapes, are 6, 14, 17 and 21 nm for respective annealing temperatures of 310, 340, 370 and 400°C. For annealing temperatures below about 300°C very little rearrangement took place, i.e. the blend appeared well mixed on the scale of 2.5 nm.

Exploration of Small (less than 100 nm) Structural Inhomogeneities in Aromatic Polymers via Susceptibility-Induced Resonance Broadening

Our studies showed that proton spin diffusion experiments can be used to probe dimensions related to orientational correlations between aromatic rings in polymers. The storage of polarization from protons in crystalline regions of semicrystalline, aromatic polymers was demonstrated to originate from the anisotropic bulk susceptibility shift which arises from aromatic rings in registry. A region of a solid which has a characteristic anisotropic bulk magnetic susceptibility (ABMS) will produce a chemical shift distribution inside of this region as well as a distribution in the immediate vicinity. The latter distribution will a) depend on the orientation of the ABMS tensor and b) will decrease in magnitude with increasing distance. A recipe for generating regions of ABMS is to have domains in which aromatic ring structures, which themselves are sources of anisotropic magnetic susceptibility, possess a net alignment of their hexad axes. Then the "bulk" susceptibility of such a region is also anisotropic.

In the experiments conducted, the level of proton polarization was correlated with chemical shift in the initial, non-equilibrium spin state. Consequently, a polarization gradient is also produced around each region of ABMS. Thus, the dissipation of this gradient, via spin diffusion, can be observed. The result is that the average size of those regions of anisotropic susceptibility can be evaluated.

In terms of the utility for characterizing polymers, this method offered some promise for determining upper limits on the domain size of orientational correlations between aromatic rings in glassy polymers. Alternatively, it may be possible to evaluate the uniformity of chain deformation in a deformed aromatic polymer glass. The obvious examples of heterogeneous regions of ABMS in polymers are semicrystalline aromatic polymers which have crystal structures with preferred orientation of the hexad axes. Such examples are poly(ethylene terephthalate), PET, and isotactic polystyrene. Both of these polymers have been studied by this technique with the result that the apparent domain sizes in the ABMS-based experiments agree with sizes obtained in more conventional spin diffusion experiments where gradients are known to relate to crystal/non-crystal differences. From preliminary examination of glassy PET it was concluded that an upper limit on the domain size for orientational correlation of aromatic rings is about 4 nm. The initial success suggests the use of such an experiment to look into far more interesting, and currently less tractable, issues in polymer science. One such problem is measuring the dimensions of orientational correlations and deformation roperties of glassy, aromatic polymers.

Asphalt NMR Characterization

The Strategic Highway Research Program (SHRP) funded a continuing effort to characterize asphalts using solid-state NMR methods. This is the second and final year of this project whose objective is to probe the size scale for compositional heterogeneity and to monitor any changes which would result from temporal aging or temperature variation.

Extensive use was made of the proton spin diffusion experiments similar to those described under the foregoing two headings. The ability to resolve aromatic and aliphatic signals provided a useful means for generating polarization gradients in spin diffusion experiments designed to probe structural heterogeneities. The major findings of the current year's effort were as follows:

a) In a mixture of asphalt cement and small particles derived from different asphalt aggregates, there was no detectable change in the average mobility of the asphalt cement as a result of the presence of the aggregate.

b) In MP spin diffusion experiments in which polarization gradients were established based on differences in the ratios of aromatic to aliphatic protons, no minimum domain dimensions (MDD's) (a concept appropriate to non-spherical domains) were identified on a distance scale much larger than a molecular diameter. In other words, these gradients in composition dissipate over distances of 3-4 nm. Through model calculations, it was determined that, for a two-phase system, this experiment will not detect nor measure the size of domains whose contrast in aromatic/aliphatic ratio is less than 1.6. Therefore, within this restriction, domain sizes are small. At the same time, chemical separations of asphalt components along with the corresponding aromatic/aliphatic proton ratios for these components, indicate that all of the asphalts have components whose aromatic/aliphatic ratios could provide the minimum contrast for observing phase separation.

c) A second kind of MP spin diffusion experiment was conducted based on mobility differences. Proposed micellar structures of asphalt are thought to consist of a core of more strongly interacting molecules surrounded by more fluid, 'peptizing' molecules. If such a model is valid then the contrast in the linewidth of the more fluid molecules versus those in the more structured core should provide the basis for initially producing a polarization gradient between the mobile and the more rigid phase. Thus, the time required for spin diffusion should indicate the MDD of the micelle. In this experiment MP detection was employed so that changes in the aromatic/aliphatic ratio could be seen as the non-equilibrium line returned to its "equilibrium" shape. It was seen that 1) the narrower portion of the line was associated with an aliphatic-rich residues and 2) the MDD's were again very small (less than 4 nm). For this experiment, there was again a minimum contrast in the ratio of mobile/immobile protons in the two phases (approx. 2.1) in order to observe phase structure. The MDD's have to be interpreted in that light.

d) An examination was made of oxidized asphalts which had been subjected to oxidation either in a pressure-oxygenated-vessel (POV) at 60°C for 3 days, or by thin-film-oxidation at 140°C followed by the same POV treatment. In general, the viscosity of any given asphalt at ambient temperature increases by a factor of about 10 because of these treatments. Unexpectedly, very little change in the proton lineshape at ambient temperature was observed as a result of the oxidation. (Normally, in the vicinity of ambient temperature, the lineshape change with temperature which accompanies a ten-fold change in viscosity is quite dramatic.) At 67°C, however, there was about a 10% increase in the broadest spectral component (which itself comprised 20-30% of the total protons) of the proton lineshape as a result of the oxidation processes. The interpretation of these observations is that oxidation increases the amount of the strongest interacting component. Yet the fraction of protons involved in this motional slowdown is only a few percent, i.e. oxidation seems to work very selectively in retarding the molecular mobility of only a few molecules. A rationalization for seeing little change in the proton lineshape at ambient temperature and a notable change at 67°C is as follows: In both the unoxidized and oxidized asphalts at ambient temperature, the most chemically modified molecules were moving too slowly (correlation times longer than 10^{-4} s) and would appear "rigid", i.e. the lineshape would not be sensitive to changes in the correlation time for molecular motion. On the other hand, at 67°C, molecular motion for these molecules would become fast enough (correlation times of 10^{-5} to 10^{-7} s) so that a retarding of molecular motion for the oxidized molecules would produce an increase in the fraction of the most rigid molecules. Thus, oxidation operates heterogeneously on the mobility of molecules, making some of the slower-moving molecules (or, in principle, molecular fragments) even more rigid.

Shifts in the Crystalline Melting and Glass Transition Temperatures of Small-Molecule Organics Confined in Polymer Gels and Porous Solids

The effect of small system size, or a confining geometry, on the liquid-solid phase transitions of non-polar organic molecules was studied in two distinctly different but related classes of porous solids, polymer gels (or networks) and porous SiO_2 glasses. The porous glass system served as a model for the freezing and melting behavior of the solvent in crosslinked and thermo-reversible polymer gels, and the possible "compartmentalization" of solvent by the network mesh. Although our basic interest is in the swollen polymeric networks, the parallel studies of controlled porous glass systems have also contributed to the understanding of finite size effects in a basic area of condensed matter physics. In addition, the glass transition, T_g, of small molecule organics in porous glasses has been studied. To date, little work has been performed to characterize the influence of finite size effects on the T_g, although it is possible that such studies could be used to differentiate among theories of the glass transition, an important area in polymer physics. Small size effects may also relate to problems such as the anomalously high molecular mobility of polymeric glasses in craze fibrils.

Solid-Liquid Phase Transition of Organics in a "Model" Porous Glass

The effect of small system size on the crystalline melting temperature, T_m, of benzene, chlorobenzene, naphthalene, cis-decalin, trans-decalin, cyclohexane, heptane confined in the pores of controlled pore glasses (CPGs) was investigated. The CPGs are narrow pore size distribution materials with cylindrical, interconnected pores with mean pore diameters of 40Å, 85Å, 156Å, 255Å and 730Å. These materials were surface treated with hexamethyldisilazane to enhance wetting by the non-polar organic materials. The transitions were measured by differential scanning calorimetry (DSC).

The melting temperatures as a function of diameter, $T_m(d)$, were studied and analyzed according to the Gibbs-Thomson equation:

$$\Delta T_m = T_m - T_m(d) = 4\,\sigma_{sl}\,T_m / (d\,\Delta H_f\,\rho_s) \qquad (1)$$

where ΔT_m is the melting point depression, σ_{sl} is the surface energy of the solid-liquid interface, T_m is the normal (bulk) melting point, $T_m(d)$ is the melting point of cylindrical crystals of diameter, d, ΔH_f is the bulk heat of fusion (per g of material), and ρ_s is the density of the solid. It is assumed that σ_{sl} is isotropic and that the crystal size is sufficiently large that the material retains its bulk properties for ΔH_f and ρ_s.

Large depressions of the melting temperature, ΔT_m, were observed at small pore diameters. For example, for benzene in the 40Å pores, ΔT_m is ~26-27K, and the breadth of the peak is ~45K. The pore solid melting endotherm moves to higher temperatures and becomes somewhat narrower as the pore diameter is increased to 85Å and 156Å, and eventually merges with the bulk (excess pore) melting peak as ΔT_m approaches zero. The results for ΔT_m were analyzed by plotting ΔT_m versus 1/d for the seven liquids studied. In general, a linear relationship was observed, in qualitative agreement with equation 1. An analysis based on the prediction of a 1/d dependence of ΔT_m according to equation 1 allowed a value of σ_{sl} to be calculated from these data, and σ_{sl} values in reasonable agreement with other methods were obtained.

This model study included other findings such as a large reduction in the bulk heat of fusion of the crystals formed in the small pores, and the apparent lack of freezing of cis-decalin and benzyl alcohol in the 40Å pores (down to 145K). The effect of pore diameter on the measured value of ΔH_f at small pore sizes was dramatic. The observed ratio of $\Delta H_f(\text{pore})/\Delta H_f(\text{bulk})$ at the 40Å pore diameter ranged from 0.28 for heptane to 0.57 for naphthalene. This may be the reason a pore melting endotherm is not detected in cis-decalin and cyclohexane in the 40Å pores. In the 85Å pores, these materials showed low ratios of $\Delta H_f(\text{pore})/\Delta H_f(\text{bulk})$ of ~0.5, compared to 0.65-0.88 for the other materials. There exists neither a model which describes such a size dependence of ΔH_f, nor other experimental studies which specifically examines the decrease in ΔH_f.

The glass-to-liquid transition temperature, T_g, of organic materials confined in CPGs was also studied as a function of pore diameter for ortho-terphenyl and benzyl alcohol. In general, a reduction in T_g was measured for liquids confined in small pores, and a linear relationship was observed in a plot of $T_g(d)$ versus the reciprocal of the pore diameter. The size of the reduction was as large as 18K for o-terphenyl in the smallest pore material (40Å). The depression in T_g, or ΔT_g, although similar in direction, was smaller in magnitude than the reduction of the crystalline melting point, reported above. For example, benzyl alcohol in the 85Å pores gave a ΔT_m of ~25K, while ΔT_g was only 3K. Other observations include the following: 1) at equivalent pore diameters, the reductions in T_g for o-terphenyl are greater than those observed for benzyl alcohol; 2) in the case of benzyl alcohol, T_g appears to more closely approach the bulk value at large pore size (within ~2K at the 730Å size) than it does for o-terphenyl (within ~4K at the 730Å size); 3) for both sets of data, the ΔC_p of the transition is not affected by the system size but is comparable to that measured for the bulk liquid.

From a theoretical viewpoint, entropy models of T_g would predict T_g to shift to higher temperatures since the entropy of a liquid in a small pore should decrease. This is counter to the observed behavior. Similarly, based on free volume concepts of the glass transition, one would expect that the free volume should increase to produce the observed shift. Either an increase in entropy or in free volume could be explained if the bulk density of the liquid in the pores is reduced, perhaps as a result of difficulty in packing the molecules. The T_g depressions observed here are contrary to results obtained by Angell et al., where size effects were not found to be significant in microemulsions of a similar size scale. The fixed nature of the controlled pore glass geometry is a better system to use than the microemulsions, which contain multiple components.

Solid-Liquid Phase Transitions of Organics in Polymer Gels

Polymer gels swollen in solvent are complex systems with multiple factors which control their freezing and melting behavior. For example, while a sizeable solvent freezing point depression, ΔT_f, and melting point depression, ΔT_m, are expected according to the lowering of the chemical potential of solvent molecules in a polymer solution as described by Flory, an additional ΔT_f has been attributed to various physical effects such as restriction of solvent crystals to small size by the network mesh or difficulty in nucleation of the solvent crystals.

Differential scanning calorimetry has been used to study solvent freezing and melting in two types of polymer gels, crosslinked natural rubber swollen in benzene and a thermoreversible gel of i-PS in cis-decalin. Low temperature x-ray line broadening studies were also used for the i-PS/cis-decalin gels, to directly measure solvent crystallite size. The nature of this system is more complicated, however, due to the possible formation of a polymer-solvent complex. The results will not be treated in detail here, except to note a possible relation to the "model" controlled pore glass system, discussed above, where a lack of freezing of cis-decalin in the smallest pores (40Å), and large reduction in the heat of fusion in small pores was observed. This behavior may be related to the behavior of the cis-decalin liquid in the i-PS gel.

The freezing and melting behavior of benzene in crosslinked natural rubber was studied for two crosslink densities, with molecular weight between crosslinks, M_c, of 3115 and 21,800 g/mole. An uncrosslinked, milled rubber sample was also studied as a control. The ΔT_f and ΔT_m values were obtained by subtracting the observed peak melting temperatures from the normal melting temperature, T_m°, of benzene (T_m°=278.5K). These values were plotted versus polymer volume fraction, v_2, respectively, and compared to the estimated ΔT_m obtained from the Flory type calculation. The theoretical curve is obtained by equating the chemical potential of the solvent crystal with that of the surrounding solution as first done by Flory using the Flory-Huggins lattice model for the chemical potential change upon mixing. The resulting equation is:

$$(1/T_m) - (1/T_m^\circ) = -(R/\Delta H_f)\,[\ln(1-v_2) + (1-(1/x))v_2 + \chi v_2^2] \qquad (2)$$

where ΔH_f is the bulk heat of fusion of the solvent, x is the degree of polymerization of the polymer and χ is the polymer-solvent interaction parameter. Usually x is assumed to be very large so that (1-(1/x)) approximately equals 1. The value of χ for the benzene/rubber system is taken as 0.43, and is nearly independent of concentration but may depend slightly on crosslink density.

The ΔT_m values for the more lightly crosslinked rubber (M_c=21,800) and uncrosslinked rubber agree well with the theoretical prediction of equation 2. The ΔT_f values, however, are much larger than the ΔT_m values, indicating that a large degree of undercooling occurs in the gels, in agreement with the other reports in the literature. The ΔT_m values for the more highly crosslinked rubber, (M_c=3115), are quite different from both the theoretical prediction of equation 2 and the experimental data for the lower crosslink density material. An additional shift of ≈5-10 K is observed beyond the theoretical prediction. One possible explanation is the effect of small crystallite size, as originally hypothesized by Kuhn et al. Based on our work on ΔT_m in the CPGs, a ΔT_m shift of 5-10K would correspond to a crystal size of ~100-200Å, which is not unreasonable but remains to be evaluated by x-ray line broadening studies. Another possible explanation is that the elastic free-energy should be incorporated into the theory of ΔT_m in crosslinked systems, in addition to the polymer solvent free-energy of mixing described by equation 2. This has not been previously considered by researchers in this area and is important in relation to vapor sorption studies of rubber as well.

MEASUREMENT AND MODELING OF MECHANICAL PROPERTIES AND PERFORMANCE

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The Impact of Physical Aging upon the Yield Behavior of Model Epoxy Glasses

When a glass forming material is cooled rapidly from above to below its glass transition temperature the resultant material is no longer in its equilibrium state. As a result, the material upon being held isothermally undergoes a spontaneous evolution of its thermodynamic properties (volume, enthalpy, etc.) towards equilibrium. Accompanying this evolution are changes in viscoelastic and other mechanical properties which have come to be understood in terms of "physical aging". In this work the effects of physical aging on the yield behavior of model epoxy glasses have been studied. These glasses are the same as those studied previously in this laboratory and one of which has been extensively studied in the Torsional Dilatometer project described below. Specifically, examinations were made of the yield behavior of two DGEBA/amine terminated PPO epoxies having poly(propylene oxide) molecular weights of 230 and 400; these specimens are referred to as the D230 and D400 epoxies, 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. In addition, it was observed that the lower yield stress, corresponding to the onset of generalized plastic flow, exhibits only a very small increase with the aging time. 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 emerged from 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 for cessation of the evolution of the relaxation modulus. This suggests that, even though the yield phenomenon is related to the viscoelastic response, the exact mechanism responsible for the yield phenomenon itself which leads to a subsequent plastic flow of the material is different. Second, in the studies of the lower yield stress, we see evidence that glassy polymers may actually be rejuvenated during yielding--a phenomenon which the dilatometric studies demonstrate does not occur below yield. Both of these observations serve as the basis for fruitful areas of future research.

Physical Aging in Epoxy Glasses, Probed by Torsional Dilatometry

A model epoxy, Jeffamine D400, is under study to determine time scales relevant to physical aging near the glass transition. Experiments in a torsional dilatometer measure volume changes and torque and normal force relaxations during a program of torsional deformations imposed following a quench from above the glass transition temperature to slightly below it. Several important time scales have emerged: For this material, torsional deformations induce volume expansions that relax on time scales similar to those of torque relaxation $\sim 10^3$ seconds. The torque relaxation evolves with the physical aging of the glass such that curves can be shifted to follow a time-aging time superposition. The volume recovery also evolves with physical aging, however, in this case, such a superposition is not possible. The time scale of the physical aging itself, $\sim 10^5 +$ seconds as determined by volume recovery, is much longer than the relaxation from mechanical stimuli, and is also different from the time scales for the evolution of the torque relaxation and volume recovery.

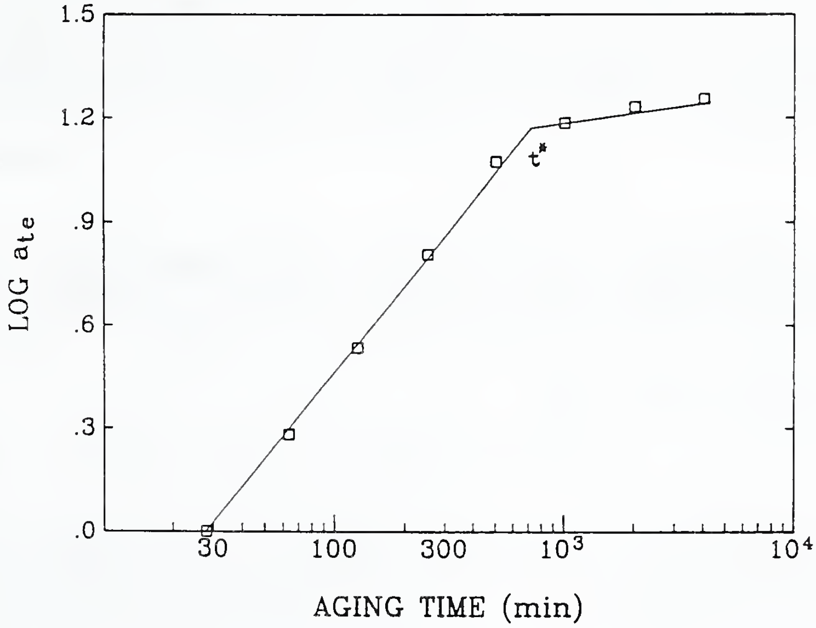

Figure 1

In Figure 1, the shift factor characterizes how torque relaxation evolves through at least two regimes, separated by the mechanical equilibration time t* ~10^4 sec, a quantity independent of strain. Prior to t*, the evolution of the torque relaxation is rapid with a rate strongly dependent on the strain. After t*, the torque evolves more slowly, if at all. It is our interpretation that prior to t* the dependence of the evolution rate on the magnitude of the strain results from the nonlinear response of the material. This contrasts with the interpretation of Struik that large deformations reverse physical aging or cause rejuvenation. Struik's rejuvenation hypothesis cannot be correct since t* is independent of strain, indicating no change in equilibration time with the magnitude of the strain. Dilatometric results also argue against a rejuvenation hypothesis since the same volume recovery underlies each quench experiment, independent of any intermittent behavior from mechanical stimuli.

Mechanical and Swelling Thermodynamics of Elastomers

In previous work, a phenomenological approach was taken in studies of important problems in rubber elasticity. From a microscopic point of view, the experimental data are examined within the context of the "Localization Model" of rubber elasticity developed by Gaylord and Douglas. According to this model w′(λ) can be expressed as:

$$w'(\lambda) = G_c\,(\lambda - 1/\lambda) + G_e\,(1 - 1/\lambda) \qquad (1)$$

where the first term in equation 1 comes from the classical network chain connectivity contribution to the free energy of the network and the second term comes from an entanglement or confinement contribution. In the limit of no entanglement interaction ($G_e=0$) the localization model reduces to classical rubber elasticity theory. Although various predictions have been made for the magnitude of the shear modulus G_c, all of the classical models indicate that it is proportional to the crosslink density ν as:

$$G_c = C_0 \nu kT \qquad (2)$$

where C_0 is a constant, k is the Boltzmann constant and T is absolute temperature. Results of fitting equation 1 to torsional data on natural rubber support the contention that $C_0 \approx 1/2$.

The confinement term has two contributions:

$$G_e = \delta(\nu kT) + G_N^* \qquad (3)$$

where G_N^* is the plateau modulus of the uncrosslinked rubber and δ is a constant. The result of fitting the data to equation 1 indeed show that G_e varies linearly in the crosslink density and that the intercept of the plot of G_e versus ν is equal to literature values given for G_N^* for natural rubber. Currently the model and data analysis are being extended to the swelling behavior of the rubber.

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

The US Department of Transportation Office of Hazardous Materials Transportation supports the development of practical and cost-effective test methods to determine whether a liquid hazardous material may be safely shipped in a particular type of polyethylene packaging.

Preliminary to the development of test methods for compatibility, a review and comparison was made of current DOT and European regulations and test methods. While in many respects the two sets of regulations are similar, there are some significant differences, the principal one lies in the area of compatibility testing. Current DOT regulations require that polyethylene packagings must be tested with each type of lading while European regulations allow for the testing to be done using one or more of six standard liquids which are regarded as being equivalent to a large class of liquid hazardous materials. The particular standard liquid is chosen on a basis of the extent to which a lading is expected to attack or swell polyethylene. One of the standard liquids, specified as a mixture of hydrocarbons, is considered as equivalent to a very large grouping of liquid chemical substances. The use of such a mixture of hydrocarbons presents a problem under current DOT regulations since according to the European regulations the mixture may have a flash point as low as 61°C while DOT regulations allow for the compatibility testing to be done at a temperature as high as 60°C.

An analysis was carried out of possible schemes for determining the compatibility of liquid hazardous materials with polyethylene. There is, as yet, no general theory which can be used to correlate the permeabilities of a large number of different ladings. However, an empirical approach to making such correlations, known as the "Permachor" scheme, has been described in detail in an earlier set of reports prepared by NIST for the DOT. The feasibility of using the Permachor scheme as a method of ranking liquid hazardous materials with respect to a set of standard liquids has been examined.

The rate at which a particular molecule permeates through polyethylene has been found to depend upon various properties of the permeant such as size, shape, polarity and other factors. Attempts to correlate permeation factors (P) with any one property of the permeant were found to give rise to a wide scatter of the data points. However, for the non-polar homologous series of straight chain hydrocarbons a plot of the P-factors verses the number of carbon atoms in the permeant was found to yield a straight line on a semilog plot. Working from this curve, numerical values were empirically assigned to other chemical species so as to force the permeability points of other homologous series to fall on the same straight line. For example, it was found that the homologous series of unsaturated hydrocarbons, when plotted on a similar semilog plot, fell on a parallel straight line shifted by a factor of 0.2. By assigning a value of - 0.2 to the double bond the P-factors of the unsaturated hydrocarbons fell on the same line with the saturated hydrocarbons. In a similar fashion, a value was assigned to the different types of organic liquids, both polar and non-polar. From these shift factors the Permachor (π) value of the molecule can be readily determined.

Another useful feature of the Permachor scheme is that once a Permachor value had been established from data at one temperature it could be used to predict the P-factor at any other temperature. In general, it is found that the compounds having the smallest Permachor number are the organic solvents such as benzene and toluene, and the low numbered hydrocarbons from C_5 through C_{10}. Correspondingly, these compounds also have the highest permeation rates through polyethylene. At a temperature of 21°C (70°F), which corresponds to one of the temperatures at which the required testing is done, the experimentally determined P-factors are in rather good agreement with the values calculated using the Permachor scheme.

On the assumption that the Permachor scheme is valid it would then appear feasible that one or more standard liquids can be substituted for a potential lading. An essential element of such a scheme is that the Permachor number of the potential lading be larger than that of the standard liquid, or that its permeation factor be smaller. This scheme appears to be most applicable in the case of pure liquids for which the Permachor numbers can be established or the permeation factors are known. If the Permachor number of the potential lading is larger than that of the standard liquid, or alternatively, its permeation factor smaller, then it would qualify to be placed in the group for which the standard liquid can be substituted. If the reverse is true, then the testing should be done using the potential lading. Classes of pure liquids or new liquids for which there is no well established data base on their permeability should be subjected to a compatibility test.

On the Long Time Creep and Lifetime Behavior in Uniaxial Extension of a Linear Low Density Polyethylene

There has been considerable interest in establishing failure criteria which can be used to predict the useful lifetime of a material or product. In the case of amorphous polymers the use of elevated temperature and/or various solvents has provided researchers with relatively successful means for predicting long time behavior based on short time tests. By collecting time to failure data at several different temperatures, for example under creep or stress relaxation, it has been possible to obtain composite curves from which the long time behavior can be predicted. With the constant evolution of new and improved materials, the time required to test these materials to failure becomes longer and longer, thus the need to devise accelerated tests becomes ever more relevant.

However, caution should be exercised in using composite curves generated in this way to predict long time behavior. One problem is that long time behavior may depend on the processing conditions. In processes such as extrusion or injection molding, where the molten polymer may experience relatively high rates of shear, it is commonly found that the melt flow rate of material taken from the processed part is either higher or lower than that of the starting resin. Such a change can come about as a result of polymer degradation, possibly the formation of crosslinks, or more importantly, the melt shearing itself. It is believed that melt shearing leads to disentanglement of the molecules and, as a consequence, to changes in the melt flow rate. The melt flow rate tends to recover to its original value only if the polymer is maintained at melt temperatures for a sufficiently long time. One consequence is that a given set of failure curves will in most cases apply to a rather limited set of preparation conditions.

Currently, an active area of research concerns the long term performance of polyethylenes used in natural gas distribution piping. Polyethylene now accounts for about 80% of newly installed gas distribution piping. The ability to establish with reliability conditions under which a natural gas piping system will last fifty years or more will likely lead to reduced cost and improved safety. The uniaxial creep behavior of one ethylene-hexene copolymer of the type used in the manufacture of natural gas distribution piping was examined over a wide range of stresses in the temperature range from 24°C to 75°C. It is found that the uniaxial creep behavior overall is quite complex, and that the time required for necking to initiate was probably the best predictor of the useful lifetime of this material.

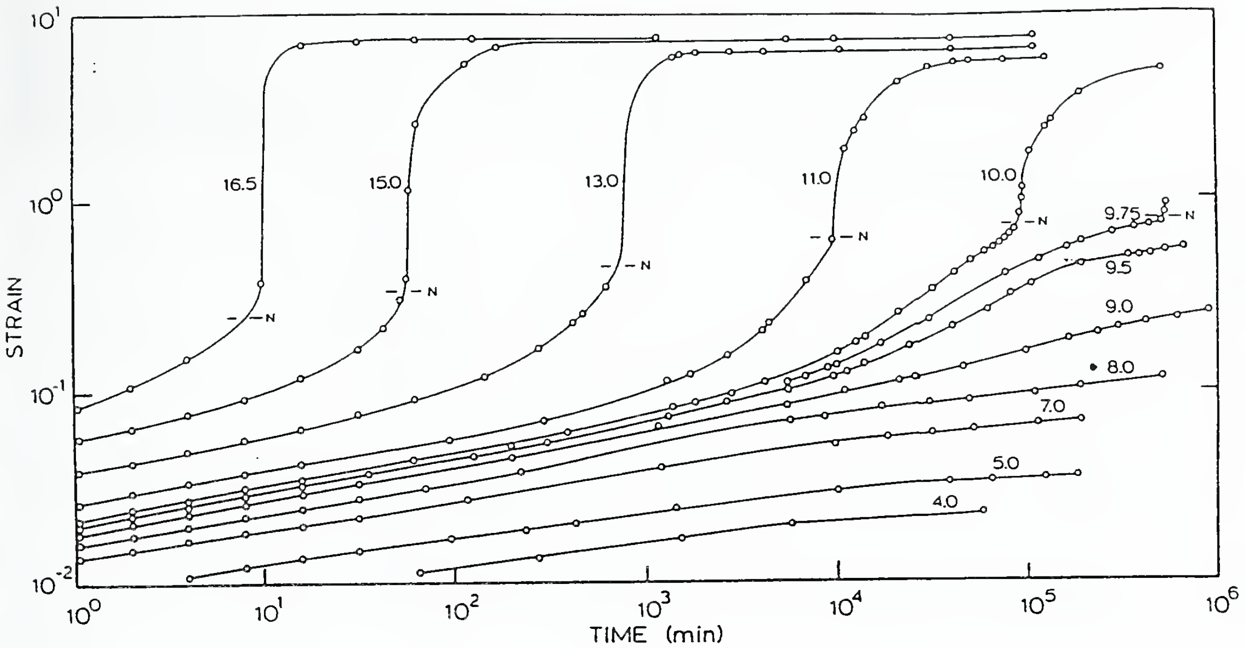

Figure 1 Log strain versus log time for an ethylene-hexene copolymer in uniaxial creep. Numbers indicate the applied stress in MPa. The letter N indicates the time and strain at which necking occurred, temperature 24°C.

Shown in Figure 1 are creep curves obtained at twelve different levels of applied stress at 24°C and times corresponding to about 1.9 years. The numbers from 16.5 to 10 indicate the magnitude of the applied stress. Where feasible, the experiments were continued to the time at which necking and cold drawing of the gauge section occurred. Data were collected until the specimen was fully cold drawn and the final plateau region well established. In Figure 1 the letter N marks the time and strain at which the onset of necking became evident. The occurrence of necking in the specimen will be considered as constituting failure of the materials. A second mode of failure commonly observed in polyethylenes is crack initiation and growth followed by fracture. This failure mode has not been observed in any of the specimens of this copolymer tested to date. Once necking occurs there is a rapid draw down until the entire gauge section has been traversed. At that point a plateau in the creep curve is reached beyond which any further creep occurs at a much slower rate.

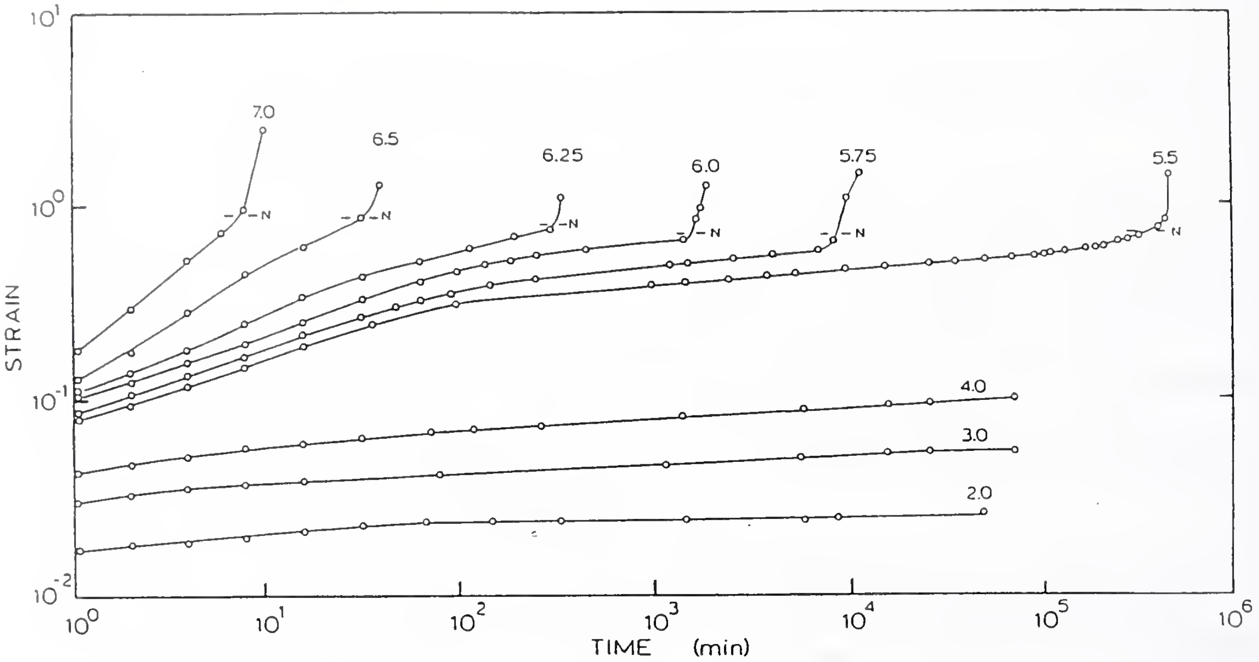

Figure 2 Legend the same as in Figure 1, temperature 75°C.

Figure 2 shows similar creep curves obtained at 75°C. Three other sets of creep curves were obtained at temperatures of 37, 50, and 63°C. Examination of all five sets of data reveals several interesting features. First, the strain at which necking occurs varies appreciably. Depending upon the temperature and the applied stress, the strain was found to be as small as 0.25 to as large as 1.00. This behavior is rather atypical of most polyethylenes in which necking generally occurs at a strain of about 0.30 or less. It can be seen that the behavior is rather complex. At 24°C the strain at which necking occurs decreases with increased stress, while at 75°C it increases. At the three intermediate temperatures it goes through a maximum, and the maximum shifts to a smaller value of stress as the temperature is increased.

In order to predict lifetimes in excess of longest times for which creep data were obtained a scheme is needed whereby all the data can be normalized to one common temperature, for example 24°C. The method of reduced variables has been successfully applied to many viscoelastic materials in the region of transition from glass-like to rubber-like behavior. In the case of creep, measurements of the compliance $D_p(t)$ made at the temperature $T\rho$ fall on a common curve if plotted as $D_p(t) = D(t)\ (T\rho/T_o\rho_o)$ versus t/a_T. In this scheme $D_p(t)$ is the compliance at temperature T, D(t) is the compliance at the reference temperature T_o, ρ and ρ_o are the values of the density at the two respective temperatures, and a_T is the shift factor between the two temperatures along the time axis. The shape of the composite curve represents the time dependence at constant temperature, which can cover a quite extended time range, and the temperature dependence of a_T describes the effect of temperature on viscoelastic properties.

It is obvious from Figures 1 and 2 that the reduced variables method cannot be applied to the creep behavior of this polymer since no two creep curves have the same shape, which is one requirement for the use of the reduced variables method. No superposition of the curves is possible, either within one set of curves obtained at a given temperature or from one temperature to another.

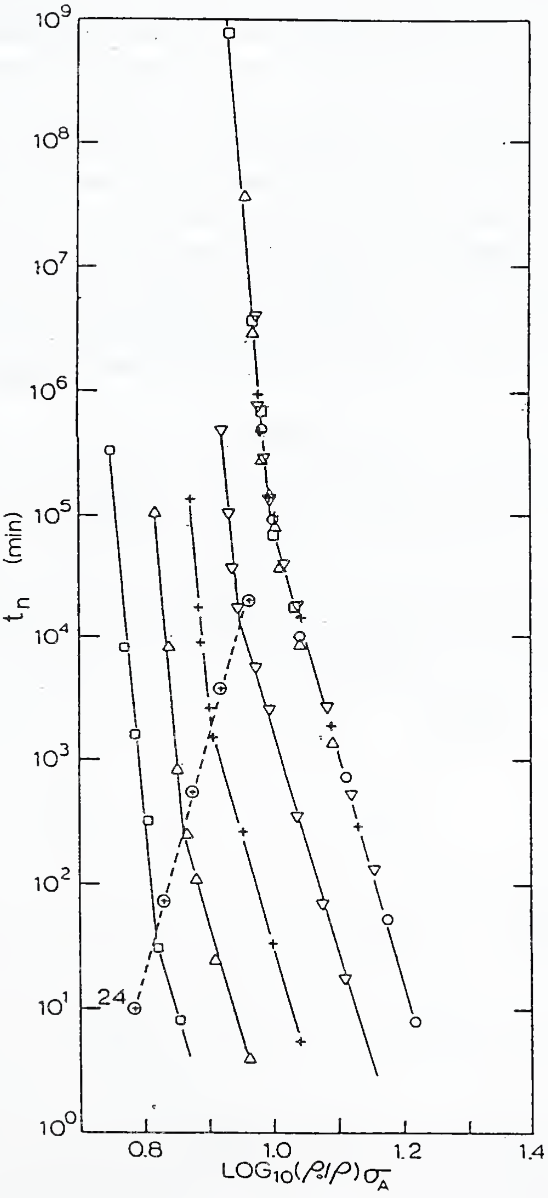

Figure 3 Log-log plot at the time for neck formation to occur versus the applied stress. The circles with crosses indicate the horizontal and vertical shift factors used to obtain the composite curve superposed on the 24° data.

An alternative approach, and one purely empirical by nature, is to use the time at which neck formation occurs as a measure of the useful lifetime of the material under conditions of uniaxial extension. In Figure 3, the logarithm of time at which neck formation occurs is plotted against the logarithm of the applied stress.

When plotted in this manner, the interesting result is that each of the five sets of data can be represented rather well by two intersecting straight lines. The abrupt change in slope, which appears in each curve, occurs at shorter and shorter times as the temperature is increased and the slopes of the upper and lower branches of each curve are independent of temperature.

Because there was a well defined breakpoint in each curve it was possible to shift all curves onto one composite curve using the 24°C data as the reference curve, as is also shown in Figure 3. The amount of shift necessary of each curve is indicated by the circles with crosses. It can be seen that on the log-log plot this set of points fall on a straight line which corresponds to the same line along which the position of the breakpoint of each curve shifts with temperature. Since both branches of the composite curve are straight lines on the log-log plot we can then calculate the time to neck as a function of stress using the relationships

$$t_{n1}\ (24°\mathrm{C}) = 4.55 \times 10^{23}\ \sigma^{-18.7} \text{ for } \sigma > 10 \text{ MPa} \tag{1}$$

$$t_{n2}\ (24°\mathrm{C}) = 3.81 \times 10^{64}\ \sigma^{-59.7} \text{ for } \sigma < 10 \text{ MPa} \tag{2}$$

It was also found that plots of $\ln b_t$ and $\ln b_\sigma$ versus reciprocal absolute temperature yielded straight lines. Therefore the break point on each individual curve in Figure 3 can be located relative to that at 24°C using the following relations

$$b_t(T) = 1.837 \times 10^{-18}\ e^{\frac{1.56\times10^4}{T}} \tag{3}$$

$$b_\sigma(T) = 0.730\ e^{\frac{778}{T}} \tag{4}$$

where T is the absolute temperature.

Thus, using relations (1-4) it is possible to reconstruct all of the curves shown in Figure 3, as well as construct curves at any other temperature in the interval from 24°C to 75°C. Such a plot can then be regarded as yielding an upper bound to the useful lifetime of this material in uniaxial extension under one set of preparation conditions.

Classical Dilatometry of Blends

The protocol for classical dilatometer studies of blends of polystyrene (PS) and polyvinylmethyl ether (PVME) near the limit of stability of the mixture is under refinement since preliminary data had indicated the surprising result of no volume discontinuity at the phase separation temperature. Further tests are exploring possible experimental artifacts: leaks in the optical seal of the dilatometer near the sample, small air bubbles in the sample, small air or oil bubbles in the mercury under the level detection device, or complications from the relative time scales of the temperature changes and the phase separation kinetics. At this point, a sample preparation method has been devised that eliminates visually-detectible bubbles, a procedure was developed to prevent leaks in the optical seal, and it was concluded that the level-measuring device works best without lubrication. Despite careful degassing procedures, the accumulation of small air bubbles beneath the level detector limits the number of tests per sample, especially at elevated temperatures. Tests at different heating and cooling rates highlight the effect of phase separation kinetics as well as vitrification kinetics, while studies of the same materials in multiple dilatometers guard against errors from leaks and bubbles, but require large amounts of polymer, often more than is available.

Studies near completion for the single phase region of the PS/PVME phase diagram focus on the effects of miscibility on density. For blends whose components are truly thermodynamically miscible on the molecular level, it is anticipated that densities exceed those from simple volume additivity rules because specific interactions between chemical groups should favor molecular arrangements that lead to an overall densification. Greater densification is expected with deuterated PS (DPS)/PVME blends than with mixtures containing protonated PS since the former is considered more miscible, phase separating at 140°C as opposed to 115-120°C for the protonated system. The effect of composition will also be studied before continuing the program into the two-phase region.

Rubber and Rubber Compounding Materials SRMs

The Polymers Division maintains a series of Rubber and Rubber Compounding ingredients as Standard Reference Materials (SRM). These materials are used widely by industry through ASTM standard test methods which specify the NIST SRM's. During the past year the program was maintained through interactions with industrial users--normally testing of samples which the users identified as defective, but which upon NIST retesting were within the original specifications of the SRM. This interaction generally leads the industrial users to reverify procedures of testing and equipment calibration. In addition, two renewal SRMs were issued this year. The SRM 388p Isobutylene-Isoprene (Butyl) Rubber standard which is used as a secondary Mooney Viscosity standard in industrial laboratories around the world was renewed. Also the SRM 388k Styrene-Butadiene (Type 1500) Rubber standard which is used in standard rubber formulations was renewed.

POLYMER COMPOSITES

The Department of Commerce recently completed a study to identify the most important emerging technologies for improving international competitiveness. The results, detailed in a report entitled "Emerging Technologies - A Survey of Technical and Economic Opportunities", indicate that Advanced Materials is a key area. The largest single item in the Advanced Materials category is polymer based composites. With an annual growth rate of 16%, polymer composites have great economic importance. The continuation of this growth rate, however, requires expanding the use of composites 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.

The program is divided into three Task areas: Processing Science, Microstructure Characterization, and Laminate Properties. Activities in the Processing Science Task during the past year focused on four areas: the sponsorship of an Industry Workshop on Polymer Composite Processing, the development of a composite fabrication facility, the continuation of research on process monitoring, and the expansion of a program on resin transfer molding.

The Task on Microstructure Characterization seeks to bridge the gap between processing and performance by developing techniques to characterize the microstructure of the resin, the fiber, the resin-fiber interface, and the composite.

The Laminate Properties Task involves the determination of properties for composite laminates and their constituents. The projects fall into three areas: test method development, failure mechanisms, and modeling.

To assist in these research efforts, the Composite Group has utilized cooperative programs and guest experts. The cooperative programs in Processing Science include efforts with the General Electric, the National Center for Manufacturing Science, the Automotive Composites Consortium, and the Department of Defense. In the area of Microstructure Characterization work is conducted with Hi-Tek Polymers, Polaroid, University of Massachusetts, Colorado State University, and Kyoto Institute of Technology (KIT). Finally, research on Laminate Properties includes cooperation with the Automotive Composites Consortium, Michigan State University (MSU), the University of Tokyo, and the Department of State.

Scientists assisting the programs as guest scientists or postdoctoral fellows were Mr. H. Kurokawa of Kyoto Institute of Technology, Dr. P. Herrera-Franco from Michigan State University, Dr. L. Coyne now with the Department of the Food and Drug Administration, Dr. A. Hampe of the Bundesanstalt fur Materialforschung und Prufurg (BAM), and Prof. H. Mizumachi from the University of Tokyo.

The 1990 Colloquium Series on Composite Materials was devoted to processing, and it continues to bring many world renown scientists to NIST for discussions. Finally, Dr. Richard Parnas was added to the staff and will work in the RTM program.

FY 90 Significant Accomplishments

- A workshop of 26 industry scientists representing the major users and suppliers of composite materials was held. The attendees identified the most important processing methods for the future and the scientific and technical barriers that limit full utilization of these methods. The most critical performance issues were also identified. The report from this workshop is a key planning document for the composites program.

- Two finite element flow modeling programs were developed to describe resin transfer molding. These "2D" programs can predict filling of shell molds containing anisotropic preforms. One program is computationally faster while the second has added terms which for the first time permit the proper modeling of boundaries such as edges, corners, and joints between preforms of different permeability.

- A new model was developed to describe flow in resin transfer molding (RTM). By considering the heterogeneous nature of the fiber preform, the model is able to predict a number of previously unexplained features observed in RTM experiments, for example, the continued increase in the inlet pressure after the mold is filled. This new model will significantly improve the ability of future finite element programs to predict RTM mold filling effects.

- Phase I in the development of the NIST composite fabrication facility has been completed with the addition of pressure molding equipment for press and autoclave fabrication. This state-of-the-art facility will permit in-house preparation of test specimens and enable experiments in on-line process monitoring and control.

- Studies with carbon fibers and nylon 66 provide strong evidence that trans-crystallization at the carbon fiber surfaces is epitaxially specific. This has obvious consequences for the control of interphase morphology during processing of thermoplastic composites.

- A patent is pending for a new thermo-acoustic technique to determine the strength of the interface between fiber and matrix (and between plies) in a composite. This method has the advantage that it can be applied to real parts and prepregs in contrast to other techniques which require special test specimens.

PROCESSING SCIENCE

S. S. Chang, W. G. McDonough, R. S. Parnas, F. R. Phelan, D. L. Hunston, B. M. Fanconi, F. I. Mopsik and F. W. Wang

The Composite Processing activities seek to generate measurement techniques for monitoring the changes that occur during composite processing, to develop a scientific understanding of these events, to formulate models that describe the changes, and to provide the basis for on-line process control. There were four areas of activity during the past year: (1) an Industry Workshop on Polymer Composite Processing was held in May to assist in program planning, (2) a composite fabrication facility was developed, (3) research on process monitoring was continued, and (4) the program on resin transfer molding initiated last year was expanded and is now the major activity in the Processing Science Task. Each of these areas will be discussed below.

Industry Workshop on Polymer Composite Processing

The Polymers Division sponsored a second Industry Workshop on Polymer Composite Processing in May, 1990 with participation by 24 organizational units representing the automotive, electronics, aerospace, marine, construction, and material supplier sectors of the composite industry. The meeting was designed to update and expand the results of a previous Workshop sponsored by NIST. That meeting identified the most promising processing methods for the future and the technical and scientific barriers that currently hinder the use of these methods. The May Workshop reconfirmed most of the earlier findings and provided a much more detailed examination of the technical barriers. In addition to addressing processing issues, the attendees also identified the most important issues in the performance of composites. The results indicated that pressure molding and liquid molding were the most important processing methods for the future. The control of resin flow and fiber orientation was considered the most important technical barrier, while process monitoring and the measurement and control of fiber-matrix adhesion were also ranked as very important. These results fit very well with the current and planned NIST research program. In the performance area, two topics, impact damage and environmental attack, were selected as critical by all industry sectors. This and other Workshop results will be used in future program development. A full description of the Meeting and its conclusions are contained in a NIST Report.

Composite Fabrication Facility

The development of the fabrication facility involves two phases. Phase I which focuses on pressure molding is virtually complete while phase II concentrates on resin transfer molding and is scheduled for completion in early 1991. In phase I, an autoclave, a prepreg machine, and a hydraulic press have been acquired. The emphasis on pressure molding is NIST's response to the importance given to this area by the first Industry Workshop. The pressure molding laboratory module will be used to fabricate specimens for testing and investigate on-line cure monitoring and process control.

Both the autoclave and hydraulic press can operate up to 538°C (1000°F). The autoclave has the ability to hold a pressure of 3.8 MPa (525 psi), and the press can impart a 900 kN (100 ton) force. The autoclave has special access ports for process monitoring sensors. Both the autoclave and press are fully automated. A variety of composite prepregs with different fiber surface treatments can be made on the prepreg machine.

The resin transfer molding module (phase II) is being designed to support the experimental program described later in this section. Details of the equipment will be described there.

Two other new facilities capabilities compliment the fabrication facility. First, a super-computing graphics workstation has been added to provide finite element modeling analysis and various types of flow modeling. Software for stress analysis and pre- and post-processing data manipulation has been acquired. The workstation is also equipped with an image analysis system to capture, store and analyze video and other image data, such as results from complex flow visualization studies.

The second facility consists of two dynamic mechanical spectrometers to characterize solids, fluids, and chemically reacting (curing) systems. One spectrometer utilizes tension, compression, and bending while the other tests torsion (shear) and normal force. Both instruments have wide frequency (100 Hz to 0.01 Hz) and temperature (400°C to -150°C) capabilities and are fully automated.

Process Monitoring Techniques

An important accomplishment of the past work in the Processing Science Task has been the development of a unique capability and expertise in process monitoring techniques. This work has produced or implemented more than 10 different measurement methods to monitor the events that occur during processing. These techniques permit measurement of mechanical (ultrasonics, viscosity), thermal (DSC), electrical (dielectric loss, conductance), optical (fluorescence, FTIR), as well as chemical and structural properties (various spectroscopies, GPC, neutron diffraction and scattering). Ultimately, a number of these methods will be implemented on-line in the new processing facility. During the past year, this expertise has been applied in two areas: a survey of process monitoring techniques and continued development of monitoring methods.

Survey of Process Monitoring Techniques: In a 1989 program, NIST assisted the National Center for Manufacturing Science (NCMS) by conducting a detailed study to determine the state-of-the-art in on-line process monitoring technology for composite fabrication. During the past year, a report summarizing many of the results from that study has been prepared. The report concludes that past development work in the areas of ultrasonics, dielectrics, optical, and spectroscopic methods make them quite promising for process monitoring. There are, however, problems that remain to be solved. The two most important challenges are the need to make more rugged and reliable sensors and to establish relationships between the properties measured by the tests and parameters more directly related to process control such as viscosity and degree of cure. The report found numerous large programs that are developing process control models and technology, and the value of such programs for the development of on-line process control was noted. For the most part, however, these programs utilize current sensors and sensor technology. Consequently, the report emphasizes the need for increased research in both sensor development and the generation of the science base required for interpretation of the sensor output.

Process Monitoring Technology: During the past year, work on process monitoring continued in three areas. First, the relationship between ultrasonics measurements on a curing system and corresponding steady-flow viscosity was studied. Data were being obtained for two model materials systems: diglycidyl ether of bisphenol A cured with either imidazole catalyst or nadic methyl anhydride and benzyldimethylamine catalyst. The temperature was varied to obtain a variety of cure rates. The results showed a clear correlation between viscosity and ultrasonics data in the early stages of cure. Efforts to predict this relationship based on simple viscoelastic relationships and models are underway.

A second area of study is differential scanning calorimetry (DSC). Although DSC is not an in-situ monitoring technique, it is an invaluable tool for studying the thermodynamics and kinetics of cure reaction, the developing an optimum cure cycle, and calibrating other monitoring techniques relative to the degree of cure in the resin.

Based on experiments with several model systems, two general observations were made. First, due to the non-equilibrium nature of DSC, a temperature gradient and an overshoot beyond the programmed temperature can occur during the initial heat up or during the cure exotherm. The overshoot can be as much as 10°C, and this can be an important source of error in data analysis. The second observation concerns the common belief that post-curing a sample produces the same final molecular structure. The results show that this is not always true. Experiments with common materials found the glass transition may vary by as much as 50°C when different curing paths are used even after extensive post-curing. This was attributed to the generation of different molecular network structures by the various cure paths. What makes this observation particularly important is the desire for more rapid processing rates in composite production. For the materials tested here, higher cure rates generally produced significantly lower glass transition temperatures. Consequently, care must be exercised when increasing production speeds to be sure the required material properties are maintained.

The third area investigated as a cure monitoring technique was fluorescence recovery after photobleaching (FRAP). This technique measures the translational diffusion coefficient of dye molecules in polymer matrices. The sensitivity of the diffusion coefficient to the degree of cure in the polymer matrix provides a means to monitor cure. The aim of the present work is to examine the potential of optic fibers to probe the interior of thick specimens by FRAP. The temporal response of the fluorescence intensity, from which diffusion coefficient of the dye molecule is determined, has been calculated for an evanescent wave type fiber optic probe. With fiber optics it should be possible to measure translational diffusion coefficients an order of magnitude smaller than those detected by the conventional microscope-based method.

Previous work utilizing optical fibers to monitor polymer cure capitalized on the sensitivity of the fluorescence characteristics of either the resin or certain probe molecules to viscosity, or the degree of cure. However, these fluorescence methods were shown to lack sensitivity at high degrees of cure which limits their usefulness in determining when the reactions are essentially complete. Another application of fluorescence spectroscopy to cure monitoring exploits the connection between resin viscosity and diffusion coefficients of photosensitive low molecular weight molecules. In this method, termed fluorescence recovery after photobleaching, FRAP, a laser beam is focussed through a microscope onto the curing sample which contains a small amount of a photosensitive dye dissolved in the resin. The intense laser beam initiates photochemical reactions in the probe molecules such that fluorescence ceases within the small volume of material illuminated by the focussed light. After photobleaching is accomplished, the high power light source is turned off and the bleached region is exposed to a low intensity probe beam. As active probe molecules diffuse into the bleached area from the surrounding region they are electronically excited by the low intensity probe beam and fluoresce. The gain in fluorescence with time is a measure of the buildup of the probe molecule concentration in the photobleached region. From the temporal behavior of the fluorescence signal and the dimensions of the bleached area the translational diffusion coefficient of the probe molecule in the polymer matrix is determined.

To examine this idea, a model consisting of a bare optical fiber with refractive index greater than that of the photosensitive probe/resin system was used. Light propagating in the optical fiber produces an evanescent field extending into the resin of intensity at a distance of r from the fiber surface given by the equation

$$I(r) = I_0 \exp(-r/\lambda_p) \tag{3}$$

where λ_p is a function of the refractive indices, the wavelength of light and the angle of incidence at the fiber-medium interface. If the initial concentration is everywhere uniform and equal to C_0 then

$$C(r,T) = C_0 \exp(-I_0 \alpha T \exp(-r/\lambda_p)) \tag{4}$$

is the concentration after bleaching time T. The dimension of the depletion zone is in tens of nanometers rather than the micrometers dimensions characteristic of microscope-based FRAP which implies that it should be possible to determine diffusion coefficients which are an order of magnitude lower than the smallest values measured in a microscope FRAP experiment.

The fluorescence recovery curves depend on the quantity $I_0 \alpha T$ as well as the translational diffusion coefficient. The fluorescence originating at a distance r from the fiber surface depends on the concentration of probe molecules, the intensity of the evanescent wave, and the probability that the fluorescent photon will impinge on the optic fiber and arrive at the detector. The fluorescence intensity as a function of time during recovery is calculated by solving the diffusion equation

$$\frac{dc}{dt}=\frac{1}{r}\frac{d}{dr}\left(rD\frac{dc}{dr}\right)$$

with boundary conditions appropriate to optical fibers. The data from FRAP measurements consist of a set of fluorescence recovery curves, each curve corresponding to a different cure time. The recovery curves cannot be directly compared since variations in the extent of bleaching are likely. For the case where only the relative changes in the diffusion coefficients are needed, the logarithm of the calculated fractional gain in fluorescence intensity is plotted against $\log(t/\tau)$, where $\tau=\lambda_p^2/4D$, for various values of $I_0 \alpha T$ to produce a family of curves. The experimental data will superimpose on the appropriate calculated curve of the same $I_0 \alpha T$ value by displacements along the two axes. The shift factor along the abscissa is simply related to the diffusion coefficients. The cure curve consists of these shift factors plotted against cure time.

Resin Transfer Molding Research Program

The final research area in Processing Science is resin transfer molding (RTM). During the past year this effort was selected for a major expansion so that a comprehensive study of this processing method would be possible. RTM was chosen as the primary focus because it was ranked by attendees at the Industry Workshop on Composite Processing as the most important fabrication method for commercial applications.

To simplify the study of RTM, the initial work will separate mold filling and polymer cure by assuming that no significant curing occurs during the filling of the mold. This is a good first approximation for many commercial applications. Ultimately, however, the program will be extended to consider simultaneous cure and mold filling since the desire for increased processing speed will move the field in this direction.

The initial effort in the RTM program addresses mold filling in three ways: (1) computer modeling studies of the fluid flow, (2) development of theoretical formulations which provide the physics for improved models, and (3) experimental research to generate the input parameters necessary for flow modeling and the results required for verification and discrimination of flow models. Each of these areas is discussed below.

Modeling: In the current modeling work for RTM, two computer programs which simulate the isothermal flow of a Newtonian fluid through a two-dimensional porous media have been constructed. A finite element technique is used to solve the governing equations in both cases. In the first simulation, the flow is modeled using D'Arcy's Law which is given by

$$v=\frac{K\cdot\nabla P}{\mu}$$

where

$$\nabla=\frac{\partial}{\partial x}+\frac{\partial}{\partial y}$$

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

The program predicts flow front vs. time and the pressure distribution during mold filling. Some sample results of flow front vs. time for two cases of highly anisotropic porous media are shown in Figure 1.

The simulation shows that the flow patterns are highly sensitive to the relative degree of fiber orientation. The results on the left are for a case where the fibers are oriented in the direction of the incoming flow, while the results on the right are for a case where they are oriented transverse to the incoming flow.

In the second simulation, the flow is modeled using the more complex Brinkman-volume averaged momentum equation (BVAME), which is given by

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

where

$$\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}$$

The BVAME differs from D'Arcy's law in that the second-order derivative terms for the velocity are retained. The main advantage of including these terms is that it provides more accurate modeling of the details of the velocity field near boundaries. Such details can be very important for the design gate and vent locations, the treatment of flow at edges, corners or inserts, and the analysis of flow between or along regions of different permeability.

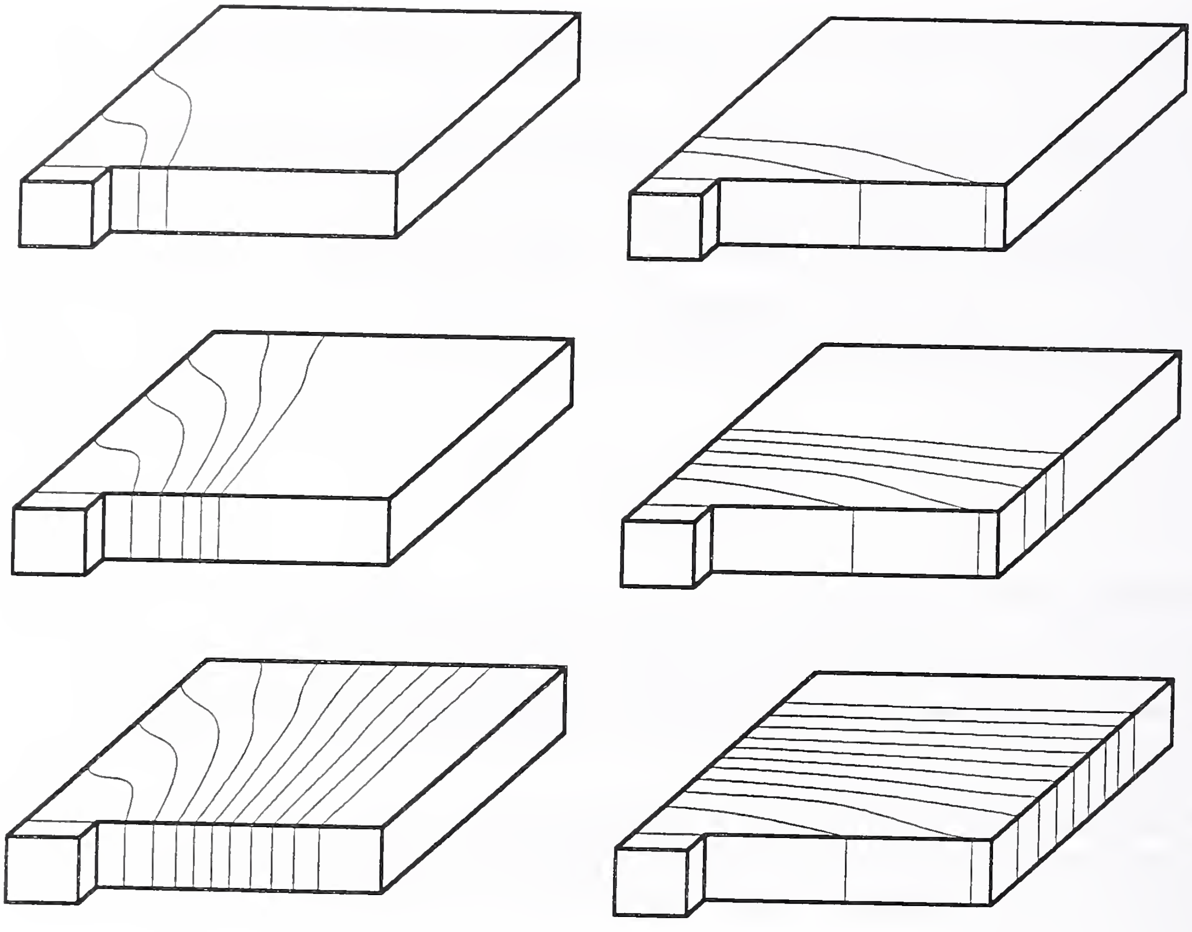

Figure 1 Some sample results of flow front vs. time for two cases of highly anisotropic porous media are shown. The results on the left are for a case where the fibers are oriented in the direction of the incoming flow, while the results on the right are for a case where they are oriented transverse to the incoming flow.

In future work, the D'Arcy's law simulation will be extended to cover three-dimensional flow, non-isothermal flow with chemical reaction, and possibly, the mold filling of (particle) filled systems and viscoelastic materials. The Automotive Composites Consortium is cooperating in the development and testing of these simulations.

Theory: An improved model for describing fluid flow in RTM was developed. The model is based on the recognition that the preforms generally used in RTM are woven not from individual fibers but from fiber bundles. Consequently, two competing flow processes occur simultaneously: the macroscopic flow of the resin through the preform and the impregnation of the individual fiber bundles which make up the preform (see cover diagram). The effect of fiber bundle impregnation is modeled by treating the fiber bundles as fluid sinks. Mathematically, this is accomplished by modifying the continuity equation in the following way

$$\nabla \cdot \mathbf{v} = Q(\mathbf{x},t-\tau,P-p_f)$$

where the sink strength, $Q(\mathbf{x},t-\tau,P-p_f)$, is a function of the position $\mathbf{x}$, the elapsed time since engulfment, $t-\tau$, and the pressure difference outside and inside the fiber bundle, $P-p_f$.

This model explains three important experimental observations. First, it predicts that the competition between the two flow processes during the filling of dry preforms leads to a reduction in the value of the mold inlet pressure relative to the non-absorbing case, thus giving the medium an effectively higher permeability. This effect is accompanied by a transient phenomenon in which the mold inlet pressure continues to rise even after the flow front has reached the outlet of the mold. Eventually, the pressure reaches the expected, non-absorbing value (see cover diagram). Finally, since flow into the bundles is slow, the model predicts this as a major source of voids. The calculations also allow for the estimation of void volume in the cured part. This model can be incorporated into either the BVAME or D'Arcy's law formulation by using the modified continuity equation. Future work will be done to pursue this idea.

Experiments: During the past year, the experimental program has emphasized the design and construction of facilities and the initiation of permeability measurements. The facilities now include a one fluid pressure pump and molds for one dimensional flow to evaluate the permeability of preform materials. This equipment will be a central element in the RTM facility and will provide the ability to investigate the effects of preform structure and orientation (with respect to gravity), and of fluid rheology on the mold filling behavior. Simple flow visualization at both a macroscopic and microscopic level can be performed to detect phenomena such as void formation, fiber wash and edge effects, which are critical issues in RTM. For more complex flow experiments a larger mold has been built and others are planned. In addition, a special pumping system has been ordered. A unique feature in this RTM pump is the capability for a large shot size (3.5 ℓ) so non-pulsating flow can be achieved for virtually all the planned flow experiments. Together with the modeling effort, this pump will be used to investigate problems such as multi-directional flow, flow around objects, and flow through complex preforms. The pump also has the ability to mix and inject two component material systems so it will be available for future studies with curing polymers. Plans for instrumented molds are also under development so fiber wetting and resin curing can be monitored inside the preform. One example is the use of optical fibers to perform spectroscopy inside the mold.

Using the equipment described above, experiments have been conducted during the past year to determine the permeabilities of saturated woven glass fabric as a function of material orientation relative to the fluid flow direction. In addition, the flow front position and mold inlet pressure were measured as a function of time, using flow visualization technology. The permeability of the unsaturated porous media was extracted from the time varying front velocity and mold inlet pressure for comparison with the saturated permeability values. As expected, the unsaturated permeability was larger than the saturated permeability. The data on front position and mold inlet pressure, as a function of time, also compared favorably with calculations made using the model described above for a heterogeneous porous media.

Results from the experimental program are being used in a cooperative program with General Electric (GE). GE is performing measurements with the same materials but using a two dimensional flow cell. A comparison will make it possible to estimate the degree to which the calculated permeabilities are independent of test method. A second objective is to verify that models can successfully predict flow in any direction using permeabilities measured in just two perpendicular directions. This is a critical assumption in all models.

MICROSTRUCTURE CHARACTERIZATION

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The major thrust in this Task is to characterize the microstructure in a composite so this structure can be related to processing and performance. The projects address one or more of four areas: the resin, the fiber, the distribution of the fibers in the resin, or the glass-resin interface region. During the past year, there were two projects on resins and one in each of the other three areas. The first project is a continuation of the investigation of the molecular network structure in thermoset (TS) polymers with an examination of a new generation of TS resins. The second is an extension of the study of crystallinity in the partially crystalline thermoplastics used in composites to include the effects of the fiber surface on crystallinity in the interface region. The structure and thermodynamics of polymer gels which can be processed into high strength fibers are under investigation. The distribution of the rigid rod molecule within a model molecular composite is under study. Finally, a new project has been initiated to study the interface between the polymer matrix and glass using neutron reflectivity. This program has just been initiated so results are not yet available. Each of the other four efforts, however, will be summarized below.

Characterization of Network Structure in Cyanate Ester Resin

Cyanate esters are a new class of resins whose performance exceeds that of epoxies which are today's baseline materials for polymeric composites. These esters are tougher, absorb less water, and have lower dielectric constants and higher T_g than conventional epoxies. In addition, a large variety of thermoplastics can be melt blended into the esters to further enhance their performance and processibility. The curing mechanism for cyanate esters is the formation of substituted triazine rings from the cyclic addition of three cyanate groups. The triazine ring, composed of three carbon and three nitrogen atoms (no hydrogen), possesses a rather high neutron scattering cross section; hence, the junctions of the molecular network in these esters are inherently labelled for neutron scattering. These resins are good candidates to extend the network characterization technique previously developed in the composites program.

Bisphenol A dicyanate (BADCY) was chosen for this study due to its simple chemical structure. A series of neutron scattering measurements using BT-6, a 3-axis diffractometer, were conducted as cure proceeded. The most conspicuous change in the scattering intensity was the evolution of a maximum at $q = 0.5\text{Å}^{-1}$ where q is the scattering vector. The presence of this maximum is consistent with the notion of triazine formation during cure. In addition, the position of the maximum indicates that the average intra-network distance between two adjacent triazine rings is 12.6Å. To explain the volume expansion observed in the later stages of the cure for these materials, some researchers have proposed the formation of many tight loops in the network structure during this period. The presence of these tight loops would result in additional intra-network correlation among the triazine rings. This, in turn, would manifest itself as additional scattering maxima in the high q region. Such a conjecture is not supported by the neutron scattering results obtained so far. On the contrary, the observed results can best be accommodated by an open tree model for the BADCY networks.

Further neutron measurements are planned. Experiments on deuterated BADCY monomer will be used to supplement the neutron results of protonated samples, especially in the high q region. This may help to unravel the observation of volume expansion in the post-gel stage of cure.

The Nucleating Effect of Carbon Fibers on the Crystallization of Polymers in Composites

Enhanced nucleation of spherulitic growth at the carbon fiber/polymer interface, as compared to nucleation in bulk polymer, results in the manifestation of transcrystallization at the interface due to the simultaneous initiation of spherulites from closely spaced sites along the fiber surface. Differences in the intrinsic ability of various types of commercially available 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 the optimization of the fine structural characteristics of the matrix for the intended uses. The studies of these effects have focused on two resins: poly(phenylene sulfide) and nylon 66.

Poly(phenylene Sulfide): The influence of various commercially available polyacrylonitrile-based (ex-PAN) and pitch-based (ex-Pitch) carbon fibers on the nucleation of spherulitic crystallization in poly(phenylene sulfide) under isothermal conditions in the range 265-280°C, has been investigated. The fibers are listed in Table I in order of increasing tensile modulus. With the exception of the AU4 and HMU all the fibers had been subjected to undisclosed

Table I

List of Carbon Fibers

Fiber	Tens. Modulus (GPa)	Tens. Strength (GPa)
(ex-PAN)		
Magnamite		
AS4	235	3.79
AU4	(235)	(3.79)
IM7	283	4.71
HMS4	338	2.48
HMU	380	2.76
(ex-Pitch)		
Thornel		
P75S	517	2.07
P100S	758	2.19
P120S	820	2.05

proprietary surface treatments in manufacture. Such treatments are usually of an oxidative nature. None of the fibers had any surface sizing except for the HMU. The polyvinyl alcohol sizing applied to the latter was extracted in boiling water for the purposes of the present study.

The surface treated and the untreated low modulus fibers (AS4, AU4) as well as the intermediate modulus (IM7) fiber did not induce any transcrystallization of the poly(phenylene sulfide). Transcrystallization was induced by all the higher modulus fibers including, it should be noted, both the surface treated and untreated ex-PAN based fibers (HMS4, HMU). These results, which extend some findings of earlier studies by others, evidence a trend connecting the nucleating ability of the fibers with increases in tensile modulus. Enhancement of both the graphitic character and the size of the constituent crystallites, as well as a narrowing of deviations from the preferred orientation of (002) planes parallel to the fiber axis, are well documented factors which underlie increases in the tensile modulus of carbon fibers. Increases in crystallite perfection, which are characterized by decreases in the spacing between the constituent graphitic layers [i.e. the (002) spacing], and improved crystallographic registry between the stacked layers, are induced by subjecting the fibers to higher temperatures in the final stages of processing. Available data indicate that such changes in crystallite perfection would be induced in the low modulus and intermediate modulus fibers used in the present study by annealing them at temperatures in the range 1000°C-1500°C. Accordingly, an immediate objective of future investigations will be the determination of whether annealing at these temperatures (initially in the absence of tension) will cause the AS4, AU4, and IM7 fibers to induce the transcrystallization of the poly(phenylene sulfide). In addition to the monitoring of changes in crystallite perfection, changes in crystallite orientation as well as fiber surface texture will be monitored in conjunction with these experiments.

Nylon 66: Nylon 66 crystallizes in the form of positively birefringent spherulites when cooled after being held in the molten state at temperatures above about 270°C. However, when the polymer, initially crystallized in the positively birefringent spherulitic form at high undercoolings (e.g. crystn. below 200°C), is rapidly heated and held isothermally at a temperature in the range 255-265°C, it melts and recrystallizes at that temperature in the form of negatively birefringent spherulites. Both the a-axis and the hydrogen bonded sheets are oriented preferentially parallel to the radius in positively birefringent spherulites, whereas the hydrogen bonded sheets are oriented preferentially normal to the radial direction in negatively birefringent spherulites. Under conditions in which positively birefringent spherulitic crystallization usually occurs, high modulus ex-PAN fibers have been reported to enhance the nucleation of such spherulites and induce transcrystallization in that form at the fiber polymer interface. In recent experiments in this laboratory a similar result was obtained using the high modulus ex-Pitch type of carbon fiber 100S (Table I). The same type of fiber however did not induce any transcrystallization under the crystallization conditions which yield negatively birefringent spherulites. Similar experiments are underway to determine whether this spherulite-structure related difference in the ability to induce transcrystallization in Nylon 66 is characteristic of high modulus carbon fibers more generally. In any event the present result is intriguing. It suggests that the interactions at the polymer melt/fiber interface are epitaxially specific, being compatible with the orientational characteristics of propagation or growth in positively birefringent spherulites, but not so in the case of negatively birefringent ones.

Microstructure of Poly(vinylalcohol) Gels

Fibers with high modulus and strength can be produced via the gel-spinning process and poly(vinylalcohol) (PVA) is one of the primary candidates for such a process. Since the structure of the gel affects the final properties of the fiber, it is important to have a good understanding of this structure, how it is formed, and how it relates to fiber performance. Such knowledge is invaluable in efforts to further improve the fibers.

The structure of aqueous PVA gels with and without adding borate ions (hereafter referred as alkaline gel and hydrogel, respectively) were investigated using small angle neutron scattering (SANS). The correlation length å, which is a measure of the wavelength of concentration fluctuations, was estimated from SANS results. The value of å showed a modest temperature dependence; it decreased with increasing temperature. The scattering intensity, I(q), within the range $0.3 < q\mathring{a} < 10$ for the alkaline gel measured at a variety of temperatures could be superimposed onto one master curve by employing these reduced variables, $I(q)/\mathring{a}^3$ and åq, where q is the magnitude of the scattering vector. This indicates that the PVA clusters can be described adequately by a single characteristic length over a broad temperature range embracing the sol-gel transition temperature, and the internal structure of the cluster is homogeneous down to a size scale of 0.1å. For the hydrogel, the superposition was valid only in the region $0.3 < q\mathring{a} < 2.0$. At high values of q where $2 < q\mathring{a} < 10$, an increase in the mass fractal dimension with lower temperatures is evident. This can be explained by the local consolidation of the polymer chains in hydrogels. Such a consolidation is absent in alkaline gels due to the presence of interchain didiol-borate complexes. For both the hydrogel and the alkaline gel, the master curve follows the Lorentzian form closely.

In alkaline PVA gels a clear-opaque-clear transition was also observed upon the addition of boric acid. The threshold concentration of boric acid depends on the polymer content as well as the concentration of added salt (NaCl). Such a transition can now be understood in terms of a Flory-Higgins type theory supplemented with a polymer-ion complex equilibrium consideration.

The hydroxy groups on a PVA chain can react with boric ion and form monocomplexes which give rise to polyelectrolyte effects. In addition, a monocomplex group can further react with a neutral chain and form dicomplexes which constitute the cross-link points in alkaline gels. The concentrations of both the monocomplex and the dicomplex are in chemical equilibrium with the boric concentration. The equilibrium constant, however, is a function of the cross-link density, Debye screen length and the solvent power. By combining all these effects via a mean field approach, the observed clear-opaque-clear transition can be shown to coincide with the theoretically predicted coil expansion-collapse-expansion transition.

Characterization of Microstructure in Molecular Composites

In a molecular composite, rigid rod molecules are dispersed in a matrix of a flexible polymer, and thus individual molecular rods act as the reinforcing fibers. Molecular composites have the potential to combine the performance of a conventional composite with the processing flexibility of short fiber composites or even simple polymers. Moreover, they retain excellent properties at high temperature. In an ultimate molecular composite, each molecular rod should be completely surrounded by flexible polymer molecules. There is, however, a strong tendency for the rigid rod molecules to aggregate and separate on a larger scale. Since aspect ratio of the reinforcement is critical to performance, this badly compromises properties.

Until recently, work in this area was hindered by the lack of test methods to directly measure the degree of dispersion of the rigid molecules. As reported two years ago, however, a new technique based on the combination of small angle X-ray and neutron scattering was developed in the composites program to address this problem. This method was first applied successfully to a polyquinoline multiblock copolymer composed of rigid rod blocks and flexible blocks. The result suggested a somewhat disappointing degree of dispersion.

Now the method has been applied to a new set of polyquinoline blends of high molecular weight prepared by Prof. J. K. Stille of Colorado State University before his untimely death. The results indicate that these blends are partially segregated but with a correlation length of 115Å. This is much less than the radius of gyration for the rigid rod molecules. One possible explanation is that the rigid rod phase has the shape of a thin cylinder, and the value of the correlation length reflects the average lateral dimension of this cylindrical geometry. Quantitative analysis of the data further suggests that the local compositional fluctuation of the rigid rod (and the flexible chain) is 20% from its mean value. This indicates a state of dispersion that is superior to that previously obtained for such materials.

LAMINATE PROPERTIES

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The objective in the Laminate Properties task is to determine the properties for simple composite structures and relating these results to the microstructure of the composite and the behavior of the individual constituents. The projects fall into three areas: test method development, resin failure mechanisms, and modeling. The current studies include four projects related to test method development. In addition, staff in the Polymer Division are advising and assisting a number of groups with test method development. These groups include: ASTM, VAMAS, and the Automotive Composites Consortium. In the area of resin failure mechanisms, there are three active projects. Finally, much of the work in modeling is supporting research in the other two areas. One additional project, however, has led to development of an analysis for the initiation of certain kinds of delamination. The results of work on these projects are briefly discussed below.

Test Method Development

Of the four projects in this area, the first is a continuation of previous research seeking to utilize tests on thin adhesive bonds as a means to help understand composite delamination. Then there are two projects to investigate measurement methods for fiber matrix interface strength. Finally, work is being done in support of the State Department to formulate test methods for evaluating laminated materials of interest to them.

Thin Adhesive Bond Test for Composite Delamination Resistance: Previous work at NIST had shown that the interlaminar fracture toughness of laminated composites can be fairly well predicted by testing the matrix phase in-situ as an adhesive bond if the bond thickness is made the same as the effective thickness of the interlaminar resin-rich zone in the composite. Thus, the adhesive bond test may provide a viable alternative to fracture toughness testing of the full-fledged composite structure. Unlike in mode I, however, the fracture of adhesive bonds under shear loading is associated with extensive matrix plasticity far down the length of the adhesive bond. Understanding the development of this plastic zone during load is thus the key to understanding the resistance of the material to delamination growth.

The evolution of the plastic zone at the crack tip during load, as well as the detailed distribution of shear strains within this zone, were monitored in real time with the aid of a video camera. An optical microscope with a large working distance was attached to the camera, thereby resulting in a magnification in excess of 200. Prior to loading, the bondline region around the crack tip was polished, and a line pattern etched on the sample surface to facilitate strain measurements. In this way, the full shear strain distribution along the plastic zone could be ascertained starting from the initial loading and ending at catastrophic crack propagation. Preliminary test results have indicated that the length of the zone as well as the strain to failure are significantly affected by the bond thickness. The zone length exceeds the bond thickness by as much as several orders of magnitude when the latter is decreased to a value resembling that of the interlaminar resin rich layer in a composite.

Comparison of Methods to Assess Fiber-Matrix Interface Strength: The behavior of the fiber-matrix interface in composites has become an increasing concern because the pace of introduction of new resins and fibers makes it impossible to use the trial-and-error approach for optimizing the interface. Moreover, as the use of composites increases, long term durability becomes more important and the interface or interphase can have a major influence on durability. Even though a number of promising techniques have been proposed, there is no well understood and widely accepted method for characterizing interfacial strength. To help address this issue, a joint program with Michigan State University (MSU) has been initiated in order to evaluate and compare results from commonly used single fiber tests (fiber pull-out, and fragmentation or critical length measurement) and newly developed composite methods (fiber indentation and thermo-acoustic tests). The last technique is a new method developed in the composite program and is described below. By combining the expertise and equipment at NIST and MSU, all four tests are included in the work. The comparisons are performed with a series of carefully prepared samples where the fiber and matrix are unchanged while the fiber surface treatment is varied to change the interface strength.

A Thermo-acoustic Test for Fiber-Matrix and Interply Adhesion: Although a number of test methods show promise for measuring the fiber-matrix interface strength, all require specially prepared test specimens. Consequently, there is a need for a test which can be applied to actual composite parts and prepregs. A new technique that meets these requirements is currently under development. This thermo-acoustic technique can be used to determine the bonding strength between fiber and matrix resin and between layers (laminae) in the composite. The method uses a laser to locally heat a region on the composite's surface, and the large differences in thermal expansion between the fibers and the polymer introduces high stresses across the interface which cause debonding. Between laminae, debonding results from dissimilarities in the principal direction of the thermal expansion as a consequence of differences in the orientation of the fibers in the neighboring layers. The debonding events produce sound waves that can be monitored with acoustic sensors. Debonding between the fiber and matrix in the first layer occurs immediately upon heating while inter-lamina debonding is delayed by the time needed for the thermal wave to propagate through the top lamina and reach the inter-laminar region. It is therefore possible to differentiate the fiber/matrix debonding and the inter-lamina debonding by monitoring the time spectrum of the acoustic emission and by controlling the heating duration. The thermal power level needed to initiate the debonding as well as the characteristics of the acoustic emission, e.g., the level of acoustic energy and the number of acoustic events, correlate well with the interface strength; hence, both serve as sensitive indicators of interfacial strength. This has been demonstrated with experiments using two graphite fiber/epoxy composites that differ only in that the fibers for one sample were surface treated to promote adhesion. Single-filament pull out tests have shown that the interface strength of the sample made with the treated fibers is about twice that of the sample made with the untreated fibers. As shown in Figure 2, the thermo-acoustic results indicate that (1) the laser power threshold needed to initiate an acoustic signal in the composite with untreated fibers is two watts compared to four watts for the sample with the treated fibers; and (2) the acoustic energy level is higher for the untreated fiber sample compared to the treated fiber sample for all the laser power levels tested.

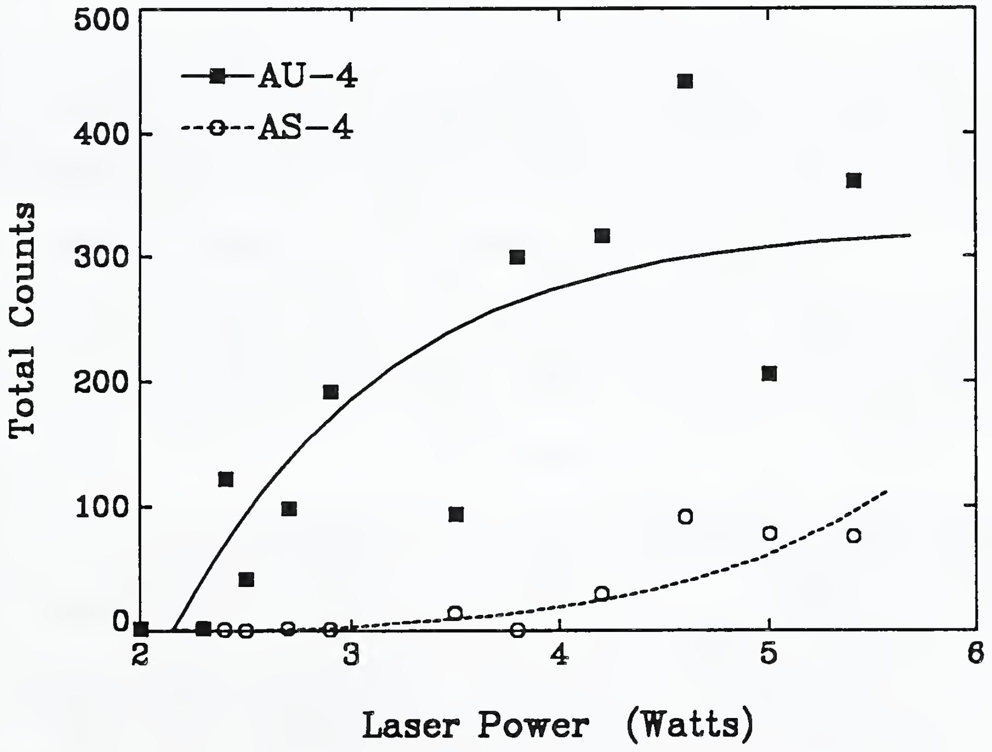

Figure 2 Total acoustic emission events as a function of laser power for samples made with fibers having a surface treatment to promote adhesion (AS4) and for samples made with fibers that have not had this surface treatment (AU4).

Test Methods for Passport Laminates: The composites program has developed considerable expertise in the evaluation of adhesion in laminated structures. This knowledge is being used to assist the State Department in developing test methods to determine bond strength and other characteristics for the laminated page in passports. This page contains the identification data and photograph and is protected by a plastic layer laminated over the top surface. During the past year, procedures were developed or adapted to evaluate the bond strength between the plastic layer and the passport page and the durability of this structure. These tests were included in a procurement request for new materials and used to evaluate the samples submitted. The program also has the long term goal of assisting the State Department to identify and test the next generation of laminating materials. In this regard, a survey was conducted to find materials with potential, and the resulting samples are now under evaluation. This work will provide both data on the strengths and weaknesses of these systems and the information necessary to make what ever modifications are necessary to update the evaluations procedures.

Failure Mechanisms

The first of the three projects in this area is characterizing the behavior of the crack-tip deformation zone prior to and during fracture for bulk samples of composite resins. The second is studying both the basic mechanical properties and the crack-tip region in geometries that simulate the constraints present when the resin is in a composite or an adhesive bond. The third program involves the physical aging of composite resins and is part of a larger program on this subject in the Mechanical Performance Group. The details of this work are covered in the Mechanical Performance Group's section of this report. Finally, the past success in increasing the toughness of thermoset resins by introducing heterogeneity into the molecular network structure continues to be of interest. A paper describing this work was published during the past year. Since the results are consistent with those reported in last years Annual Report, however, they will not be presented here.

Micromechanics of Fracture in Toughened Resins: Previous studies have shown the importance of the crack-tip deformation zone in toughening of resin systems for high performance composites and adhesives. To characterize the formation and growth of this zone and its relationship to the crack growth process involved in fracture, video tape recordings were made through a microscope focused on the crack-tip region during loading. A series of rubber-toughened epoxies with fracture energies ranging from 0.2 kJ/m^2 (no rubber) to 5.0 kJ/m^2 were examined. The results show that increasing toughness is associated with not only increasing size of the deformation zone at the failure point but also changing growth characteristics of the zone and the crack. Obtaining such information is a critical step in developing an understanding and predictive capability for the fracture of these toughened materials.

The Role of Yielding in Composite Resin Failure: Polymeric materials are widely used in a variety of technological applications such as traditional adhesive bonding, composites, electronic packaging, and protective or functional coatings. When a damage tolerance analysis is performed for such applications, it is generally assumed that the mechanical properties of the constrained film or bond are the same as those of the unconstrained or bulk material. Recent experimental work at NIST and elsewhere, however, has shown that this assumption may be critically erroneous. For example, tests on thin-bondline adhesive systems demonstrated that the adhesive fracture energy under shear loading may be as little as a small fraction of the bulk toughness. To help understand this effect, the present research is determining the mechanical properties and yield behavior for materials constrained to a thin layer between rigid substrates. The properties are measured from the early stages of elastic deformation and up to final rupture. This thin adhesive bond geometry is used to simulate the constraint that is present in all of the applications cited above.

The test configuration is a napkin ring torsional specimen which leads to essentially pure shear deformation in the adhesive layer over the entire spectrum of deformation. This test configuration eliminates the complex tri-axial state of stress which usually characterize the more commonly used tensile napkin ring test or shear lap test configuration. Preliminary test results on a toughened epoxy system have shown that while the yield stress is only slightly affected by the layer thickness, the failure strain may change by a factor of more than ten as the thickness is decreased from a value which gives bulk behavior to a size corresponding to the effective thickness of the interlaminar resin-rich layer in composites. This study is currently being extended to include epoxy matrices covering a wide range of toughnesses.

Modeling Stress Concentrations that Generate Delaminations

One cause of composite delamination is the stress concentrations (or stress singularities) that can be generated at free edges when the composite is under load. Although studied for some years, the exact nature of these singularities is not clearly established for all conditions.

Recent investigations have shown that a logarithmic singularity may be present at a free edge irrespective of the conditions on the boundary remote from the singular point. This is in contrast with the r^δ type singularity, which may exist at the free edge of any laminate. The parameter r indicates distance from the stress concentration point while the exponent δ indicates the strength of the singularity. Although the r^δ singularity is much stronger than the logarithmic singularity and, if present, can be primarily responsible for the onset of delamination, the role of the logarithmic singularity should not be ignored. Therefore, it was decided to examine relative importance of the two singularities, their interaction and their influence on stress distribution. The enriched finite element technique was used.

Numerical results have been obtained for three different composite laminates: (45°/-45°), (90°/15°) and (-15°/75°). Various solutions exists for the (45°/-45°) lay up which does not have any logarithmic singularity. Consequently, this case has been selected as a benchmark problem. For the (90°/15°) lay up a strong logarithmic singularity should exist. Davet and Destuynder seem to suggest no other (than logarithmic) singularity is present in the case of a -15°/75° lay up. However, our eigenvalue solution gives $\delta=-0.0303$, which clearly shows a singularity of the type r^δ.

In a similar way, other results for this study show that incomplete theoretical information on the number and/or the type of the singularities can significantly distort the picture emerging from the calculations. Such incompleteness also affects various parameters related to the singularities, such as the stress intensity factors. In addition, this analysis suggests that, in terms of accuracy and performance, the enriched finite element technique parallels other powerful methods, including the hybrid stress method.

POLYMER BLENDS AND SOLUTIONS

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

The importance of polymer blends is evident from their ubiquitous presence in consumer products in recent years. These products include automobile and airplane parts, business machines, appliances, furniture, packaging materials, housewares, toys and clothing materials. Blending and alloying technology has significantly expanded the number of grades and types of plastics available, providing a wide variety of property profiles for applications needs. The world wide consumption of polymer blends and alloys is expected to increase from 1.6 billion pounds in 1989 to 2.4 billion pounds by 1994, at an annual growth rate of over 8%.

Polymeric 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 material properties, such as mechanical properties, flame retardancy, processibility, and barrier properties can be improved through blending. High cost 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 which will allow an extension of the study to structures of larger size is under construction.

FY 90 Significant Accomplishments

- Phase diagrams of bulk polymer blends of deuterated polystyrene/poly(vinylmethyl ether) and deuterated polystyrene/polybutadiene have been studied by simultaneous SANS and viscosity measurements at various temperatures and shear rates. The suppression of the concentration fluctuation modes has been observed as a function of shear rate. This gives fundamental physical understanding of the mechanism of shear induced miscibility of polymer blends.

- Spinodal decomposition of a hydrogen bonded binary blend which consists of a polystyrene with 1.5 mole % of p-(1,1,1,3,3,3, hexafluoro-2-hydroxy-isopropyl)-α-methylstyrene co-monomer and a poly(butylmethacrylate) has been studied. This is the first time the spinodal decomposition kinetics of a miscible polymer pair which is stabilized by strong interacting monomer pairs has been studied in detail. Not only have new phenomena been observed, but also important technical applications may be derived from this study.

- The 10-meter SAXS facility had active outside users which include: 7 industrial laboratories, 2 academic institutions, and 3 other federal laboratories. Activities of users include: structure/property/processing relationships in blown polyethylene films, microstructure in polypropylene, polyester and nylon fibers, morphology of amorphous/semicrystalline nylon blends and properties of carbon aerogels.

- A digital image acquisition and analysis system based on a Zeiss optical microscope and a Silicon Graphics computer has been assembled. The late stage phase separation of polystyrene/poly(vinylmethylether) is being studied. Preliminary results suggest phase inversion in the late stage phase separation of a 40/60 blend of PS/PVME. Polystyrene/ poly(2-vinylpyridiene) system is also being studied.

- Theory for calculating the entropy of a polymer chain (with excluded volume) immersed in an anisotropic matrix has been developed. This theoretical approach allows us to solve many important problems such as: 1. The collapse transition of a polymer in a field of oriented rods; 2. Polymer dissolved in block copolymers; 3. Polymer dissolved in a stretched rubber; 4. Self-consistent treatment of a system of stretched molecules and 5. Dimensions of polymer molecules in bulk polymer.

- A standard reference material, SRM-1476a was recertified for melt flow this year. Also the certification of a polypropylene with a melt flow rate of about 11g/10 min is currently being carried out. 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. This work is supported by a group of polymer companies represented on the ASTM subcommittee.

EXPERIMENTAL

C. C. Han, R. M. Briber, J. D. Barnes, B. J. Bauer, C. M. Guttman, J. R. Maurey, A. I. Nakatani, P. H. Verdier, D. A. Waldow, S. Sakurai[1], H. Hasegawa[1], T. Hashimoto[1], H. Kim[2], Y. Takahashi[3], Y. Matsushita[3], A. Takano[4], M. He[5], Y. Feng[5], M. Jing[6], S. Wu[6], E. Gholz, Pei Sung[7], Q. Tran-Cong[8]

[1]Kyoto University, [2]Korea Institute of Science and Technology, [3]Nagoya University, [4]Tokyo Institute of Technology, [5]East China University of Chemical Technology, [6]Fudan University, [7]FDA, [8]Kyoto Institute of Technology.

Shear Stabilization of Critical Fluctuations in Bulk Polymer Blends Studied by Small Angle Neutron Scattering

The small angle neutron scattering (SANS) technique has been used to study the concentration fluctuations of binary polymer mixtures under shear. Two polymer systems, deuterated polystyrene/ poly(vinylmethylether) and deuterated polystyrene/polybutadiene, have been studied as a function of temperature and shear rate. Due to the small wavelength of the incident neutron radiation compared with light, the shear dependencies of concentration fluctuations in the one-phase region and in the strong shear limit have been obtained from the q dependence of the scattering structure factor for the first time. From a detailed analysis of the scattering structure factor S(q) a crossover value of the wave number q_s has been obtained as a function of temperature and shear rate. This crossover wave number represents the inverse of the lowest fluctuation mode which is not affected by shear. The temperature, viscosity, and shear rate dependence of this experimentally determined q_s agree well with a simple rotatory diffusion model and also the dynamic mode-mode coupling analysis of Kawasaki and Ferrell. The apparent spinodal temperature as a function of shear rate is shown to be consistent with the prediction of Onuki.

Chain Dimension Determination of Deuterated Polybutadiene by Small-Angle Neutron Scattering on the Basis of Random Phase Approximation

The chain dimension of a deuterated polybutadiene (DPB) which is mixed in the matrix of a protonated polybutadiene was measured by the small-angle neutron scattering technique. The Kuhn's statistical segment length for this particular DPB with 20% 1,2-unit, 36% cis-1,4-unit, and 44% trans-1,4-unit was determined by two methods, the Zimm's method and the random phase approximation (RPA) calculation analysis. The most reliable estimate of the statistical segment length for this DPB was 6.88Å, the value obtained by the latter method.

Spinodal Decomposition in a Hydrogen-Bonded Polymer Blend

The spinodal decomposition of a hydrogen-bonded binary blend which consists of a polystyrene with 1.5 mole % of p-(1,1,1,3,3,3 hexafluoro-2-hydroxy-isopropyl)-α-methylstyrene co-monomer and a poly(butylmethacrylate) has been studied. This system has a LCST with an asymmetrical phase diagram. The critical point of the system does not coincide with the temperature minimum of either the spinodal or the cloud point curves. The kinetics follow the Cahn-Hilliard-Cook model for early spinodal decomposition and a self-similar mechanism for late stage coarsening for most cases. For cases of a shallow quench and cases close to glass transition temperature, double peaks have been observed during spinodal decomposition which suggests that a second or an alternative relaxation mechanism may be dominating the coarsening process. A special procedure has been developed to measure the cloud point for this system which should be applicable for any polymer blend system which has a cloud temperature close to the glass transition temperature.

Small Angle Neutron Scattering and Light Scattering Study on the Miscibility of protonated Polyisoprene/Deuterated Polybutadiene Blends

Binary mixtures of protonated polyisoprene and deuterated polybutadiene with particular microstructures exhibit an LCST-type phase behavior. Small-angle neutron scattering (SANS) and time-resolved small-angle light scattering (SALS) techniques were employed to study the static and dynamic phase behavior of the mixtures. From the static study by SANS, binary interaction parameters, χ, and the phase diagram were obtained. The spinodal temperature at the critical blend composition obtained by the analysis of SANS profiles from the single-phase state were in good agreement with that obtained by the time-resolved SALS measurement. The component polymers are prepared by living anionic polymerization, and hence have well-defined molecular characteristics. Therefore, this system is considered to be an excellent polymer mixture system to study the relationships between static and dynamic phase behaviors of the polymer mixture and the molecular parameters such as molecular weight, polydispersity, microstructure, etc.

Temperature Dependence of Probe Diffusion in Bulk Polymer Matrices

The temperature dependence of the diffusion coefficients for a photobleachable molecular probe in various polymer matrices has been studied using forced Rayleigh scattering (FRS). The probe molecule, a cyclophane derivative, is demonstrated to be a suitable probe for the FRS experiment due to the characteristics of the photodimerization reaction. The dynamic range of the FRS experiment enabled the measurement of the self diffusion coefficients over a range of nearly eight orders of magnitude. The temperature dependence of the self diffusion coefficients is well described by the Williams, Landel, Ferry (WLF) equation for all the polymer matrices studied. In addition, the data from the individual polymer matrices can be shifted to construct a universal curve which is also well described by the WLF equation.

Image Analysis of the Late Stage Coarsening Dynamics of Polymer Blends

A digital image acquisition and analysis system based on a Zeiss optical microscope and Silicon Graphics Computer has been assembled. The first data is being obtained on the polymer blend system polystyrene/poly(vinylmethylether) (PS/PVME), a compatible blend with a lower critical solution temperature. Temperature jump experiments from the single phase region into the two phase region are being preformed. The earliest stages of the phase separation occur at a length scale too small to observe with the optical microscope, but as the domains coarsen they become observable. The emphasis of this work will be the late stages of phase separation where the domains form isolated droplets, rather than an interconnected spinodal structure. This blend appears to show interesting behavior at a composition of 40/60 PS/PVME where the blend begins to phase separate with the PVME as the continuous phase, but then the phase inverts to give PS as the matrix. Preliminary experiments are also being performed on the incompatible blendsystem polystyrene/poly(2-vinylpyridine). In this system, the components are dispersed by rapid solvent evaporation and then the coarsening is studied from this kinetically determined state. This system is similar to that used by industry in many cases to create multicomponent materials.

Morphology Changes in Polyurethanes Subjected to Cyclic Deformation

The behavior of polyurethanes subjected to cyclic deformation has been studied with SAXS using a new deformation stage which was built and brought into operation this year. This allows in situ deformation in the NIST 10m SAXS camera. It is known from previous work that the hard segment domain structure in polyurethanes is disrupted by deformation. Experiments have been started to examine the effect of cyclic deformation.

Protection of Archival Records

Protection of the records of the National Archives and Records Administration from atmospheric pollutants has been a matter of long time concern. This research program is a study of the protection mechanism provided by containers commonly used in protecting archival materials from atmospheric pollutants. The degradation mechanism of paper by these pollutants and the relation of the degradation mechanism to various possible storage modes are under investigation.

Measurement of the diffusion coefficient and the binding coefficient of SO_2 in the boxboard used to make archival boxes is currently underway. A model of the adsorption of the pollutant SO_2 using data previously collected on various papers has been developed and issued as a NISTIR. The model describes the time dependence and gas concentration dependence of the data by assuming both reversible and irreversible binding of the pollutant to paper as well as a saturation concentration for the reversible binding.

Studies of the degradation of newsprint and rag paper using aging experiments have been done. The aging of paper in an enclosed environment was studied in order to observe degradation products which might catalyze the degradation of the paper itself. To obtain information on the degradation products resulting from the aging process in a reasonable time, accelerated aging, aging at higher temperatures, or at higher concentration of active species, have been done.

The results indicate low molecular weight acids are formed in the aging of paper at 60°C. Further work to detect these and other products is currently underway.

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 studied by measuring the change in local swelling using a fluorescence microscope and a FTIR microscope.

Phase Behavior of Blends with Cyclic Components and the Effects of Cyclization on Diffusion in Polymer Blends

M. M. Santore, G. B. McKenna, and C. C. Han

Cyclic polystyrene (PS) was mixed with linear polyvinylmethyl ether (with both above the entanglement molecular weight) and this blend compared to one with exclusively linear components to determine the effects of cyclization on the phase diagram and on diffusion near critical conditions. (These mixtures exhibit lower critical solution temperature behavior.) Cloud point studies showed that the cyclization of one component has a stabilizing effect on the blend over a wide composition range, shifting the binodal to higher temperature by 7-8°C. This result is not predicted by Flory-type theories, but is consistent with the depressed theta temperature for solutions of cycles. Time resolved light scattering following a temperature jump into the two phase region near the critical composition facilitated the calculation of an apparent mutual diffusion coefficient and mobilities. At the critical composition (80% PVME, 20% PS for both linear and cyclic systems) the apparent mutual diffusion coefficients for the two blends exhibited nearly the same dependence on temperature relative to the spinodal temperature. The mobility calculation which accounts for the difference in spinodal temperatures, allows comparison of the two systems at any one temperature in the range of our experiments, showing that cyclics are slightly less mobile than their linear counterparts. Though the difference is significant, it is worth emphasizing that cyclization does not seem to hinder motion as much as would be expected from reptation arguments.

THEORY

E. A. Di Marzio, J. F. Douglas, C. M. Guttman, P. H. Verdier, A. Yang[1] and D. Kranbuehl[2]

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Orientation Dependent Entropies of Polymer Systems

The entropy of a polymer chain (with excluded volume) immersed in a bath of oriented fixed obstacles uniformly placed on a lattice is calculated. The obstacles are represented by aligned or partially aligned rigid-rods, or by stretched polymers of a known length and concentration. The effect of the obstacles is to reduce the number of configurations of the polymer, and to stretch the polymer in the direction of alignment. The size of the polymer increases at small concentrations of obstacles, but for large concentrations, it decreases.

These statistics permit solution of the following five problems in polymer science: [1] The collapse transition of a polymer molecule immersed in a field of oriented rigid rods. The transition behavior is now more complicated because not only volume, but also asymmetry ratio are needed to characterize the system. [2] A free polymer dissolved in a block copolymer. The block copolymer molecules are stretched and oriented; therefore they orient the dissolved polymer. [3] A free polymer dissolved in a stretched rubber. These polymers will be elongated by the stretched cross-linked rubber even though they are not part of the network. They therefore contribute to the stress-strain relation as do polymers attached at one end only to the network. [4] Self-consistent treatment of a system of stretched molecules. Applications can be made to a) rubber elasticity, b) diblock copolymers, c) polymers crowded onto a flat surface and attached at one end. [5] Dimensions of polymer molecules in bulk polymer. We should now be able to show that the shape of polymer moelcules in the bulk is the same as that in theta solvent.

Glass Temperature of Polymer Rings

The glass temperatures of four separate ring systems have been predicted and compared with experiment. They are polyvinypyridine, polydimethysiloxane, polyphenylmethylsiloxane and polystyrene. In all cases we predict the qualitative fact that the glass temperature T_g for rings rises as we lower the molecular weight while the T_g of the corresponding linear polymer falls as we lower molecular weight. Although the quantitative fit for the linear chains is satisfactory, the quantitative fit for the rings needs improvement, thereby suggesting that the configurational entropy of rings needs to be calculated more precisely. The usefulness of this work lies in the ability of the Gibbs-Di Marzio entropy theory to predict from first principles the glass temperature of all varieties of polymer systems. The glass temperature is an important processing variable.

Peeling a Hydrogen Bonded Polymer Off of a Surface

Hydrogen bonds provide a means for compatabilizing polymer blends. This suggests that a polymer molecule that is connected to its environment via hydrogen bonds should be studied. The solution is sought for the problem of a polymer molecule pulled off of a plane surface (or off of a line) to which it is attached with hydrogen bonds. The elastic entropy force pulling off the polymer competes with the energetic force zippering the segments onto the surface (or line). The energy equation of state and the force equation of state are both obtained. It is found that there is a critical force. Above this force the polymer pulls off completely; below this force the polymer zippers down onto the surface.

A hydrogen bonded polymer system mimics a cross-linked system but the cross-links consisting of 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 such a system flow no matter how small the value of the applied force? The answer to this question determines whether the compatabilized polymer system is viewed as a gel or as a liquid and is being pursued.

Characterization of Branched Polymers

Ratios of the mean dimensions of a branched polymer (star, ring, comb) in dilute solution to those of a linear polymer of the same molecular weight provide a useful means of characterizing branching architecture. A comparison is made between renormalization group calculations for these basic dimensionless ratios and experimental measurements on carefully prepared model branched polymer solutions. Variable excluded volume and hydrodynamic interaction complicate the interpretation of these dimensionless ratios in practice and conditions and properties which minimize these complications are identified.

Relaxation in Disordered Materials with Applications to Polymer Melt 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 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 crosslined network (network connectivity, entanglement interaction, finite chain volume) into a simple theory of rubber elasticity which they call the "localization model". In this model the change in the network free energy with deformation is given by

$$\Delta F(elastic)/V_o = (G_c/2)\sum_{i=1}^{3} (\ddot{a}_i^2 - 1) + G_e \sum_{i=1}^{3} (\ddot{a}_i - 1)$$

where ΔF(elastic) is the elastic contribution to the free energy of the network, V_o is the volume of the rubber sample and the $\ddot{a}_i$ are the principal extension rations ("stretches"). G_c and G_e are connectivity and entanglement contributions to the network modulus.

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 is in progress.

Dynamics of Polymer Chains

Better understanding of the dynamics of polymer chains is important to improving both the characterization and the processing of polymers. Gel permeation chromatography and intrinsic viscosity, the former the only method available at present for estimating distribution in molecular weight, are dynamical, nonequilibrium experiments which depend in part upon the relaxation of polymer chains in dilute solution. 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 both plastics and elastomers 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 elastomers, which must start with more realistic treatment of the dynamical behavior of the individual chains, 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 two areas. The first of these is a study of the effects of changing the chain move rules upon relaxation behavior, in an attempt to resolve discrepancies between results obtained by different groups of investigators using different model systems. The second is a series of studies of size and knotting effects in systems of closed-ring chains. Although these latter are primarily studies of equilibrium effects, dynamical models are needed to carry them out for closed-ring systems. The results of this work may help to explain anomalies found in experimental data on such systems.

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

We are producing two polyurethane SRM's with weight-average molecular weights and with 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 the usual commercial polyurethanes, but rather is a model compound to which the usual techniques for determining molecular weights of homopolymers can be applied. We are also developing methods for estimating compositional variation in polyurethanes, both for checking our own SRM's and for investigating the range of variation in commercial polyurethanes.

Polyolefin Melt Flow Rate Standards

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

A branched polyethylene, SRM-1476a, with a melt flow rate of 2.0 g/10 min was recertified this year. This work was supported by OSRM.

Work on the certification of a polypropylene with a melt flow rate of 11 g/10 min is currently in progress 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 Visiting Committees, during staff visits to industrial characterization laboratories, and in the responses to market surveys.
By far, the most pressing need is for calibration standards for aqueous size exclusion chromatography (SEC). For this purpose, samples of narrow molecular weight distribution are preferred.

Work has begun on the certification of two narrow molecular weight polyethylene oxides, one with a molecular weight of about 30,000 daltons and another with a molecular weight of about 120,000 daltons. The polyethylene oxide SRM's should be usable on most aqueous SEC columns without the special column conditioning. This work is supported, in part, by OSRM.

SAXS AND POLE FIGURE FACILITIES

J. D. Barnes

Digital Camera for Small-Angle X-Ray Scattering

The currently active roster of outside users includes seven industrial laboratories and two academic institutions. There are also three activities involving other federal laboratories.

Activities by internal NIST users have focused on polyurethane materials and deformation of polyethylenes.

Development work aimed at enhancing the facility's capabilities for quantitative measurements on an absolute intensity scale are proceeding on several fronts:

Efforts at developing standards for absolute intensity calibration are conducted in collaboration with workers in the NIST Ceramics Division. These workers claim that scattering measurements using a double crystal instrument at the National Synchrotron Light Source to study specially prepared glassy carbon materials provided absolute scattering cross sections. The materials are also said to be suitable for SANS measurements, so that intercomparisons among the various scattering methods should be possible.

Software that permits direct interchange of image files between the SAXS facility's VAX and other computers has been developed. Files have been successfully shared with Macintosh II and IRIS systems.

Our collaboration with Dr. Edward S. Clark has evolved into an effort to simulate the three-dimensional small-angle scattering function from simple specimens exhibiting an orthorhombic wide-angle orientation texture. The small-angle patterns from these materials also exhibit an overall orthorhombic symmetry that reflects the processing conditions that produced the specimens. Reconstruction of the three-dimensional scattering pattern should provide a means for correlating the features observed in SAXS patterns with microstructural features observed in electron microscopy. SAXS patterns collected for various specimen orientations constitute two-dimensional sections through the 3-d scattering function. The observed patterns can be compared with contour maps of the corresponding sections in the 3-d scattering functions.

Recent measurements, in collaboration with Dr. Christian G'Sell, on polyethylene specimens that have been subjected to shear deformation, have yielded SAXS patterns that exhibit monoclinic symmetry. Work is continuing to determine whether the shear process leads to a simple destruction of crystalline order or to a transformation of the crystallite orientation in the specimens.

X-Ray Pole Figure Facility

Recent work on orientation texture in semicrystalline polymers has been aimed at providing a means of simulating pole figures based on model crystallite orientation distribution functions. While the statistical literature does contain references to distribution functions for vectors on the surface of a sphere, there are no known distribution functions that possess the correct properties for describing three-dimensional distributions of rigid-body rotation angles.

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. Although no current effort is in progress on diagnostic systems, plans do include these activities for the future.

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.

A multidisciplinary effort on the effects of microwave generated gas plasma sterilization treatments on medical and dental instruments may result in improved health care delivery in the future.

The partnership between the Federal Government and the American Dental Association, which extends back to 1928, was further strengthened during the past year with the establishment at NIST of a Center of Excellence for Materials Science Research, 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 will be pursued by scientists in the Dental and Medical Materials Group and the American Dental Association Health Foundation/Paffenbarger Research Center over the next five years.

FY 90 Significant Accomplishments

- Novel, highly fluorinated difunctional and multifunctional vinyl monomers were prepared based on a modification of the method used for the syntheses of analogous hydrocarbon cyclopolymerizable monomers.

- Vinyl metal carboxylate monomers based on mono-[2-(methacryloyl)oxy ethyl]phthalate were synthesized and shown to have a number of potential dental applications, e.g. as radiopacifying resins.

- Glass ceramic compositions with intrinsic tooth-like colors were evaluated for potential clinical uses.

- Results from liposome studies suggest that fragments from the enzymatic degradation of putative proteoglycan, an essential extracellular component of cartilage, are equally effective in inhibiting calcification.

- Calculations from a viscoelastic model of residual stresses in porcelain-metal strips show that surface and interfacial stresses vary inversely with the 1/7 and 1/2 power of the strip curvature; hence, unlike the result from elastic calculation, curvature is not a sensitive indicator of stress.

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

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Software implementation for the second generation automated pin-on-disc wear apparatus has been completed. The new machine permits continual exposure to food-simulating liquids during wear experiments which should advance our understanding of how environment influences wear. In addition, the original pin-on-disc wear machine has been overhauled, recalibrated and upgraded with a PC interface to increase our capabilities for wear studies. Tests are in progress to assess the reproducibility of the two machines in preparation for our participation in a round-robin wear test on commercial posterior composites sponsored by the American Dental Association.

Clinical trials of two related dental enamel bonding systems have continued. The original three-step procedure involved sequential application of ferric oxalate, N-phenyl glycine (NPG) and the diadduct of 2-hydroxyethyl methacrylate and pyromellitic anhydride (PMDM); the newer two-step method utilizes acidified NPG plus PMDM. Attempts to further improve and refine the two-step system have led to the development of analogs of NPG and PMDM that have demonstrated improved adhesion to dentin. These materials are currently being evaluated for storage stability and proper packaging.

Significant progress has continued in the development and evaluation of radiation shielding materials for protecting soft tissues from radiation damage during head and neck tumor therapy. Elastomeric materials based on microspherical metal alloys and auto-setting polysiloxanes were shown to be capable of blocking over 40% of ^{60}Co gamma rays and 10 MeV x-rays and almost 100% of the 7MeV electron beams with thicknesses of 2 cm or less of the composite.

Several new types of polymeric calcium phosphate cements were developed using tetracalcium phosphate (TTCP) and dicalcium phosphate (DCP) and water soluble polymers such as gelatin, poly(vinyl alcohol), etc. Stoichiometric mixtures of TTCP and DCP in minimal amounts of water have been shown to form hydroxyapatite. Hydroxyapatite formation also was observed from TTCP/DCP using these types of aqueous polymeric solutions. With aqueous solutions of poly(alkenoic acid), e.g. poly(acrylic acid), a competing acid-base reaction occurs involving carboxylic acid groups and TTCP. The latter types of polymeric calcium phosphate were fast-setting and generally stronger than the original TTCP/DCP cement. The new cements also showed modest but significant adhesion to dentin and are expected to have excellent biocompatibility.

MEDICAL MATERIALS INSTRUMENTS AND DEVICES

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Research has continued on the use of microwave generated gas plasmas for sterilization of dental and medical instruments. Previous reports of sterilization of dental burs in 30 seconds may have to be revised in light of the FDA stringent process definition of sterilization which requires probability of sterility studies to determine the rate of disinfection and insure a failure rate of only 1 in 1,000,000 devices. New plasma system configurations were designed, constructed and investigated by both physical monitors (temperature and current probes) and biological indicators (B Subtilis spores). Spore kill kinetics have been investigated as functions of microwave power/pressure, spore loading, material substrate and material geometry. Results indicate that several minutes may be necessary for complete sterilization. The temperature increases that may accompany these longer exposure times may present a problem for certain types of devices. Consequently, the effects of the plasma under different conditions on the material properties of candidate substrates needs to be determined.

A device to test the cutting efficiency of dental burs has been designed and constructed. A cooperative research project with the U.S. Navy Dental School has been initiated to assess the statistical variability of the device when cutting MACOR (a machinable glass-ceramic). If the project is successful, the cutting efficiency of dental burs exposed to microwave generated gas plasmas will be investigated.

The principal phases and structural states of calcium phosphate substances formed upon coating titanium implant surfaces by a plasma technique using hydroxyapatite sources were identified and semi-quantified. Knowledge of the chemical and physical composition of these implant coating is essential for evaluating and controlling in vivo bonding with the contiguous tissue when the implants are used for bone and tooth restorations.

DENTAL POLYMER, COMPOSITE, CEMENT SEALANT AND ADHESION CHEMISTRY

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The synthesis of vinyl metal carboxylate monomers was extended to several types derived from mono-[2-(methacryloyl)ethyl] phthalate, MMEP. Water soluble salts, e.g. Ca, can be used to formulate resin-modified glass ionomer cements. Those having redox metals, e.g. Fe, Ti, act catalytically with certain free radical initiator systems. Liquid resins were formulated with the organophilic zirconyl derivative of MMEP which yielded composites with excellent esthetics, enhanced radiopacity and acceptable strength. These types of organometallic monomers have a number of potential dental and medical applications.

The lack of di- and multifunctional fluorinated vinyl monomers has hampered the development of low surface energy thermoset polymers and composites. The formaldehyde-acrylate insertion reaction has been extended to the synthesis of novel, highly fluorinated difunctional and multifunctional acrylate monomers and oligomers. The use of aprotic solvents such as dimethyl sulfoxide appears to be essential for successful reaction of highly fluorinated mono- and diacrylates with paraformaldehyde. The new synthetic procedures have been extended to acrylate siloxane monomers.

The polymerization of a liquid, symmetrical saturated spiroorthocarbonate was achieved at ambient temperature using $BF_3 \cdot OEt_2$ as the initiator. Complete double ring-opening occurred to yield the expected polycarbonate polymer as a viscous oil. Exposure of the same liquid monomer to a microwave generated plasma (30 seconds, 100 torr) also resulted in highly efficient double ring-opening but now yielded a tough solid polymeric film. The polymerization of other spiro and other types of cyclic monomers by this technique is under investigation.

Previous research identified α-methylene Ç-butyrolactone as a potentially useful dental monomer. Solvent resistant poly(vinylactones) have now been prepared from several newly synthesized substituted α-methylene Ç-butyrolactones. The synthesis of difunctional vinyl lactones is under investigation.

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 was shown to be highly effective in several dentin bonding systems.

The adhesive properties of polymer- and resin-modified glass ionomer cements were evaluated for their ability to bond to dentin and composites. Acceptable bond strengths to both substrates were observed with the tensile strengths to composites often being significantly higher than those obtained with unmodified glass ionomer cements.

NIR-SPECTROSCOPIC INVESTIGATION OF WATER SORPTION CHARACTERISTICS OF DENTAL RESINS AND COMPOSITES

S. Venz and B. Dickens

Dental composites spend their service lives in aqueous environments and are expected to absorb some water. To some extent, absorbed water counteracts polymerization shrinkage by causing swelling and thus closing marginal gaps. However, water has been found to have deleterious effects. Prolonged storage of dental composites in water leads to reduction in transverse strength and in some chemically cured composite systems also leads to a reduction in modulus of elasticity and tensile strength. The coupling agents at the filler/resin interface are adversely affected by water. Although silane agents can improve the performance of composites in water, they do not prevent leaching of the filler itself.

Because of its large dipole moment, the OH group absorbs strongly in the IR region of the spectrum. The IR frequency of the O-H bond decreases with increasing hydrogen bonding for the stretching modes and increases for the bending mode. Thus, IR methods are useful to probe the environment of OH groups.

An isolated water molecule has three modes of vibration: the symmetric stretch (v_1), the bend (v_2), and the antisymmetric stretch (v_3). These three vibrations absorb strongly in the "fundamental" part of the IR spectrum (300 to 4000 cm^{-1}) at 3450 to 3700 cm^{-1}, 1595 to 1650 cm^{-1}, and 3550 to 3750 cm^{-1}, respectively. Overtones (such as $2v_1$) and combination bands (such as v_2+v_3) of these bands are observed in the near-infrared (NIR).

The position of the absorption maximum in the NIR spectrum of small quantities of water in solvents depends on the nature of the solvent. The maximum is at 1.89 µm (5291 cm^{-1}) for water in toluene, 1.91 µm (5234 cm^{-1}) for water in dioxane and polyethylene glycol, and 1.96 µm (5102 cm^{-1}) for water in ethylene glycol. The v_2+v_3 combination band for water vapor occurs at 1.875 µm (5332 cm^{-1}). That for liquid water is at 1.94 µm (5155 cm^{-1}).

These numbers show that water in toluene is isolated from other hydrogen bonding molecules, including other water molecules, whereas water in ethylene glycol is in a water-like environment.

Investigating the relationship between NIR absorptivity and water content to examine the absorbed water has several advantages:

1) NIR spectra are much less crowded than spectra in the fundamental region because most observable NIR absorptions are vibration modes involving hydrogen.

2) NIR absorptions are much less intense than absorptions in the fundamental region. Because the attenuation of the beam is small, sample thickness is not critical.

3) The water band at 1.9 μm is one of the strongest in the NIR region. Thus, it was possible to detect water in specimens ranging from 0.5 mm to 2mm in thickness, even in small amounts. For faster equilibration, films less than 100 μm thick can be used and spectra can be taken by means of a sandwich technique on a stack of these films.

4) The position and intensity of the NIR absorbance of a given amount of water depends on the matrix in which the water is absorbed.

A Near InfraRed (NIR) method using the 5200 cm^{-1} absorption of water has been employed to examine water absorbed in photo-polymerized dental resins and composites in the form of 0.01 cm to 0.15 cm thick films. The concentration, c [Mol L^{-1}], of absorbed water in specimens of thickness t [cm] was calculated by means of Beer's law, $A=\varepsilon ct$. A is the NIR absorbance and ε is the absorptivity of absorbed water. The NIR absorptivity, ε, of water absorbed in a polymeric medium is inversely related to the degree of hydrophilicity and hydrogen bonding capability of the polymer and to the presence of water clusters and it is therefore necessary to estimate ε for water in each material. A series of measurements was carried out where the water sorption was determined gravimetrically and correlated to the absorbance in the NIR spectrum. Once the relationship between ε and water content is known for a material, water sorption can be determined rapidly on very thin specimens for faster equilibration. If dissolution of the specimen occurs, the solubility behavior of the specimen may be evaluated from a comparison of NIR and gravimetric measurements.

Typical dental methacrylate resins and composites were photo-polymerized. All polymerized resins were found to contain water when stored in room air. The NIR absorptivity values ε of water in the various resin matrices are correlated with decreasing water content in the matrices at ambient conditions and after six months equilibration time at 100% relative humidity. To a first approximation, the NIR absorptivity values provide estimates of the degree of hydrophilicity of each resin.

The water absorbance spectra show slight but distinct differences in the position of the absorbance maxima for the various polymers. Shifts to lower wavenumbers (higher wavelengths) correlate with increasing hydrogen bonding capacity of the resin matrix. The degree of hydrophilicity (roughly defined as the capability of forming hydrogen bonds), as estimated from the position of the maximum of the water absorbance peak, agrees with that estimated from the absorptivity.

Water sorption is significantly less in a polymer made from monomers dried before polymerization than in a polymer made from the same monomers that were not pre-dried. Drying of an already polymerized resin removes any water clusters and thus may lead to the formation of microvoids. Where microvoids exist and sufficient water has been re-absorbed, water clusters would reform in these microvoids. Polymers made from predried monomers are expected to contain fewer microvoids than polymers from nonpredried monomers and therefore re-absorb less water.

MODIFIED SURFACE-ACTIVE MONOMERS FOR ADHESIVE BONDING TO DENTIN

S. Venz and B. Dickens

An adhesive system of bonding of dental composites to dentin based on a 10% acetone solution of a solid acidic methacrylate was developed by Bowen of the Paffenbarger Research Unit of the American Dental Association. In an extension of that earlier work, several new liquid acidic monomers were synthesized and evaluated as dental adhesives. Because they are liquids, the new monomers can be applied in thicker layers than solid monomers. Weibull analysis showed that the adhesive bonds of at least one of the new monomers to dentin are significantly stronger than those of the earlier system and that the new bonding system is more reliable because the bonds have a narrower range of failure.

CALCIUM PHOSPHATE CHEMISTRY, BIOCHEMISTRY, STRUCTURE AND CLINICAL IMPLICATIONS

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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 suggest that putative proteoglycan (PG) control of the spread of mineralization in cartilage and possibly other hard tissues, such as dentin, may not be weakened by the enzymatic breakdown of the PG into its principal constituent parts, chondroitin sulfate and core protein. Other liposome studies showed that the effect of cholesterol, an essential component of biomembranes, on ionophore-mediated transmembrane calcium ion movements is not significantly affected by the specific phospholipid makeup of the rest of the membrane. In turn, cholesterol does not appear to directly influence the interaction of these other lipids with the developing mineral phase in membrane-centered calcification processes.

Under physiological conditions octacalcium phosphate (OCP) is a precursor that hydrolyzes 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 completed. The structure was not compatible with the proposed model for OCP-succinate double salt, indicating that there could be different models for 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.

A two step experimental calcium phosphate solution and a commercial acidic potassium oxalate solution (PROTECT)[*] were evaluated for their effects on dentin permeability and sensitivity. Both treatments reduced the permeability of dentin significantly.

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.

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[*] Certain commerical materials and equipment are identified in this article 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.

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

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Computer simulations show that the surface residual compressive stress increases about four times faster than tensile interfacial stress in porcelain-metal strips when the cooling rate is increased from 1°C/sec to 50°C/sec (for 0.8 mm thick body, 0.2 mm opaque porcelains and 0.5 mm thick alloy). Another study of stress shows that the failure stresses for 50 and 200 µm thick bond sections for resin-to-metal bond specimens, tested in tension and bending, can be related to each other by use of Weibull analysis; risks-of-rupture calculations indicate interfacial failure origins for all but the 200 µm thick bond specimens tested in tension, in agreement with fractographic analysis.

An analysis of the stress in the diametral compression test and complementary test specimens indicates that data from only single-cleft fractures can be used for calculation of tensile failure stresses.

A patent application has been submitted for ternary alloys of the class $Zr(A_{1-x}B_x)$, where A is a noble metal such as Ru, Os or Co and B is another noble metal such as Pd. These alloys are strengthened and hardened by martensitic transformations that occur at room temperature under stress and are expected to have excellent biocompatibility. Studies continue to elucidate the nature of various factors that enhance the ductility and other characteristics of these alloys for use in dental and medical applications.

The intrinsic coloration 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 using the characteristic strength (S_o) and the Weibull modulus (m). It was found that m is independent of storage time while S_o shows a small but significant increase between 15 and 30 min. and a much larger increase between 30 and 1440 min (24 hours).

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Industrial and Academic Interaction

Industrial

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.

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.

A Research Associate Program with **Enimont America** has been initiated to evaluate fluorescence techniques for cure monitoring of crosslinkable polycarbonate polymers.

Molecular composites supplied through an agreement with **duPont** are characterization for structural heterogeneities by solid state nuclear magnetic resonance spectroscopy.

The **Strategic Highway Research Program** and Montana State University are collaborating on measurements of the structure of asphaltic cements and concretes of the sort used in road pavements. The work involves application of solid state nuclear magnetic resonance techniques to characterize heterogeneities in asphalt cements.

Industrial visits were made to **Kodak, General Electric, IBM, and Xerox** 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 the crash worthiness and developing test methods for automotive composites.

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.

A workshop attended by 24 industry representatives of the automotive, aerospace, electronics, marine and building sectors reviewed progress of the division's polymer composites processing effort and provided input into future programmatic thrusts in processing and performance.

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.

The Cooperative Research and Development Agreement (CRDA) on microwave generated gas plasma sterilization was renewed with **Air Techniques**. In addition, an agreement regarding this project was established with **Fusion Systems**. A new CRDA is being pursued with **Dentsply International**.

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.

A joint program with **Hi-Tek Polymers** and the University of Massachusetts analyzes the molecular network structure of thermoset resins. **Hi-Tek Polymers** provides samples of a new resin system based on dicyanate, while 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 cooperative program involving **Polaroid**, the University of Massachusetts and Kyoto Institute of Technology explores relationships among properties of high performance fibers and films and the structure and solution thermodynamics of the precursor polyvinyl alcohol gel.

Academic

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.

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

A cooperative program with Professor I. K. Varma of Indian Institute of Technology, Dehli explores the role of interface in the mechanical performance 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 envolves 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 investigates test methods for fiber-matrix interface strength in composites. A variety of currently available test methods will be evaluated using model materials carefully prepared to have different interface strengths. The results as well as the advantages and disadvantages of each method will be compared to determine the current state-of-art in this field.

A joint research program with Colorado State University examines polymer blends where one component contains a rigid segment that acts as a reinforcement to form a "molecular composite". The materials are synthesized at Colorado State University and analyzed by Polymers Division staff using a technique they developed to determine the degree of dispersion for the rigid segments.

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), 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 Dental School of Georgetown University, The University of Texas (San Antonio), Taiwan University, Howard University, Alfred University (NY), 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.

Associated Activities

Invited Talks

Division personnel presented a total of 111 invited talks on research activities at the following types of organizations and symposia: industrial laboratories, 23; international symposia, 10; universities, 28; topical symposia, 8; national and government laboratories, 21; professional society meetings, 17; and Gordon Conferences, 4.

SRMS and Patents

Dr. Gregory B. McKenna and Kathleen M. Flynn: SRM 388p, Isobutylene-Isoprene (Butyl) Rubber Standard for Mooney Viscosity

Dr. Gregory B. McKenna and Kathleen M. Flynn: SRM 386k, Styrene-Butadiene (Type 1500) Rubber Standard for Standard Rubber Formulations.

Dr. Charles M. Guttman and Dr. John R. Maurey: SRM 705A, Polystyrene.

Dr. Charles M. Guttman and Dr. John R. Maurey: SRM 1476a, Polyethylene melt flow rate.

Dr. Charles M. Guttman and Dr. John R. Maurey: SRM 1477, Polypropylene melt flow rate.

Reference Materials 8455 Pyrite Ore Bioleaching Substrate.

A.S. DeReggi, C.K. Chiang and G.T. Davis: Superconductor Polymer Composites. U.S. Patent 4,954,487, September 4, 1990.

J.M. Antonucci: Non-aqueous dental cements based on dimer and trimer acids. U.S. Patent 4,832,745, May 23, 1989.

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, CL. Thomas and F.W. Wang. (Pending)

Thermal Technique for Determining Interface and/or Interply Strength in Composites. W.L. Wu. (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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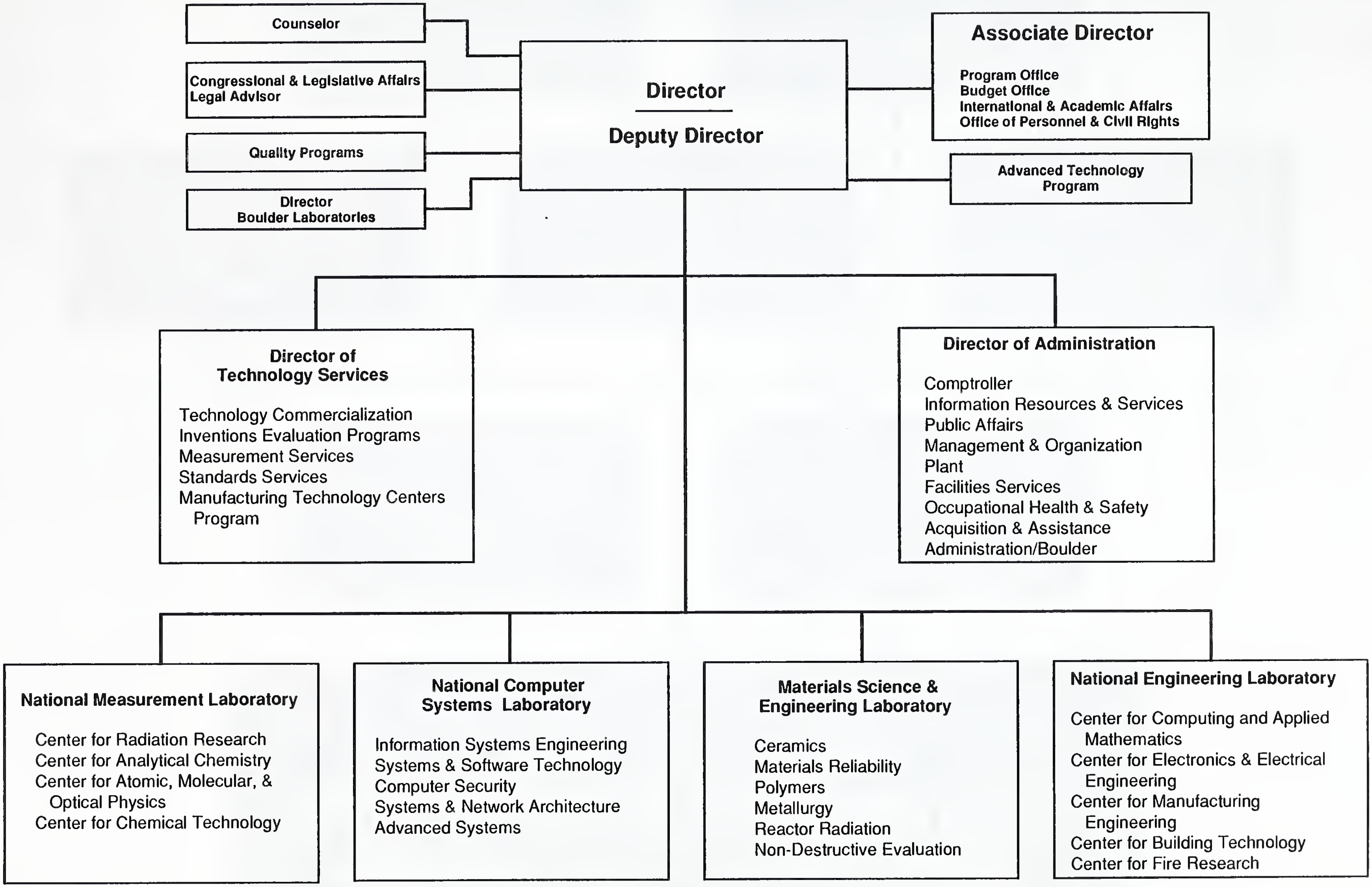

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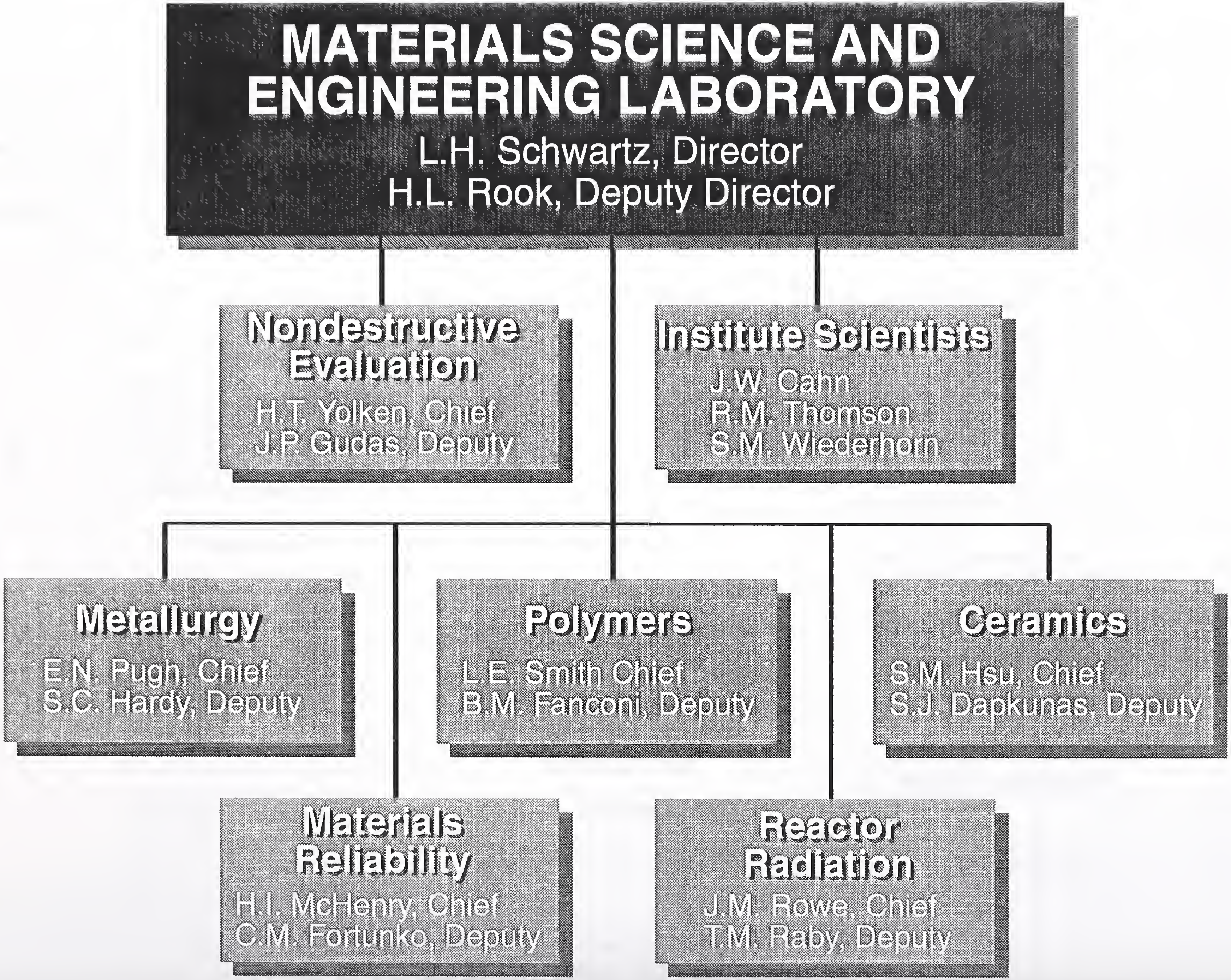

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Technical Activities of the Polymers Division for FY 90 are reviewed. Included are descriptions of the 6 Tasks of the Division, project reports, publications, and other technical activities.

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